

## Centered Accumulation and Equilibrium of PAHs on Indoor Window Films and the Influence of Central Heating

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### Introduction

Organic films can be formed on impervious surfaces (e.g., windows, roadways and roofs) through gaseous and particle deposition from air and have an important influence on the transportation and fate of organic pollutants in surrounding environments.<sup>1</sup> A variety of organic pollutants have been monitored in window films, including PAHs,<sup>2</sup> polychlorinated biphenyls (PCBs)<sup>3</sup>, phthalate esters (PAEs)<sup>4</sup> and polybrominated diphenyl ethers (PBDEs)<sup>5</sup>. Window film has the ability to respond rapidly to changes of air pollution in the indoor environment.

Since the film works as a passive sampler, the gas phase concentration of PAH can be estimated in principle if the partition coefficients between the window films and air can be determined at equilibrium condition. The window film can represent the air condition at the time of sampling and allows for the prediction of short-term variability of organic compounds in air.<sup>4</sup> Thus it is crucial to determine whether the chemicals in the organic film is at equilibrium with those in air. Therefore, the objective of this study is to evaluate the accumulation of PAHs and congener profiles along with their partition status developed in indoor window films weekly collected during the heating season and non-heating season in a typical northeastern Chinese city. Obtaining such data to evaluate the temporal variability is very important, and then the potential human health risks for people who working in the buildings can be estimated.

### Materials and methods

**Sample Collection and Process.** A total of 8 time-serials of window film samples with exposure duration of 7-77 days were collected in winter of 2014 (heating season) and summer of 2015 (non-heating season) from two different buildings (A and B) of a university in Harbin, Northeast China. The windows selected for sampling were pre-cleaned with ethanol soaked Kimwipes (Kimberly Clark, Roswell, Georgia, USA) prior to the sampling campaign. All the collected film samples were extracted by shaking with acetone: dichloromethane (1:1, Volume: Volume) and analyzed for 15 priority PAHs by gas chromatography /mass spectrometry.

**QA/QC and Statistical Analysis.** Each batch of 12 samples consisted of two procedural blanks and two method spikes. All samples were spiked with surrogate recovery standards containing naphthalene-D<sub>8</sub>, fluorene-D<sub>10</sub>, pyrene-D<sub>10</sub> and perylene-D<sub>12</sub> prior to extraction to determine analytical recovery efficiencies. Mean recoveries for the film samples were 73 ± 11%, 79 ± 11%, 83 ± 10% and 86 ± 11% for naphthalene-D<sub>8</sub>, fluorene-D<sub>10</sub>, pyrene-D<sub>10</sub> and perylene-D<sub>12</sub>, respectively. The statistical analyses were performed using SPSS 22.0 for samples.

### Results and discussion:

**Comparison between two seasons.** PAH concentrations are presented in two ways, one is area-normalization which reflects the total concentrations of PAHs in the surrounding environment; the other is mass-normalization which shows the content of PAHs associated with window film<sup>6</sup>. The geometric mean (GM)

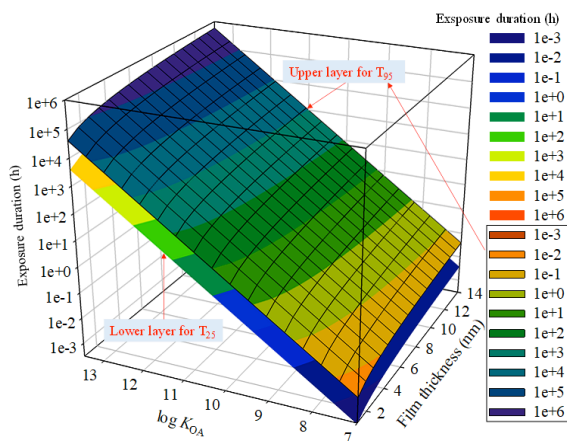


Figure 1. The 3D maps for log  $K_{OA}$  vs film thickness vs exposure duration.

concentration of  $\Sigma_{15}$ PAHs in heating season samples was 1300 ng/m<sup>2</sup> film, approximately 30 times higher ( $p < 0.001$ ) than that in non-heating season samples with the GM levels of 45 ng/m<sup>2</sup> film. Among the PAHs determined in heating season, BbF was the most abundant compound with GM concentrations of 200 ng/m<sup>2</sup>, followed by Fluo (190 ng/m<sup>2</sup>), Chr (160 ng/m<sup>2</sup>) and Pyr (150 ng/m<sup>2</sup>). In non-heating season, the dominant compound samples were Phe, BbF and Fluo with the median concentrations of 12 ng/m<sup>2</sup>, 5.7 ng/m<sup>2</sup>, and 3.5 ng/m<sup>2</sup>, respectively.

