

DIRECT OBSERVATION OF THE UPTAKE OF GASEOUS POLYCYCLIC AROMATIC HYDROCARBONS BY A FOREST CANOPY

Choi S-D¹, Li H X¹, Su Y¹, Gevao B¹, Harner T², Wania F¹

¹Department of Physical and Environmental Sciences, University of Toronto at Scarborough, 1265 Military Trail, Toronto, Ontario, Canada, M1C 1A4; ²Science and Technology Branch, Environment Canada, 4905 Dufferin Street, Toronto, Ontario, Canada, M3H 5T4

Abstract

Rapid uptake of PAHs by a forest canopy was observed at the Borden forest in Southern Ontario, Canada during budbreak in early spring 2003. High volume air samplers were taken for 12 days at three different heights (44.4, 29.1, 16.7 m) on a scaffolding tower and on the forest floor below the canopy (1.5 m). An analysis of the temporal variations, vertical profiles, and gas/particle partitioning of the PAHs showed that gaseous PAHs established a concentration gradient with height, whereas levels of particulate PAHs were relatively uniform, implying that only the uptake of gaseous PAHs by the forest canopy was sufficiently rapid to be observed. Specifically, the gaseous concentrations of intermediate PAHs, such as phenanthrene, anthracene, and pyrene, during budburst and leaf emergence were reduced within and above the canopy. When a gradient was observed, the percentage of PAHs on particles increased at the elevations experiencing a decrease in gas phase concentrations. These results are the most direct evidence yet of the filter effect of forest canopies for gaseous PAHs in early spring.

Introduction

Forests have been shown to effectively filter many semi-volatile organic compounds (SOCs) from the atmosphere, thereby reducing air concentrations and increasing deposition to the forest floor.¹ Despite several field measurements and modeling efforts devoted to quantifying this forest filter effect, the magnitude, variability, and mechanisms of this process remain to be fully characterized. Simultaneous sampling of air concentrations and bulk deposition below a canopy and at a nearby clearing can be applied to estimate the SOC deposition to forest canopies during an entire growing season.^{2,3} While these studies can yield long term average gaseous deposition velocities to forests, they only provide indirect evidence of SOC uptake in the canopy and the resulting reduction of air concentrations. The purpose of this study was to determine concentration gradients of polycyclic aromatic hydrocarbons (PAHs) developing above a forest as a result of their rapid uptake in the canopy. The temporal variations of gaseous and particulate PAHs, their vertical profiles and gas/particle partitioning at different heights on a 45 m scaffolding tower were investigated in a Canadian deciduous forest.

Materials and Methods

The sampling site (44° 19' N, 79° 56' W), located on the Canadian Forces Base Borden (Figure 1), is a mixed deciduous forest with an average canopy height of 22 m. Sampling was carried out in early spring 2003 (April 24–June 2) when PAH uptake in the forest canopy is expected to be largest. Three samples at different heights on the scaffolding tower (44.4 m, 29.1 m, and 16.7 m) and one sample on the forest floor below the canopy (1.5 m) were taken for 12 days using high volume air samplers (Figure 2). Prior to budburst (April 24 and 25), 24-hr samples were collected for two continuous days to characterize the situation without the presence of a canopy. While leaves were developing, 24-hr samples were collected every three days until leaves were completely developed, which lasted about one month (May 5–June 2).

PUF plugs and GFFs were individually Soxhlet extracted and concentrated by rotary evaporation. Extracts were cleaned and separated into two fractions on a column of silicic acid/neutral alumina. 16 US EPA PAHs were analyzed by gas chromatography-electron impact mass spectrometry (GC-EIMS) in the selected ion monitoring (SIM) mode using an Agilent 6890 GC-5973 mass spectrometric detector. Because the three most volatile PAHs (naphthalene, acenaphthylene, acenaphthene) were subject to apparent breakthrough, they were not considered in the data interpretation. More details on sample preparation, cleanup, instrumental analysis, and QA/QC can be found elsewhere.⁴

