FURTHER CHARACTERIZATION OF PUF DISK PASSIVE AIR SAMPLERS FOR PAHS AND PARTICLES

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Introduction

Since its introduction in 2002[1], the polyurethane foam (PUF) disk passive air sampler (PAS) has become widely used for research and monitoring of persistent organic pollutants (POPs) and other priority chemicals in air. As these simple samplers are increasingly used for measuring a growing and diverse set of chemicals, it is important that a calibration is performed for each chemical class to characterize and confirm the uptake and sampling behavior. Templates are available for assessing sample air volumes (in m^3) and for describing uptake and loss of chemicals and surrogates for the PUF disk sampler for a wide range of chemicals.[2] This allows data on the amount of chemical accumulated on the PUF disk sampler (e.g. pg/sampler) to be converted to a volumetric air concentration (e.g. pg/m^3). Recent studies of the PUF disk sampler have shown that the samplers collect both gas-phase and particle-phase chemicals at the same sampling rate, typically about 4 ± 2 m^3/day.[3] The sampling rate is known to vary from this average value during conditions of high and low wind speeds.[4,5]

In the current work, further studies are carried out to assess performance of the PUF disk sampler. First, the particle sampling behaviour of the PUF disk sampler used under the Global Atmospheric Passive Sampling (GAPS) Network is compared to other passive sampler types and to the conventional PS-1 high volume sampler.[6] Results from these tests inform on the comparability of the different passive and active sampling approaches. Second, the stability of polycyclic aromatic hydrocarbons (PAHs) spiked onto PUF disk is assessed through controlled chamber experiments that simulate O_3 exposure for a typical deployment period lasting a few months (Jariyasopit et al., submitted). In most studies involving passive sampling it is assumed that chemicals are stable on the sampling substrate during the deployment period. For most POPs, which are inherently persistent, this is the case. However for some less stable chemicals such as the PAHs, heterogeneous oxidation may result in losses that need to be assessed. Lastly, the application of the new passive dry deposition sampler (PAS-DD) will be discussed [8] and new developments on the 'Toxicity Mapping" concept will be introduced as important areas of future research and application for PUF disk samplers.

Materials and methods

Particle Infiltration Efficiencies for PUF disk passive samplers and PS-1 active sampler
Field experiments were carried out in the fall of 2014 to assess particle infiltration efficiencies (PIE) for different passive sampling chamber designs as well as a typical high volume PS-1 sampler. The PIE provides a measure of the representativeness of air samplers in matching particle distributions in ambient air. This was accomplished by using an online aerosol spectrophotometer to measure the number concentration and size distributions of particles inside and outside of samplers with high time resolution. The comparison of the measured particle distributions provides insight to the comparability of the passive and active samplers for measuring particle-associated chemicals in air. Additional details are provided in Markovic et al., (2015). [6]

Flow tube chamber experiments for assessing stability of PACs in PUF disks exposed to O_3
A pre-cleaned PUF disk was spiked with individual PAHs using a pipet and placed in the flow tube chamber. An illustration of the experimental setup for the flow tube chamber is shown in Figure 1. Additional details are provided in Jariyasopit et al. (submitted).[7] The setup consisted of three air streams delivered into the flow tube: (1) O_3 generated by a TG-10 Ozone Generator (Ozone Solutions, IA), (2) zero air for dilution generated by a zero air source (AADCO Model 737), and (3) humid air generated by passing zero air through a gas-washing bottle filled with deionized water. O_3 levels were monitored using an Ozone analyzer (Model 205, 2B Technologies, CO). Relative humidity (RH) of the air stream in the flow tube was measured using a probe. PUF disk in the flow tube were exposed for ~4.5 h with the average O_3 concentrations at ~40 ppm (total flow of 11 LPM) and ~14 ppm (total flow of 4 LPM) at 0% RH and 50% RH respectively and experiments were conducted

