

A Prototype Passive Air Sampler for Measuring Dry Deposition of Polycyclic Aromatic Hydrocarbons

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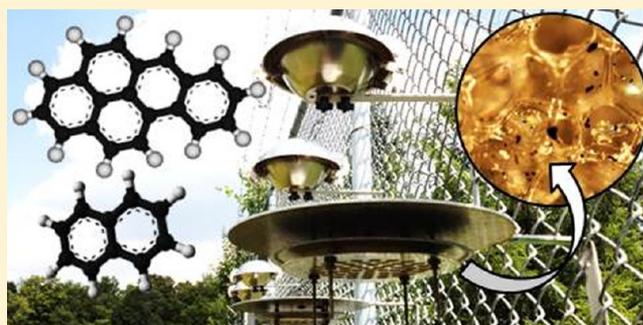
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S Supporting Information

ABSTRACT: The passive dry deposition (Pas-DD) collector is presented as a tool for estimating atmospheric loadings (dry deposition fluxes or maps) for polycyclic aromatic hydrocarbons (PAHs) and other semivolatile compounds. Pas-DD collectors based on a parallel plate design were codeployed with conventional polyurethane foam (PUF) disk passive air samplers (PAS) in outdoor urban air over different seasons. Two configurations of sampling media (PUF only vs stacked glass fiber filter on PUF) were used. For both samplers, a higher level of accumulation of PAHs was observed when only the PUF disk was used as the sampling medium. The Pas-DD collector and the PAS accumulated gas-phase PAHs (dry gaseous deposition component) to a similar extent. For the higher-molecular weight PAHs that are associated with particles, the Pas-DD collector was enriched relative to the PAS. Dry deposition velocities derived from the Pas-DD collector were approximately 0.16 cm/s for gas-phase PAHs and up to 0.8 cm/s for particle-phase PAHs.



1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous atmospheric pollutants that are a concern because of their toxicity. Investigations of their deposition fluxes are often conducted to assess loadings to environments that may be at risk. A common approach for estimating deposition of PAHs and other semivolatile air pollutants is based on sampling of ambient air.¹ Deposition estimates based on ambient air data require additional meteorological information and physical chemical property data for the estimation of deposition fluxes for individual compounds.^{2,3} This results in uncertainty in the deposition estimates because of limitations in the availability and quality of input data and various assumptions inherent in the calculations. For instance, passive and high-volume sampling methods typically collect <30 μm particles, with the particle-phase mass dominated by the fine particle fraction, whereas deposition is dominated by coarse particles.^{4,5} It is also possible to directly measure and/or assess deposition through collection of precipitation,¹ snow,^{6,7} and the use of bulk deposition collectors.^{8–10}

In this study, we introduce a prototype passive dry deposition (Pas-DD) collector. This time-integrated sampler is particularly well suited for deployment in remote sites over large regions, where sampling using conventional air sampling equipment is logistically challenging because of the nature of

the environment and the lack of access to electricity and infrastructure. Such a need exists in the Athabasca oil sands region, where there are concerns associated with deposition of PAHs to terrestrial and aquatic environments and the associated health risks.^{6,11} The use of the Pas-DD collector to collect PAH dry deposition data at a high spatial resolution to generate deposition maps is analogous to the way that mosses, lichens, and other biomonitors are used to map spatial deposition, but overcoming some of the inconsistency and interpretation challenges associated with biomonitoring. For example, natural climate variabilities (temperature, altitude, etc.) along with the biomonitor's nutrition can greatly influence their cumulative response.^{12,13}

Field deployments of the Pas-DD collector were performed during a summer and winter season and alongside conventional polyurethane foam (PUF) disk passive air samplers like those currently used in the oil sands air monitoring program.¹⁴ Two configurations of collection media were also tested for their ability to capture dry gas- and particle-phase deposition of PAHs.

