

Assessing the feasibility of passive air samplers: A complementary method for monitoring persistent organic pollutants in Great Lakes air

Todd Gouin¹, Tom Harner², Pierrette Blanchard², Don Mackay¹

¹Trent University

²Environment Canada

Introduction

To characterize the environmental fate and transport of persistent organic pollutants (POPs) it is necessary to map their spatial and temporal distribution in different environmental media. Recently, passive air samplers (PAS) have been deployed at various geographic scales, from local to continental, to assess the distribution of POPs in air¹⁻³. A major goal of mapping the spatial and temporal distribution of POPs in air is to assess how regulatory initiatives are influencing the environmental levels of banned substances, and to identify potential source regions or 'hot spots'⁴.

It is proposed that a complementary method to the collection of active, high-volume air samples (AAS) for monitoring long-term trends are PAS, which can enable the cost effective collection of monthly or seasonally integrated air samples deployed throughout a large geographic region. In this study, the performance and reliability of the PAS as a complementary method for monitoring POPs is assessed by comparing with AAS that were collected at several sites located in the Laurentian Great Lakes basin.

Materials and Methods

Sampler design and theory: PUF disks consisting of the same polyurethane foam typically used in the sorption of gas-phase organics used in AAS were housed in a stainless steel domed chamber². The uptake of organic contaminants by the PUF disks from the atmosphere has been described elsewhere⁵. Air samples were extracted and quantified for 19 organochlorine (OC) pesticides and 48 polychlorinated biphenyl (PCB) congeners. Details regarding preparation, handling, instrument method and analysis are reported elsewhere⁵.

Sampling Sites: PAS were deployed throughout the Laurentian Great Lakes on a seasonal basis between July – October 2002 (period 1, i.e. summer), October – December 2002 (period 2, i.e. autumn), January – March 2003 (period 3, i.e. winter) and March – June 2003 (period 4, i.e. spring). Several of the Integrated Atmospheric Deposition Network (IADN) stations were used as sampling sites, including 5 master stations, located at Burnt Island (BNT), Eagle Harbor (EGH), Sleeping Bear Dunes (SBD), Point Petre (PPT), and Sturgeon Point (STP) and 7 satellite stations, located at Chicago (CHI), St. Clair (STC), Point Pelee (PPL), Burlington (BUR), Rock Point (RPT), Egbert (EGB), and Grand Bend (GDB). In addition, 3 other sites, located in Toronto (TOR), Downsview (DOW), and at a field research site operated by Trent University (TNT), were included. The selection of these 15 sites ensures that samples were collected on the shores of each of the five Great Lakes in both remote and urban areas as well as within the interior of the watershed.

Results and Discussions

QA/QC: Quality assurance measures included the collection of 24 duplicate samples, with six of the samples being extracted and analyzed separately by the Organic Analysis Laboratory at Environment Canada in Toronto following the IADN method protocol⁶. Duplicates were collected and analyzed to provide an indication of the overall precision of both the sampling and laboratory methods. Duplicates with a coefficient of variance (COV) that is <35% indicate very good agreement between paired samples (i.e. a COV <35% indicates concentration differences that are about a factor of 1.5 between paired samples). Results for the deployment of all duplicate samples for PCBs and four OC pesticides show that 87% of duplicates had a COV <35%, and 96% with a COV <50% for the PCBs and OC pesticides. These results suggest that the sampling method for the PAS is consistent, and further implies that concentration differences that are greater than a factor of 2 are significant.

Passive air concentrations: In the interest of brevity, the spatial and temporal distribution of air concentrations for only α -HCH and γ -HCH are shown in Figure 1.