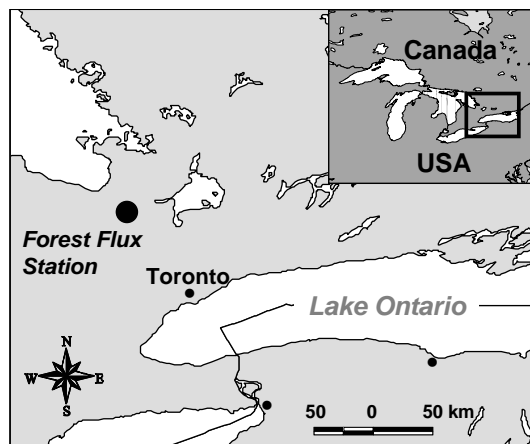


Figure 1. Location of the forest flux station at Borden, Ontario, Canada.

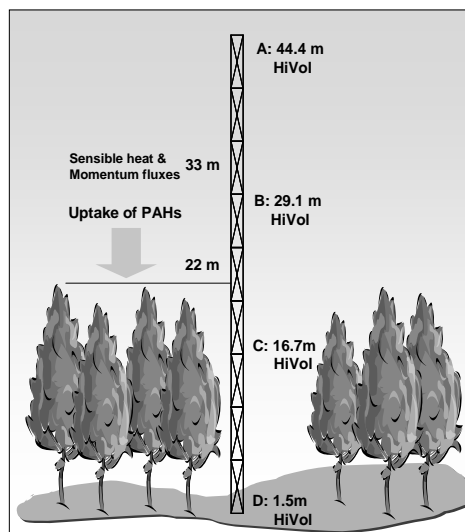


Figure 2. High volume air sampling at the different heights (A: 44.4 m, B: 29.1 m, C: 16.7 m, and D: 1.5 m) on the 45-m scaffold tower.

Results and Discussion

Temporal variations of PAHs

The temporal variation of total gaseous PAHs and the average PAH composition at different heights (A, B, C and D) are shown in Figure 3. Only gaseous PAHs showed different concentrations at different heights (Figure 3a), while those of particulate PAHs were relatively uniform (data not shown). The average composition of gaseous PAHs also showed differences with height (Figure 3b). For instance, the contribution of phenanthrene ranges from 51% to 62%. There was no variation in the particulate PAH compositions with height. These results indicate that only the level and composition of gaseous PAHs might be highly influenced by the forest canopy.

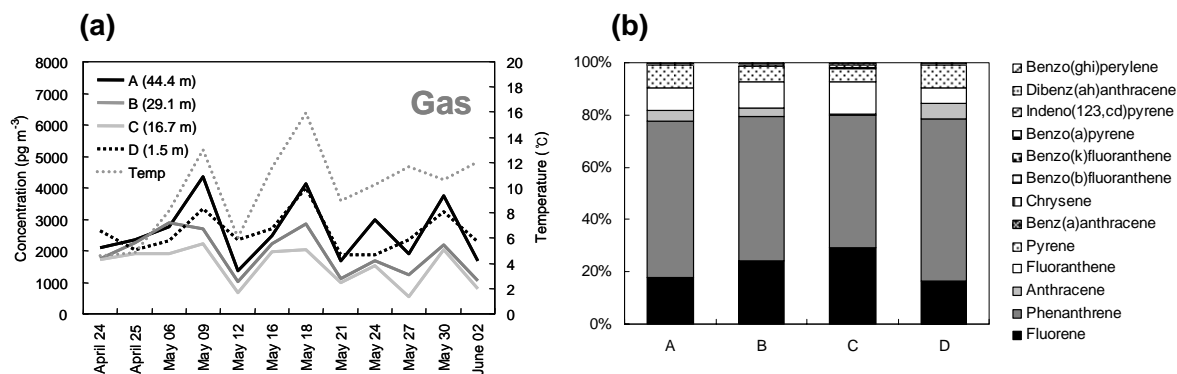


Figure 3. Temporal variations of the total gaseous PAH concentrations (a) and the average composition in the gaseous phase (b) at the different heights.