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2. METHODS

2.1. Passive Dry Deposition (Pas-DD) Collector and Passive Air Sampler (PAS). A schematic of the Pas-DD collector is shown in Figure 1. The sampler comprises two

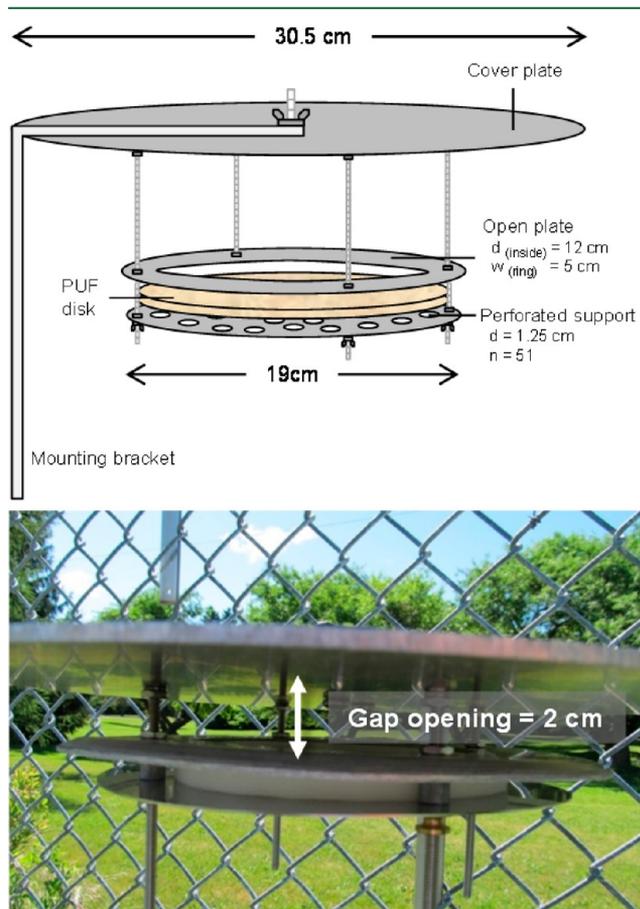


Figure 1. Schematic and photo of the passive dry deposition (Pas-DD) collector.

parallel flat plates (cover plate and open plate) and a PUF disk as the sampling medium. The PUF disk is positioned below the open plate and is held in place by a perforated support. The edges of the open plate are tapered slightly to promote unobstructed flow of air between the two plates with minimal turbulence.¹⁵ Compounds subject to dry gas- and particle-phase deposition are captured on the PUF disk. The larger diameter of the top cover plate provides shielding of the PUF disk from wet deposition and direct sunlight that may enhance degradation for some target analytes.¹⁶

Testing was performed on the Pas-DD collector to evaluate the effect of the gap opening between the cover plate and open plate (from 2 to 7 cm) on the number of particles that were deposited onto a glass fiber filter situated on top of the PUF disk (see Text 1 of the Supporting Information). It was shown that even for gap openings as small as 2 cm, the full size range of particles was able to deposit onto the sampling medium (i.e., the larger particles were not excluded). For field testing of the Pas-DD collector in this study, the 2 cm gap configuration was used as this provided optimal protection for the PUF disk from wet deposition and sunlight (Text 1 of the Supporting Information).

2.2. Sampler Deployment. Samplers were deployed during two sampling campaigns at the Environment Canada (Downsview) field station in Toronto, ON (43.780611°N, -79.467953°W). This is a background urban site that receives PAHs from a wide range of typical urban sources (e.g., vehicle traffic, residential and recreational emissions, and light industry). The first campaign took place during the summer (June to August 2012, lasting 63 days) and the second campaign during the winter (November 2012 to January 2013, lasting 61 days). During each campaign, a total of eight samplers were deployed side by side: four Pas-DD collectors (Figure 1) and four conventional PUF disk PAS (Figure S1 of the Supporting Information). The samplers were mounted approximately 1.5–2 m above the ground (see Figure S2 of the Supporting Information).

Two configurations of the sampling media were tested in duplicate for both the Pas-DD collector and PAS. Configuration 1 used the PUF disk alone as the collecting medium (Tisch Scientific TE-1014, 14 cm diameter × 1.35 cm thick), whereas in configuration 2, a Whatman 1824-042 glass microfiber filter (GFF) was placed on top of the PUF disk (i.e., GFF-PUF) to attempt to differentiate the particulate (collection on GFF) and gas (collection on PUF) components of dry deposition. This was repeated in both campaigns, and field blanks were collected for PUF disks ($n = 3$) and GFFs ($n = 2$).