in triplicate. The combination of high O_3 concentrations and experiment duration were approximately equivalent to exposing the PUFs to an ambient O_3 concentration of ~50 ppb for two months. Additional information on the validation of the system (i.e. blank and recovery tests and results of control experiments) are provided in Jariyasopit et al. (submitted).[7]
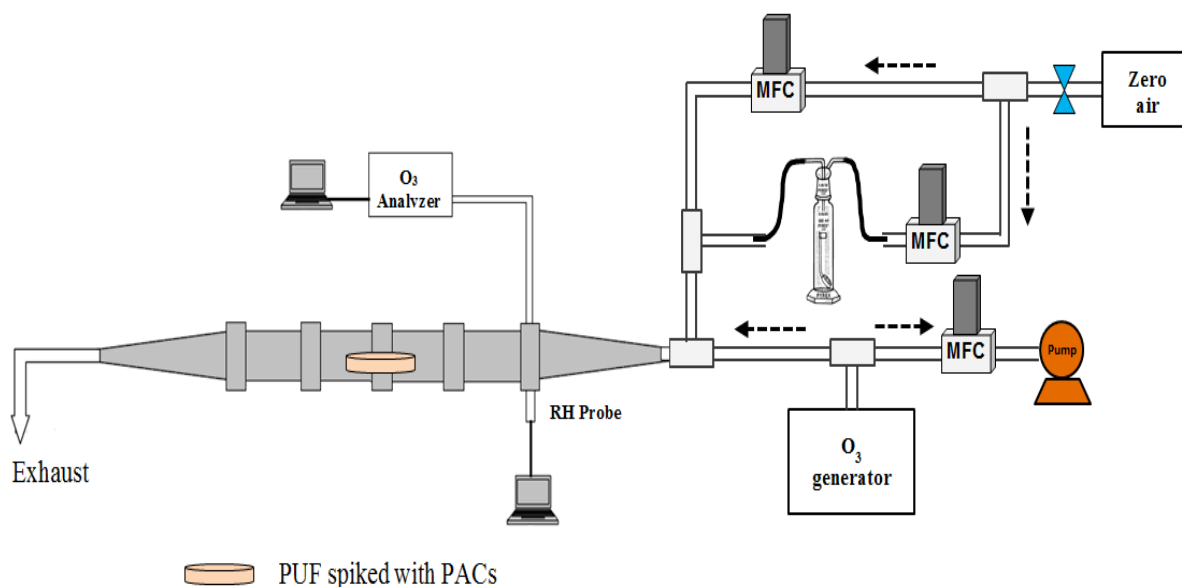

Figure 1. Experimental setup for the flow tube chamber (from Jariyasopit et al., submitted).[7]

Samples were prepared and analyzed using methods described previously.[8] Briefly, PUFs were spiked with the labeled recovery PAH surrogates and extracted with pressurized liquid extraction using petroleum ether and acetone (75:25, v:v; 2 cycles). The extracts were evaporated under a purified N_2 stream with a Turbovap II (Biotage, NC). Sample extracts were spiked with the labeled PAH internal standards and were analyzed by gas chromatography / mass spectrometry (Agilent 6890 coupled with an Agilent 5975 MSD), in electron impact in selected ion monitoring mode, on a DB-XLB column (30 m × 0.25 mm I.D., 0.25 µm film thickness, Agilent Technologies).