Indoor window films are expected to collect gas-phase chemicals as well as chemicals in the particulate matter, therefore similar to the indoor dust chelating chemical pollutants. The median concentration of  $\Sigma_{15}$ PAHs in heating season samples was 240  $\mu\text{g/g}$  film, approximately 23 times higher than that in non-heating season samples with the median level of 10  $\mu\text{g/g}$  film. For the dust samples in non-heating season, the concentrations ranged between 4.2 and 21  $\mu\text{g/g}$  with the median value of 6.9  $\mu\text{g/g}$  dust, which were very close to that of window film samples collected in the same season.

**Accumulation Characteristics of PAHs.** The accumulation characteristics of PAHs concentrations in the window films in heating season and non-heating season showed that the correlation between the concentrations of PAHs (in ng/m<sup>2</sup> film) and exposure duration were positive and significant at  $p < 0.05$ , suggesting that the concentrations of PAHs (ng/m<sup>2</sup> film) were growing in a near-linear pattern with time exposed. Near-linear accumulations of window films were observed in this study, similar to what had been reported in previous studies.<sup>2</sup> This growth patterns suggested that the concentrations of PAHs (in ng/m<sup>2</sup>) would continue to increase with the accumulation of films.

The exposure duration is an important factor affecting the accumulation of PAHs in window films. Meanwhile, significant higher concentrations of PAHs were found in window film samples collected in heating season (heating season) than those collected in non-heating season ( $p < 0.001$ ). The exchange between air and window films, and the similarity in trends between these two matrixes suggested that the influence of outdoor air was very important to the indoor environment because there were no major sources of PAHs inside these two building.

**Growth of bulk film thickness as a function of exposure time.** The bulk film thickness was then plotted against exposure duration of the window films in order to derive an equation to fit the monitoring data. The derived equation was given by

$$FT = (0.16 \pm 0.01) \times GD - (0.65 \pm 0.33) \quad (1)$$

where FT is the bulk film thickness (nm), and GD is the growth days of the film. The correlation coefficients were significant with growth days explained 71% of the variances ( $r^2$ , with  $p < 0.01$ ) in film thickness. The result showing that the bulk film thickness was positively and significantly correlated with the exposure duration (1-7 weeks) of the window films.

A multicomponent partitioning model predicted a pure film thickness of 7.9 nm and 13.9 nm over one year period based on some assumptions (see Figure 1 of the cited reference).<sup>7</sup> This pure film thickness was converted into the bulk film thickness with the values of 32 nm and 56 nm, respectively. An initially faster growth rate of the films and an almost steady growth rate subsequently were observed.<sup>5</sup> For example, a near linear film growth with an average growth rate of 1.6-2.6 nm/day was found for a sheltered glass beads.<sup>8</sup> It should be pointed out that higher TSP and total SVOC concentrations in China would result in faster film growth.

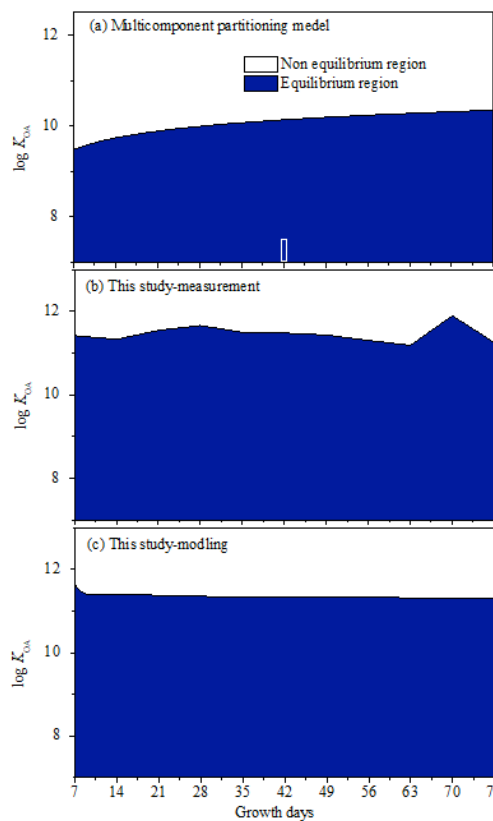
**Gas/film partitioning.** To determine the certain time of the window film uptake in which stage of the uptake curve was, the condition is derived from  $K_U$  as follows:<sup>9</sup>

$$T_{95} = \ln(0.05) / K_U \quad (2) \quad T_{25} = \ln(0.75) / K_U \quad (3)$$

where  $K_U$  is the uptake rate (1/h). The equilibrium condition was achieved when the exposure duration ( $T_{exp}$ ) of the window film was higher than  $T_{95}$  (the time to 95% equilibrium); when  $T_{exp} < T_{25}$  (the time to 25% to equilibrium), the uptake of chemical was in a linear stage; and if  $T_{25} < T_{exp} < T_{95}$ , the chemical in the window films can be assumed to be in the curve stages.