2.3. Analysis Using Optical Microscopy. At the end of each deployment period, an ~15% portion of each collected PUF disk and GFF were cut out and removed for visual analysis by optical microscopy using an Olympus BX51 instrument fitted with an MPLN5xBD lens. The percentage of the portion removed was calculated on the basis of the weight by difference (Table S1 of the Supporting Information). Optical microscopy is sensitive enough to provide a visual assessment of particles as small as ~1 μm that have deposited onto the GFF and PUF disk surfaces. In the context of assessing depositing particles, the dominant contribution comes from particles that are larger than 1 μm and can be easily viewed by this technique.⁴

2.4. GFF and PUF Disk Sample Extraction, Analysis, and QA/QC. The remaining portion (~85%) of the GFFs and PUF disks was analyzed according to the methods used by Harner et al.,¹⁴ and results were scaled up accordingly to represent 100% of the sample. Field blank results were used to calculate corresponding limit of detection (LOD) values as mean field blank values + 3 × the standard deviation. When PAH target analytes were not detected in the field blanks or samples, $2/3$ of the instrument detection limit (IDL) value for the corresponding analyte was substituted. The IDL was calculated by extrapolating the lowest calibration standard to a concentration that would result in a signal-to-noise ratio of 3:1, assuming a linear response. Field blank, LOD, and IDL values are summarized in Tables S2 and S3 of the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Optical Microscopy. Figure 2 is a 50× magnification of a portion of a PUF disk and GFF following the winter deployment in the Pas-DD collector under the PUF only and GFF-PUF configurations, respectively. Many of the collected particles have passed through the pores (~200–250 μm in diameter) on the exterior surface of the PUF disk and have become entrained in the matrix, with little chance for resuspension or chemical desorption. In contrast, particles

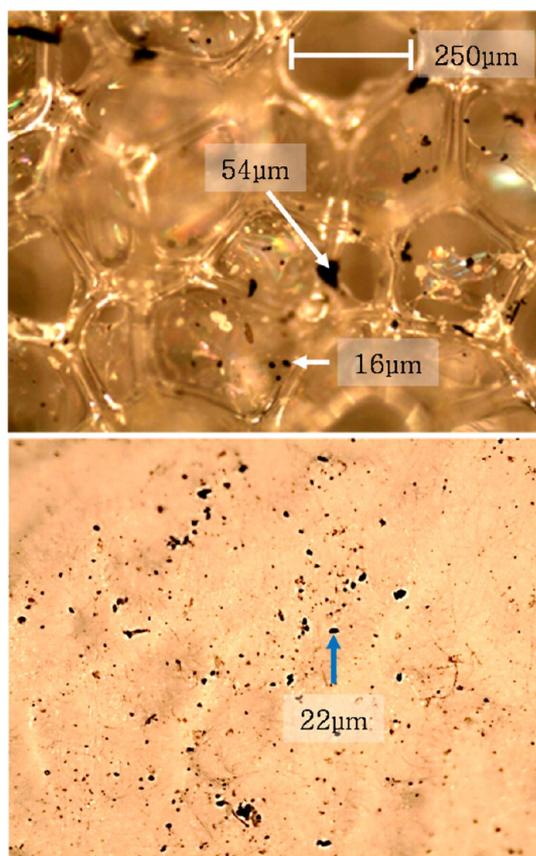


Figure 2. Optical microscopy images of a PUF disk (top) and GFF (bottom) collected from the Pas-DD collector during the winter campaign. The PUF disk shown is from the “PUF only” configuration. The images are at 50X magnification.

collected on the GFF are positioned on the surface of the more densely woven GFF matrix, where pore sizes are approximately $<0.1 \mu\text{m}$. These particles are more exposed to air with the potential for revolatilization of the bound chemical. Inspection of the underside of the PUF disk and GFF samples by optical microscopy revealed very few particles, indicating that particle collection was predominantly to the top surfaces of the sampling substrates. Analysis of PUF and GFF from the PAS revealed a finer particle composition compared to that of the Pas-DD collector, which is attributed to the “closed” design of the PAS sampling chamber that excludes larger particles.^{17–19}

3.2. PAH Analysis. Final compound concentrations (nanograms per PUF disk and nanograms per GFF) are listed in Table S4 of the Supporting Information, with results for selected PAHs illustrated in Figure 3 (for representative particle-associated PAHs) and Figure S3 of the Supporting Information for representative gas-phase PAHs. Of the four configurations tested [Pas-DD_(PUF only), Pas-DD_(GFF-PUF), PAS_(PUF only) and PAS_(GFF-PUF)], the largest amounts of PAHs were collected on the Pas-DD collector that used only a PUF disk as the collection substrate (Figure 3). This was even more apparent for the winter period when the partitioning of PAHs shifts to the particle phase because of the reduced volatility at colder temperatures.^{20,21} The double-domed PAS also showed greater levels of accumulation of PAHs for the PUF only configuration compared to the GFF-PUF arrangement.