Results and discussion
The results of the evaluation of PIEs for the four common air samplers are shown in Fig. 2 and indicate that the PS-1 high volume sampler and the GAPS and LANCS passive samplers possess high sampling efficiencies for ambient particles in 250 – 4140 nm size range, to within the uncertainty of the experimental method of ~ 15 %.[6] This confirms the application of these samplers for studies of particle–associated chemicals in air. The PIE value of the MONET passive sampler was determined to be low by a factor of approximately 1.8.
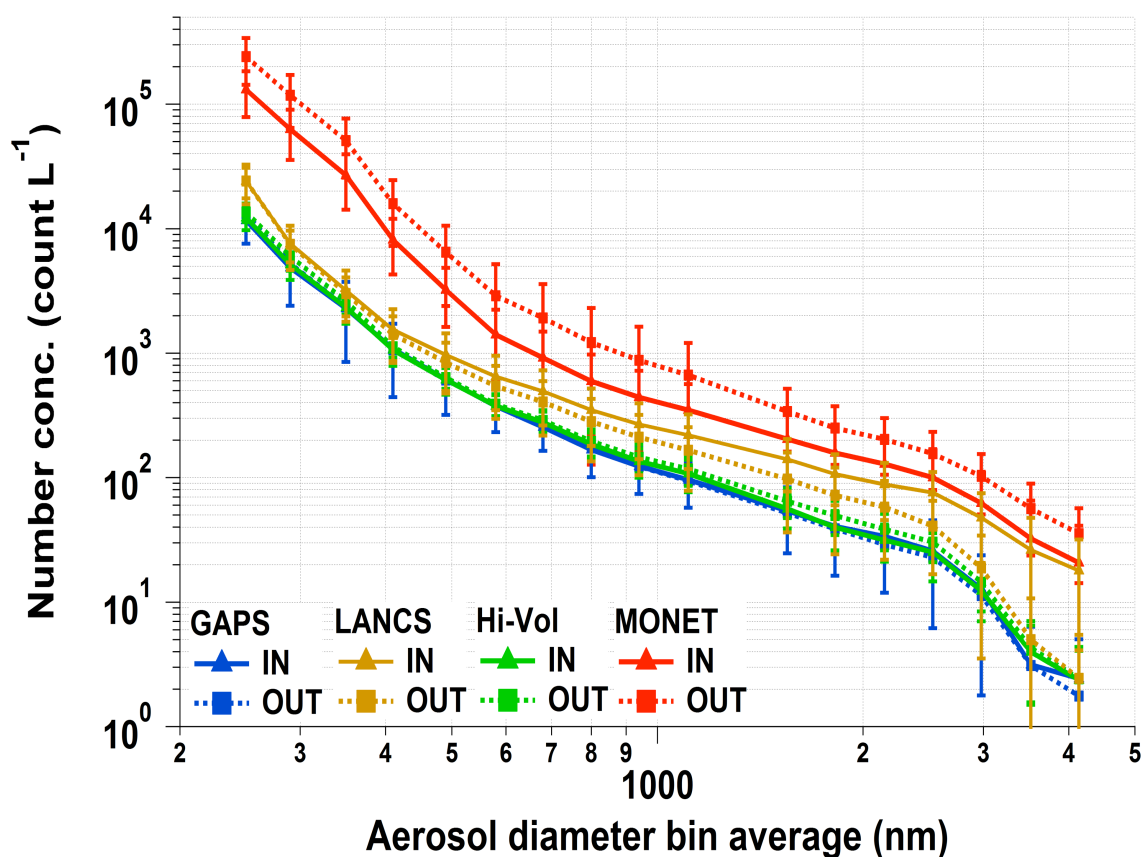
Figure 2. Number size distribution of particles in the 250 - 4140 nm optical diameter range (in 17 size bins) inside and outside of the four commonly used offline samplers. The y-axis represents the number of particles measured per 1 L of sampled air on a logarithmic scale. The x-axis represents the averages of the optical size bins of measured particles on a linear scale. The results for passive air samplers used by the GAPS Network (GAPS), Lancaster University (LANCS), and the MONET program (MONET), and a conventional PS-1 high volume active air sampler (Hi-Vol) are illustrated in blue, orange, red, and green respectively. The dashed lines represent the ambient aerosol sample measured outside and solid lines represent the ambient aerosol samples measured inside of the four offline samplers. Figure modifed from Markovic et al. [6].

The results of the flow tube experiments for PAHs are shown in Figure 3.[7] At 0% RH, 7 of the 19 PAHs yielded more than 50% loss after exposure. At 50% RH, the majority of PAHs were stable upon O_3 exposure indicating that the PUF disk sampler can adequately sample PAHs over extended deployment periods. It is also noteworthy that the experimental conditions in this study represent a worst case scenario for the stability of PACs sorbed to PUF. In reality, the sampling of PACs in ambient air represents an 'aged' component of PACs where the most reactive species have already partially been removed. Also, PACs in ambient air will be associated with the particle phase to varying extent, which will help to enhance their stability.