Vertical gradient of gaseous PAHs

In Figure 3a, the levels of gaseous PAHs at height B (29.1 m) and C (16.7 m), just above and below the top of the canopy, are clearly lower than those at height A (44.4 m) and D (1.5 m). This vertical gradient for the total gaseous PAHs is mainly due to phenanthrene which is dominant in all samples (Figure 3b). In order to confirm which compounds have vertical gradients, plots of the sampling heights versus concentrations of 13 PAHs for the gaseous and particulate phase were made. Concentration gradients with lower concentrations close to the canopy were established for gaseous PAHs with three and four rings, such as pyrene (Figure 4). They have $\log K_{OA}$ values of 7.8 to 8.9 (estimated from sub-cooled liquid vapor pressure^{5,6}), which is in the expected range for a

pronounced filter effect ($7 < \log K_{OA} < 11$).⁷ No such gradients were observed for highly volatile PAHs because of the low uptake capacity of the canopy for these PAHs, which may quickly establish equilibrium between air and the canopy. Gradients for less volatile PAHs were neither observed, because they were strongly associated with particles during the sampling period.

When a gradient was observed, the percentage of PAHs on particles increased at the elevations which experienced a decrease in concentration (Figure 4), suggesting that it was mostly the gaseous compounds that were taken up in new foliage. This is consistent with the lack of a gradient for the less volatile compounds. As expected, no strong gradients were observed on the first two sampling days in late April, which was prior to the emergence of the new foliage at the Borden forest. After budburst, the gradient was maintained throughout May and early June. This suggests that it is indeed the newly emerging foliage which results in the rapid uptake and a decrease in air concentrations. In addition to the gradients above the canopy, inverse gradients were often observed below the canopy, i.e. the PAH levels measured at the forest floor (1.5 m) were typically higher than the levels within and above the canopy. Again, this phenomenon was only observed for the more volatile PAHs, suggesting volatilization from forest litter.

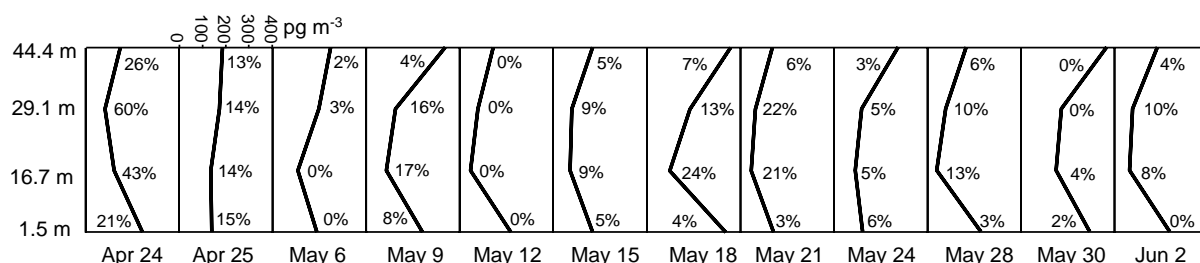


Figure 4. Vertical profile of gaseous pyrene during the sampling period. Percentages of these compounds on particles are assigned at the different heights.

Previous studies had identified critical $\log K_{OA}$ values of 9.9 and 9.7 for the gaseous deposition of SOCs to a German and a Canadian deciduous canopy, respectively.^{2,3} Compounds with $\log K_{OA}$ below that threshold approached equilibrium between air and the forest canopy during a growing season, whereas the uptake of less volatile SOCs is kinetically controlled. In this study, however, even relatively volatile PAHs with $\log K_{OA} < 9$ (phenanthrene, anthracene, and pyrene) were likely subject to kinetically limited dry gaseous deposition. This can be explained by the sampling date in early spring, when leaves had just been emerging and had not had time to approach equilibrium with atmospheric PAH levels. In contrast, the $\log K_{OA}$ thresholds in the previous studies were determined from data covering the entire growing season.

