

Evaluation of performance reference compounds in PUF passive air samplers at different wind speeds

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Introduction

Polyurethane foam (PUF) samplers are being used in an increasing number of studies to passively sample semivolatile organic compounds (SOCs) in the atmosphere (e.g. ^{1, 2}). However, recent research shows that the uptake and loss kinetics of passive air samplers is influenced by changes in wind speed ³. According to theory, the rate of chemical exchange between the sampler and atmosphere can be limited by the thickness of the air-side boundary layer. If this is the case then an increase in wind speed can reduce the thickness of the boundary layer resulting in higher rates of exchange. The loss of performance reference compounds (PRCs) loaded into the sampler prior to deployment should reflect exposure to different wind speeds at different sites.

This approach has been used successfully with passive water samplers (e.g. Huckins et al.⁴) however studies using PRCs in passive air samplers are limited to SPMDs and a tristearin-based sampler ^{5, 6}. We tested whether PRCs could be loaded reproducibly into PUF samplers and then exposed the samplers to different wind speeds in a wind tunnel. Data was examined in order to determine whether the loss of PRCs responded to changes in wind speed. In addition, the capacity of sampling chambers to control for the effects of varying wind speeds was investigated.

Methods and Materials

Preparation

PUF disks (total external surface area: 365 cm² disk⁻¹) were pre-extracted in dichloromethane (DCM) using Accelerated Solvent Extraction. All samplers (including field blanks) were wrapped in solvent rinsed aluminium foil immediately after preparation and stored at -17 °C.

PRCs were loaded by soaking each PUF disk in 200 mL of pentane containing 2 µg of ²D₁₀-acenaphthene (²D₁₀-Ace), ²D₁₀-fluorene (²D₁₀-Flo), ²D₁₀-anthracene (²D₁₀-Ant), ²D₁₀-pyrene (²D₁₀-Pyr) and ²D₁₂-benz[*a*]anthracene (²D₁₂-B[*a*]A). Samplers were removed after the pentane had evaporated (approx. 2 hours). Seven of these samplers were kept as field blanks and not deployed. These samplers were also used to determine the reproducibility of the loading technique.

Deployment

Samplers were deployed in four scenarios. Samplers were deployed inside a wind tunnel and exposed to high wind speeds of approximately 3.5 to 4.5 m s^{-1} ($n=6$) and low wind speeds of approximately 0.5 to 1.5 m s^{-1} ($n=6$). A third set of samplers ($n=4$) placed inside the wind tunnel were deployed inside aluminium bowl sampler chambers to investigate whether the chambers reduced the effect of wind. Although wind speeds around the chambers ranged between 3 and 4 m s^{-1} , wind speeds inside the chambers were generally $<0.3 \text{ m s}^{-1}$. A fourth set of PUF samplers ($n=6$) were placed outside the wind tunnel where wind speeds were negligible. Replicate samplers were collected after 7 and 14 days.

Extraction and quantification

PUF samplers were Soxhlet extracted in redistilled hexane for 12 hours. All samples were cleaned using a mixed alumina silica column and gel permeation chromatography. For quantification the samplers were spiked, prior to extraction, with an internal standard mix containing known amounts of 7 deuterated PAHs ($^2\text{D}_{10}$ -phenanthrene, $^2\text{D}_{10}$ -fluoranthene, $^2\text{D}_{12}$ -chrysene, $^2\text{D}_{12}$ -benzo[*b*]fluoranthene, $^2\text{D}_{12}$ -benzo[*a*]pyrene, $^2\text{D}_{12}$ -indeno[1,2,3-*c,d*]pyrene and $^2\text{D}_{12}$ -benzo[*g,h,i*]perylene). The separation and quantification of the PAHs was performed using a Varian 3400 GC, coupled to a Finnigan SSQ 710 single stage quadrupole mass selective detector.

Results and Discussion*Reproducibility of PRC loading*

Several PUF samplers were loaded with PRCs but not exposed (field blanks, $n=7$). Of the total amount of PRCs added to the pentane, less than 40% of $^2\text{D}_{10}$ -acenaphthene and $^2\text{D}_{10}$ -fluorene and greater than 90% of $^2\text{D}_{10}$ -pyrene and $^2\text{D}_{12}$ -benz[*a*]anthracene originally added was recovered from the samplers (Table 1). Coefficients of variation for the PRCs loaded into the PUF samplers were between 7% and 28% and only exceeded 10% for the more volatile compounds, $^2\text{D}_{10}$ -acenaphthene and $^2\text{D}_{10}$ -fluorene.

Table 1. Results from PRC loading experiment.