The greater sampling of PAHs by the PUF only configuration versus the GFF-PUF configuration may be

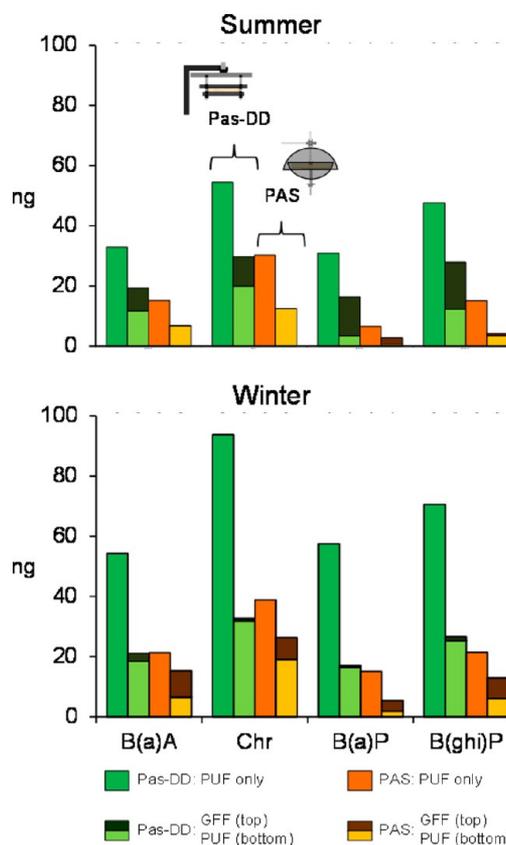


Figure 3. Concentrations (nanograms per PUF disk and nanograms per GFF) of representative particle-phase PAHs measured by the passive dry deposition (Pas-DD) collector and passive air sampler (PAS) during the summer and winter campaigns. GFF-PUF results are presented as stacked bars. Variability in the range of values for Pas-DD and PUF only ($n = 2$) was within $\sim 20\%$ of the mean value for 88% of target compounds in summer samples and 82% of compounds in winter samples. There was no bias in the percent variability for particle-phase vs gas-phase PAHs.

attributed to the porosity of the PUF that allows depositing particles to become entrained (see Figure 2), thereby reducing the likelihood of resuspension or rebounding (i.e., particles blowing off the substrate). This entrainment of particles into the PUF matrix has been previously reported.¹⁸ Loss of chemical from these particles by revolatilization is also less likely as the PUF disk itself has a high sorptive capacity and is likely to scavenge PAHs that are bound to or released from the particles. Particle rebounding and revolatilization of the chemical is more likely to occur for the GFF where deposited particles are associated with the surface of the GFF (that has limited sorptive capacity for PAHs) and are more vulnerable to episodic wind gusts.^{20,22–25}

The higher level of accumulation of PAHs by the Pas-DD collector compared to that of the conventional PAS (for both PUF only and GFF-PUF configurations) is attributed to the double-dome chamber used for the PAS that filters out the larger depositing particles.^{17–19} Dry deposition of PAHs is a combination of dry gaseous deposition and dry particle deposition. In essence, the two sampler configurations should be sampling gas-phase PAHs at similar rates (i.e., dry gaseous deposition has no downward bias as it is a function of diffusivity in air), with slightly higher sampling expected in the open Pas-DD collector design because of the reduced boundary layer

thickness. However, a slightly lower total level of accumulation of the gas-phase component might be possible in the Pas-DD collector compared to the PAS chamber (when results are expressed as nanograms per sample) because of the positioning of the PUF disk in the Pas-DD collector. Approximately 36% of the PUF disk total outer surface area is covered by the open plate and perforated support that holds the PUF disk in place; countering reduction in sampling for the Pas-DD collector is the higher wind speed through the Pas-DD collector plates that will reduce air-side mass transfer resistance and enhance chemical sampling rates.^{26–28} Because of its open design, the Pas-DD collector provides a better measure of the downward flux of PAHs (i.e., dry particle deposition) as the Pas-DD collector is collecting the full size range of depositing particles and most importantly the larger particles that dominate the dry particle deposition component.⁴