In summary the results of these studies provide further suport for the application of PUF disk passive air sampler for studies of particle and gas-phase chemicals in air, including PAHs. The validation of PUF disk samplers for particle-associated compounds is a key development as many of the new priority chemicals for air (e.g. new flame retardants) are higher molecular weight chemicals with low volatility and therefore partially or totally associated with particles in air.
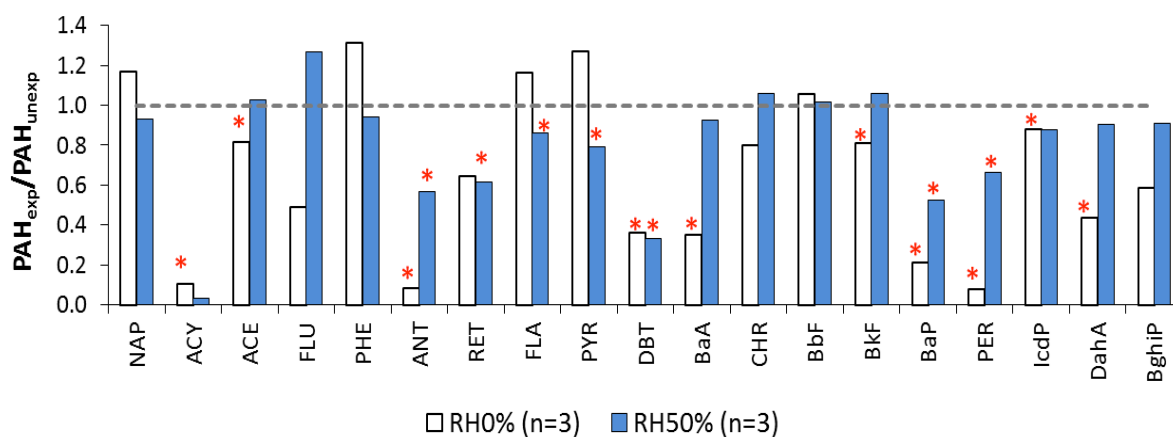
Figure 3. Ratios of parent $PAH_{exposed}$/parent $PAH_{unexposed}$ for the O_3 exposures at RH 0% and RH 50%. A red asterisk denotes a statistically significant difference between the unexposed and exposed masses. (NAP = napthalene, ACY = acenaphthylene, ACE = acenaphthene, FLU = fluorene, PHE = phenanthrene, ANT = anthracene, RET = retene, FLA = fluoranthene, PYR = pyrene, DBT = dibenzothiophene, BaA = benz(a)anthracene, CHR = chrysene, BbF = benzo(b)fluoranthene, BkF = benzo(k)fluoranthene, BaP = benzo(a)pyrene, PER = perylene, IcdP = indeno(1,2,3-c,d)pyrene, DahA = dibenzo(a,h)anthracene, BghiP = benzo(ghi)perylene).

References:
1. Shoeib, M., Harner, T. (2002) *Environ. Sci. Technol.* 36, 4142-4151.
2. Harner, T., 2014_GAPS Template for calculating PUF and SIP disk sample air volumes_November 6 2014, *ResearchGate*. Retrieved date?www.researchgate.net/profile/Tom_Harner?ev=hdr_xprf
3. Harner, T., Mitrovic, M., Ahrens, L., Schuster, J. (2014) *Organohalogen Compds*. 2014, 76, 442-445.
4. Petrich, N.T., Spak, S.N., Carmichael, G.R., Hu, D., Martinez, A., Hornbuckle, K.C., (2013) *Environ. Sci.Technol*. 47,8591-8598.
5. Tuduri, L., Harner, T., Hung, H., (2006) *Environmental Pollution* 144, 377-383.
6. Markovic, M., Prokop, S., Staebler, R.M., Liggio, J., Harner, T. (2015) *Atmos. Environ.* (in press).
7. Jariyasopit, N., Liu, Y., Liggio, J., Harner, T. (2015) *Atmos. Environ.* (submitted)
8. Eng, A., Pozo, K., Harner, T. (2014) *Environ. Sci. Technol. Letters* 1, 77-81.
9. Schuster, J.K., Harner, T., Su, K., Mihele, C., Eng. A. (2015) *Environ. Sci. Technol*. 49, 2991-2998.