Gas/particle (G/P) partitioning behavior

Rapid uptake of gaseous PAHs by the forest canopy is expected to affect the G/P partitioning behavior. Since models based on the fraction in the particle phase (Φ) were found more suitable for fitting PAH data,⁴ we used the following two equations:

$$\text{One-parameter model: } \Phi = A / (P_L + A) \quad (1)$$

$$\text{Two-parameter model: } \Phi = 1 / (1 + 10^{-m \cdot \log(PL/Pa) - b'}) \quad (2)$$

where P_L is the vapor pressure of the sub-cooled liquid (Pa), and A , m , and b' are fitting parameters. The regression results (A , m , and b') for all 48 samples were listed and plots of observed G/P partitioning and fitting curves for the two models were made (data not shown). Both models have on average correlation coefficients of 0.96 and 0.97, respectively, and their fitting curves for the same sample are highly comparable. The curves for level B (29.1 m) are generally shifted to the right, implying an increased contribution of particulate PAHs above the forest canopy. In order to compare G/P partitioning at different heights, correlations between fitting parameters ($\log A$, m , and b') at two heights (A-B, A-C, A-D, B-C, B-D, and C-D) were investigated (Figure 5). Eight data sets (out of 48) with extreme slopes ($m > -0.6$ and $m < -2$) were excluded.⁴ Data points clustered close

to the diagonal 1:1 lines in Figure 5, imply a small difference in the fitting parameters between two heights.

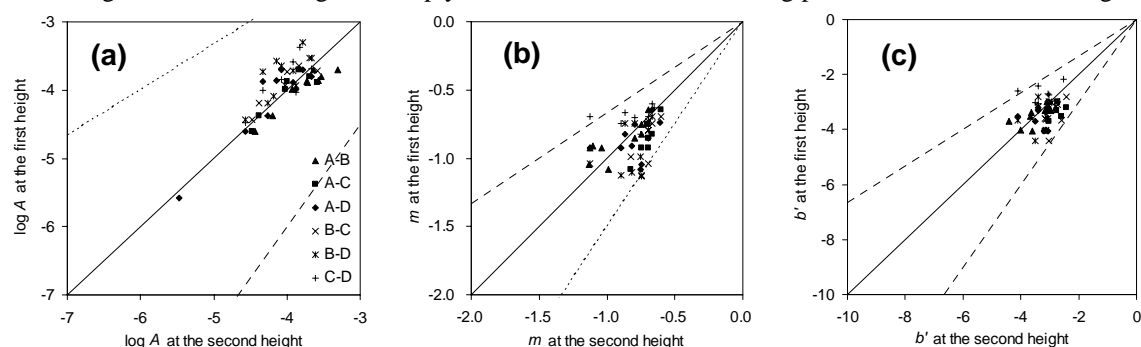


Figure 5. Correlation plots of the fitting parameters of $\log A$ (A), m (B), and b' (C) describing the gas/particle partitioning behavior of PAHs between the different heights (A-B, A-C, A-D, B-C, B-D, and C-D).

According to paired students' t-test with a two-tailed distribution, significant differences ($p < 0.01$) were observed in $\log A$ (A-B, B-D), m (A-C), and b' (A-C). This suggests that the G/P partitioning behavior above and within the canopy is statistically different. As parameter A is directly related to the capacity of the particles, the triangles for A-B to the upper right of the diagonal line (Figure 5a) indicate that air samples at level B have a higher fraction of PAHs on particles. This is consistent with the observation of increased Φ with decreased PAH concentrations above and within the canopy (Figure 4). Explanations for m and b' (Figure 5b,c) are also possible; the higher values of m and b' at level C produced shallower and rightward-shifted S curves, resulting in higher Φ for intermediate PAHs. This supports our assertion that canopy uptake of gaseous PAHs resulted in a change in G/P partitioning.

Acknowledgements

This work was financially supported by the Canadian Foundation for Climate and Atmospheric Sciences (Project GR-007: Forest as Filters of Persistent Organic Pollutants).

References

1. Simonich SL, Hites RA. *Nature* 1994;370:49.
2. Horstmann M, McLachlan MS. *Atmos. Environ.* 1998;32:1799.
3. Su Y, Wania F, Harner T, Lei YD. *Environ. Sci. Technol.* 2007;41:534.
4. Su Y, Lei YD, Wania F, Shoeib M, Harner T. *Environ. Sci. Technol.* 2006;40:3558.
5. Lei YD, Chankalal R, Chan A, Wania F. *J. Chem. Eng. Data* 2002;47:801.
6. Xiao H, Wania F. *Atmos. Environ.* 2003;37:2867.
7. McLachlan MS, Horstmann M. *Environ. Sci. Technol.* 1998;32:413.