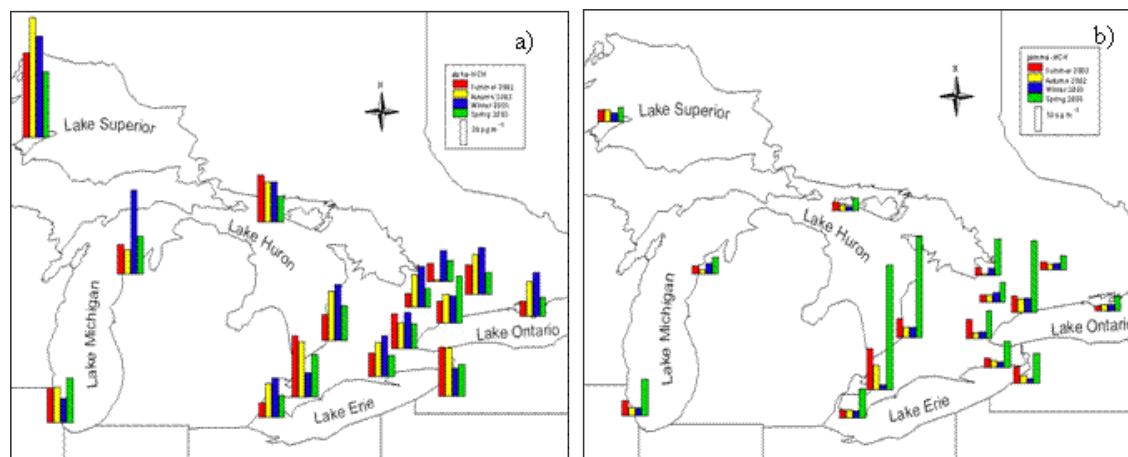


Figure 1: Spatial and temporal distribution of a) α -HCH and b) γ -HCH in air ($\text{pg}\cdot\text{m}^{-3}$) in the Laurentian Great Lakes between July 2002 and June 2003.

The uniform distribution of α -HCH is consistent with previous observations^{2,3} and is expected based on the relatively high volatility and persistence of this banned chemical, enabling it to attain fairly uniform concentrations globally. The results for α -HCH lend confidence to the PAS dataset since concentrations of α -HCH are in the expected range, between 15 and 73 $\text{pg}\cdot\text{m}^{-3}$, and show minimal seasonality. The small variability in α -HCH concentrations thus makes it an ideal compound to compare between PAS and AAS. Figure 2 compares AAS results with PAS data for α -HCH at IADN stations located at EGH, CHI, SBD, and STP for the 4 deployment periods. The AAS data were averaged to correspond to the deployment period of the PAS. The error bars for the high-volume air data represent the standard deviation of the averaged concentrations, whereas the error bars for the PAS are based on the results obtained from the analysis of duplicate samples. The agreement is quite good (i.e. within a factor of 2 to 3) especially considering the temporal variability (error bars) of the AAS data.

γ -HCH, which is the major constituent of Lindane, was in the process of being phased out in Canada in 2003. Thus, the elevated levels of γ -HCH during the spring (Fig. 1) are most likely associated with agricultural activities in the region. Concentrations of both α - and γ -HCH are consistent with ambient concentrations in the Great Lakes region²⁻⁴.

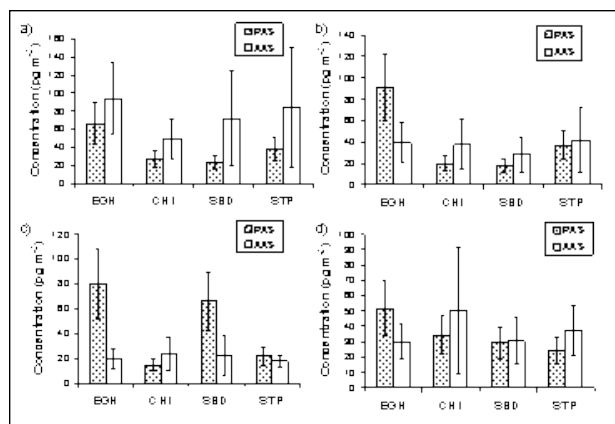


Figure 2: Comparison of α -HCH air concentrations between PAS and AAS for each of the deployment periods. a) summer; b) autumn; c) winter; d) spring. Error bars for the AAS indicate the observed standard deviation while the error bars for the PAS indicate the range of certainty, based on results obtained from duplicate samples.