The ability of the Pas-DD collector to capture the dry particle deposition component of the deposition flux is further illustrated in Figure 4, which shows enhancement ratios of the

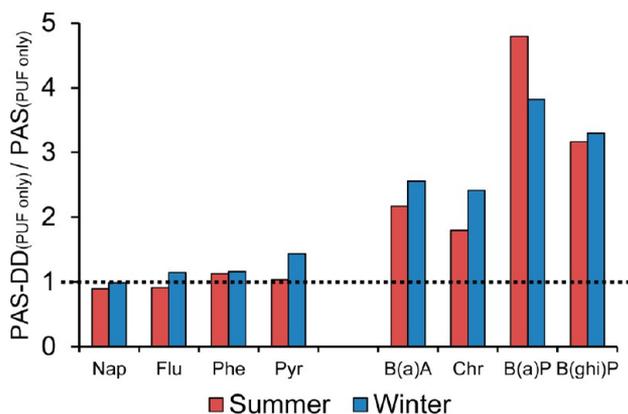


Figure 4. Enhancement ratios [Pas-DD_(PUF only)/PAS_(PUF only)] for gas-phase (left) and particle-phase (right) PAHs during summer and winter deployments.

Pas-DD collector versus the PAS when only the PUF disk is used as the collection substrate. For mainly gas-phase PAHs such as naphthalene, fluorene, phenanthrene, and pyrene, there is a negligible difference between the results for the two samplers with ratios near 1 for both summer and winter deployments. Both samplers are collecting dry gaseous deposition at similar rates. On the basis of the recent field calibration of the PUF disk passive air sampler for PAHs,¹⁴ this sampling rate is equivalent to $\sim 5 \text{ m}^3/\text{day}$ (equivalent to $\sim 58 \text{ cm}^3/\text{s}$), which can be converted to a deposition velocity of $\sim 0.16 \text{ cm/s}$ for gas-phase PAHs based on the exposed PUF disk surface area of 365 cm^2 [i.e., $(58 \text{ cm}^3/\text{s})/(365 \text{ cm}^2) = 0.16 \text{ cm/s}$]. This is in the range of deposition velocities reported by Chang et al.¹¹ for low- to medium-molecular weight PAHs (0.01–0.29 cm/s respectively). However, it is important to note that for the most volatile PAHs (e.g., naphthalene and fluorene), the PUF disk has a limited sorptive capacity and will eventually approach equilibrium (e.g., <1 week for naphthalene and ~ 3 weeks for fluorene). The process for accounting for a reduced level of accumulation as equilibrium is approached in PUF disks is discussed by Harner et al.¹⁴ In the real environment, the lower-molecular weight PAHs are likely equilibrating with surface compartments (e.g., vegetation, soil,

etc.),^{29,30} so their equilibration in the PUF disks used in the Pas-DD collector would be analogous.

The enhancement ratios (Figure 4) for the Pas-DD collector increase above unity for the higher-molecular weight PAHs benzo(a)anthracene, chrysene, benzo(a)pyrene, and benzo-(g,h,i)perylene, which are increasingly associated with atmospheric particles.^{21,31,32} Ratios as high as 3.5–5 are observed for PAHs that are entirely particle bound [i.e., benzo(a)pyrene and benzo(g,h,i)perylene]. Results for other PAHs are summarized in Table S5 of the Supporting Information and show a similar behavior. The enhancement ratios for the high-molecular weight PAHs that are totally particle-bound can be translated to deposition velocities associated with dry deposition and are in the range of 0.56–0.8 cm/s (i.e., 3.5–5 times greater than the estimate of 0.16 cm/s for dry gaseous deposition). This finding is consistent with other reports of PAH deposition velocities.^{2,11,33,34}

In summary, the Pas-DD collector is introduced and demonstrated as a simple tool for mapping atmospheric dry deposition of PAHs and potentially other semivolatile priority chemicals and even metals. Future optimization of the Pas-DD collector (e.g., gap opening) will be explored using fluid dynamic models and wind tunnel testing.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional text, figures, and tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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