PRC	% of total quantified in PUF	Mean amount quantified in sampler (ng)	% Coefficient of Variation
$^2\text{D}_{10}$ -Ace	29%	570	28
$^2\text{D}_{10}$ -Flo	35%	700	25
$^2\text{D}_{10}$ -Ant	59%	1180	9
$^2\text{D}_{10}$ -Pyr	95%	1900	7
$^2\text{D}_{12}$ -B[<i>a</i>]A	99%	1980	10

Relationship between loss rate constants and octanol to air partition coefficients (K_{OA})

Loss rate constants, k_L (day^{-1}) were calculated according to the following equation:

$$k_L = \ln(C_{PRC-0}/C_{PRC})/t$$

where C_{PRC-0} represents the concentration of the particular PRC in the sampler at time zero (measured from unexposed field blanks) and C_{PRC} is the concentration of the particular PRC in the deployed sampler at time t (7 or 14 days). The C_{PRC} at 7 days was used when the compound could not be detected at 14 days. Octanol to air partition coefficients for the respective compounds were taken from Beyer et al.⁷.

Loss rate constants decreased with increasing $\log K_{OA}$ in all exposure scenarios. Modelling theory suggests that where loss rate constants are negatively related to $\log K_{OA}$, air-side resistance is dominating chemical exchange (Table 2).

Table 2. Log K_{OA} values and corresponding mean PRC loss rate constants for each exposure scenario.

PRCs	$\log K_{OA}$	Mean loss rate constants (d^{-1})		
		No wind	Low wind	High wind
$^2D_{10}$ -Ace	6.09	0.30	0.56	0.65
$^2D_{10}$ -Flo	6.76	0.10	0.21	0.28
$^2D_{10}$ -Ant	7.70	0.06	0.13	0.23
$^2D_{10}$ -Pyr	8.70	0.01	0.05	0.09
$^2D_{12}$ -B[a]A	9.85	<0.01	0.01	0.02

Loss rate constants and wind speeds

Loss rate constants generally increased with increasing wind speeds (Table 2 and Figure 1). This relationship was less evident for the heavier molecular weight compound $^2D_{12}$ -benz[a]anthracene possibly due to the relatively short deployment period.

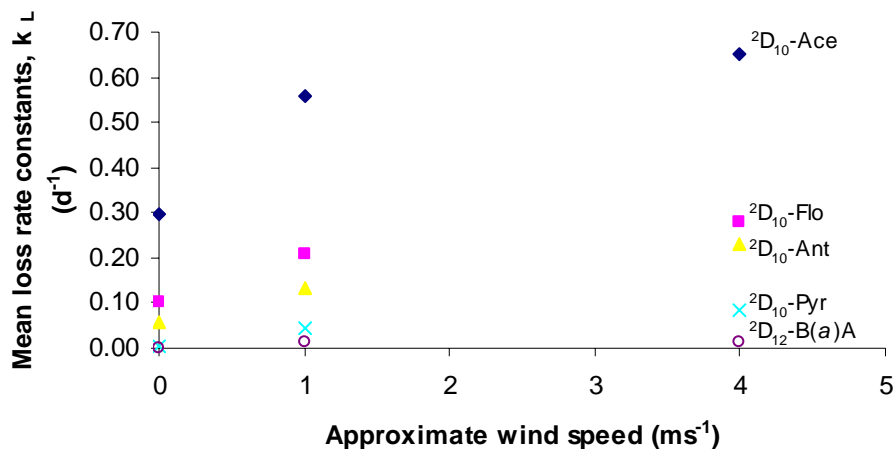


Figure 1. Mean loss rate constants for each PRC at different wind speeds.

Influence of sampler chamber on wind speed effects

Figures 2 and 3 show the effect of wind speed on the loss of ²D₁₀-anthracene and ²D₁₀-pyrene from PUF samplers deployed inside and outside the wind tunnel. The loss of both PRCs from samplers deployed inside protective sampler chambers and samplers deployed outside the wind tunnel were similar, suggesting the chambers provided sufficient buffering of wind effects.

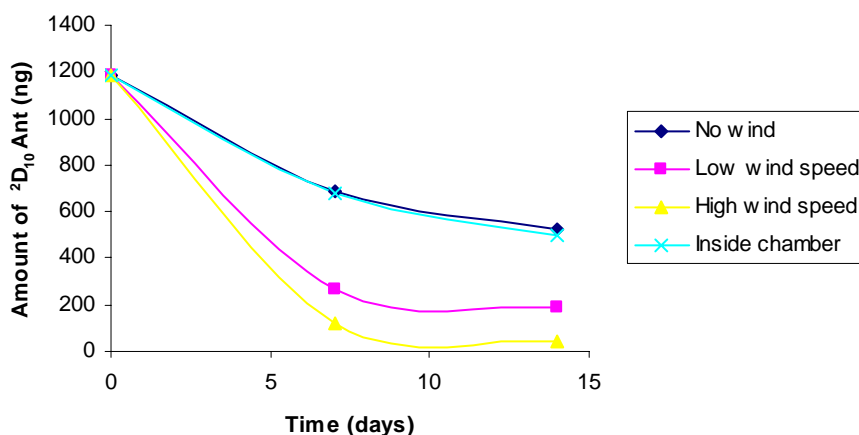


Figure 2. Loss profile showing the mean amount of ²D₁₀-anthracene quantified in PUF samplers from the four exposure scenarios.