When comparing between PAS and AAS data for the PCBs, a large discrepancy can be seen for the summer deployment period. In this instance, it is interesting to examine air parcel back trajectories for the days when AAS were collected in order to determine if the AAS that were collected are representative of the entire period integrated by the PAS.

Figure 3 shows the 3-day back-trajectories for STP for each day AAS were collected, the temporal trend for AAS PCB data (inset) a comparison of AAS and PAS data for PCBs and selected OC pesticides, and the back trajectory probability density maps for the PAS during the summer and spring deployment periods. Previous studies have shown that sites to the south and east of STP are source regions of PCBs⁷. However, of the 5 AAS collected during the summer period, only the sample collected on Aug. 31 is shown to be sampling air that has passed over this region and exhibited higher PCB levels (Fig. 3a). The back trajectory

probability density maps for the PAS collected at STP, on the other hand, indicate that the air integrated by the PAS for the entire period shows a much larger contribution from the PCB source regions (Fig. 3e). These probability maps are derived from daily air parcel back trajectories computed for each day of the sampling period using the Canadian Meteorological Centre Trajectory Model. These findings explain the higher levels of PCBs in the PAS versus the AAS in Fig. 3c. In contrast, an example of where the AAS and PAS data agree well is shown in Figure 3d for STP during the spring period. In this case the air parcel back trajectories (Fig. 3b) are consistent with the back trajectory probability maps for the entire period (Fig. 3e).

Generally, the good agreement between the AAS and PAS data suggests that the PAS can be reliably used to monitor the spatial and temporal trends of POPs, complementing the data obtained from the AAS.

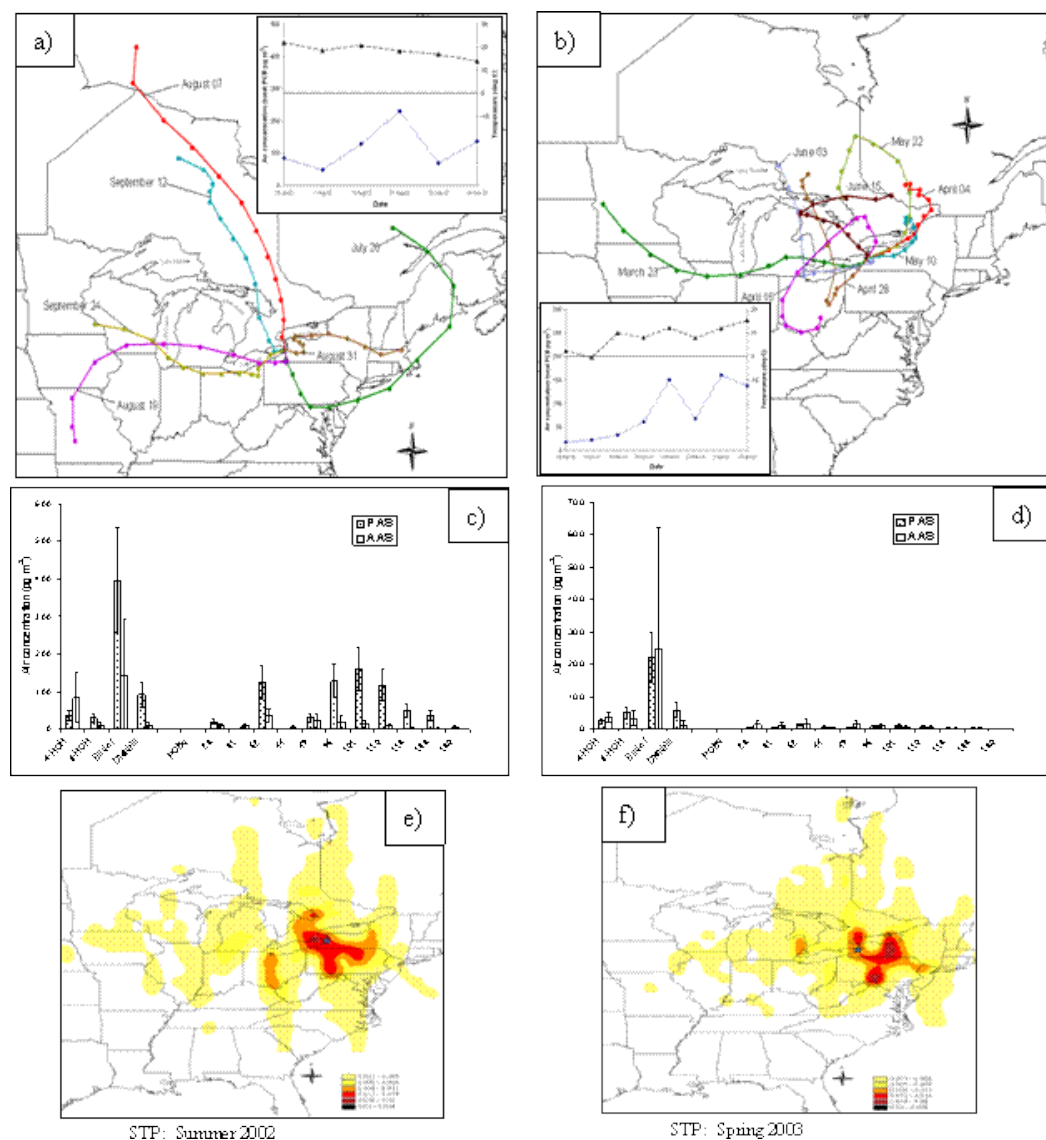


Figure 3: 3-day air parcel back trajectories (10 m) for each day AAS were collected at STP during the PAS a) summer and b) deployment periods and comparison between AAS and PAS for OC pesticides and PCBs during c) summer and d) spring periods. Back trajectory probability density maps for STP during the e) summer and f) spring deployment periods are also shown.

Acknowledgements

The authors thank NSERC, Environment Canada, and the consortium of companies that support the Canadian Environmental Modelling Centre for financial support, Celine Audette for deploying PAS, Jacinthe Racine for back trajectory data, Ken Brice and Ky Su for participating in an inter-laboratory study and Ron Hites and Ilora Basu for providing IADN AAS data.

References

- (1) Jaward, F. M., Farrar, N. J., Harner, T., Sweetman, A. J., Jones, K. C. (2004) *Environ. Sci. Technol.* 38: 34-41.
- (2) Harner, T., Shoeib, M., Diamond, M., Stern, G., Rosenberg, B. (2004) *Environ. Sci. Technol.* 38: 4474-4483.
- (3) Shen, L., Wania, F., Lei, Y. D., Teixeira, C., Muir, D. C. G., Bidleman, T. F. (2004) *Environ. Sci. Technol.* 38: 965-975.
- (4) Buehler, S. S., Basu, I., Hites, R. A. (2002) *Environ. Sci. Technol.* 36: 5051-5056.
- (5) Pozo, K., Harner, T., Shoeib, M., Urrutia, R., Barra, R., Parra, O., Focardi, S. (2004) *Environ. Sci. Technol.* 38: 6529-6537.
- (6) Blanchard, P., Audette, C. V., Hulting, M. L., Basu, I., Brice, K. A., Chan, C. H., Dryfhout -Clark, H., Froude, F., Hites, R. A., Neilson, M. "Atmospheric deposition of toxic substances to the Great Lakes: IADN results through 2000," PWGSC#En45-156/2000-1E, USEPA Report #905-R-04-900, 2004.
- (7) Hafner, W. D., Hites, R. A. (2003) *Environ. Sci. Technol.* 37: 3764-3773.