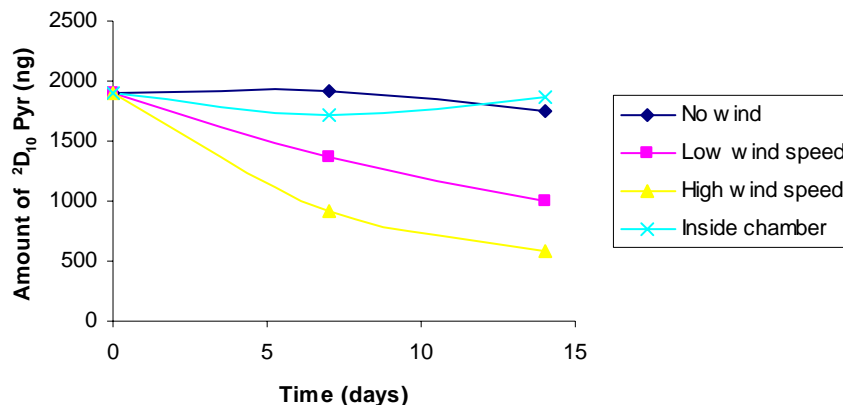


Figure 3. Loss profile showing the mean amount for ²D₁₀-pyrene quantified in PUF samplers from the four exposure scenarios.

In order to reliably determine loss rate constants, approximately 20% to 80% of the original amount of PRCs added to the samplers should be quantified in the samplers subsequent to exposure⁸. After the 14 day deployment, <5% of ²D₁₀-acenaphthene remained in any of the samplers. For ²D₁₀-fluorene, the only samplers with >20% remaining were those deployed outside the wind tunnel. In the case of ²D₁₀-anthracene, approximately 45% remained in the samplers deployed inside sampler chambers and outside the wind tunnel, while <20% remained in samplers exposed to wind. For the heavier molecular weight compounds, ²D₁₀-pyrene and ²D₁₂-benz[*a*]anthracene, >90% remained in samplers outside the wind tunnel and inside sampler chambers, whereas the amounts remaining in samplers exposed to wind were within the acceptable range.

Results suggest that PUF samplers can be reproducibly loaded with PRCs, although percent coefficients of variation exceeded 20% for the more volatile PRCs. Loss rate constants were negatively related to corresponding log *K*_{OA} values, suggesting air-side resistance dominates chemical exchange for these compounds. Loss rate constants generally increased with increasing wind speeds, showing that PRCs are potentially a useful tool for detecting differences in exposure to varying wind speeds between sites.

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References

1. Jaward, F.M., N.J. Farrar, T. Harner, A.J. Sweetman, and K.C. Jones, Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environmental Science and Technology*, 2004. 38(1): p. 34-41.
2. Shoeib, M. and T. Harner, Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environmental Science and Technology*, 2002. 36(19): p. 4142-4151.
3. Harner, T., N.J. Farrar, M. Shoeib, K.C. Jones, and F.A.P.C. Gobas, Characterization of polymer-coated glass as a passive air sampler for persistent organic pollutants. *Environmental Science and Technology*, 2003. 37(11): p. 2486-2493.
4. Huckins, J.N., J.D. Petty, J.A. Lebo, F.V. Almeida, K. Booi, D.A. Alvarez, W.L. Cranor, R.C. Clark, and B.B. Mogensen, Development of the permeability/performance reference compound approach for in situ calibration of semipermeable membrane devices. *Environmental Science and Technology*, 2002. 36(1): p. 85-91.
5. Müller, J.F., D.W. Hawker, D.W. Connell, P. Komp, and M.S. McLachlan, Passive sampling of atmospheric SOCs using tristearin-coated fibreglass sheets. *Atmospheric Environment*, 2000. 34(21): p. 3525-3534.
6. Ockenden, W.A., B.P. Corrigan, M. Howsam, and K.C. Jones, Further developments in the use of semipermeable membrane devices as passive air samplers: Application to PCBs. *Environmental Science and Technology*, 2001. 35(22): p. 4536-4543.
7. Beyer, A., F. Wania, T. Gouin, D. Mackay, and M. Matthies, Selecting internally consistent physicochemical properties of organic compounds. *Environmental Toxicology and Chemistry*, 2002. 21(5): p. 941-953.
8. Huckins, J.N., J.D. Petty, H.D. Prest, C.E. Orazio, and R.C. Clark, A guide for the use of semipermeable membrane devices (SPMDs) as samplers of waterborne hydrophobic organic contaminants. Report for the American Petroleum Institute (API). 2000, API: 1220 L. Street, N.W. Washington DC: American Petroleum Institute - API publication No 4690.