The  $T_{95}$  as a function of  $\log K_{OA}$  and film thickness was shown in Figure 2. Using the time to reach 25% of equilibrium and time to reach 95% of equilibrium, the relationship for  $\log K_{OA}$  versus film thickness versus exposure duration showed that the increasing values of  $\log K_{OA}$  and film thickness would increase the exposure duration required to reach 25% or 95% of equilibrium between air and films (Figure 1). The time to reach 95% equilibrium ( $T_{95}$ ) is generally longer than the time of linear stage ( $T_{25}$ ) by a factor of 10. When the  $\log K_{OA}$  values are known for a certain compound, the relationship between film thickness (nm) and exposure duration (h) could be illustrated. For example, when film thickness = 12 nm, PAHs with  $\log K_{OA} = 11$  would be in linear stage ( $T_{25}$ ) within 81.3 h of exposure and reach 95% equilibrium with exposure duration greater than 847.5 h.

**Relationship between  $\log K_{OA}$  of PAHs and exposure time under equilibrium.** Figure 2 shows the modeling results of the predicted equilibrium regions for  $\log K_{OA}$  as the function of film growth days (7-77 days) under three scenarios. In Scenario 1, the predicted pure films growth over time by Weschler and Nazaroff<sup>7</sup> was firstly converted into the bulk film thickness. Then  $\log K_{OA}$  threshold to reach the equilibrium stage can be calculated using the known film thickness at certain film growth days. The  $\log K_{OA}$  was plotted against exposure duration to show the equilibrium regions using  $\log K_{OA}$  as a surrogate (Figure 2(a)). Initially ( $T_{95} = 1$  h), the



**Figure 2.** Modeling the predicted equilibrium regions for  $\log K_{OA}$  as the function of indoor film growth (7-77 days).

PAHs with  $\log K_{OA}$  values  $\leq 8.7$  could reach the equilibrium stage at thinner films. With increasing exposure time and film thickness, the equilibrium regions increase rapidly and then diminish to an almost steady rate and limited to  $\log K_{OA}$  values  $\leq 11.8$  within 500 days of exposure. In Scenario 2, using the film thickness of at each sampling event from our measurement, the  $\log K_{OA}$  vs exposure duration plot showed that the  $\log K_{OA}$  values of PAHs should be less than or equal to  $11.5 \pm 0.2$  (Figure 2(b)). In Scenario 3: the equilibrium region was predicted using the linear regression model for the growth of bulk film thickness as described by Equation (1), showing that the PAHs with  $\log K_{OA}$  values  $\leq 11.6$  could reach the equilibrium stage at thinner films (Figure 2(c)). Under this circumstance, the equilibrium regions decrease slowly and then diminish to an almost steady rate and limited to  $\log K_{OA}$  values  $\leq 11.3$  within 77 days of exposure.

Considering that the exposure days is the time to reached 95% equilibrium, and the relationship between film growth days and film thickness is actually the film growth rate. Accordingly, the relationship between equilibrium regions for different  $\log K_{OA}$  and the film growth rate can be established (Figure 3). This figure shows that equilibrium can be reached for higher  $\log K_{OA}$  compounds under slower film growth rate. As film growth rate increased, it would require a lower  $\log K_{OA}$  value for a certain compound to reach the equilibrium. The equilibrium condition for compounds is that the  $\log K_{OA}$  less than the values ranged from 10.85 for faster film growth rate (0.50 nm/day) to 12.39 for slower film growth rate (0.01 nm/day).

**Prediction of Air Concentration.** The predicted median air concentrations of  $\Sigma_{15}$ PAHs in heating season and non-heating season were 900 and 240  $\text{ng}/\text{m}^3$ , respectively. Greater levels of PAHs were obtained in heating season than in non-heating season, which was a consistent result of the window film data.

Generally, the estimated concentration of PAHs were reported to be higher than the real measurement.<sup>6</sup>

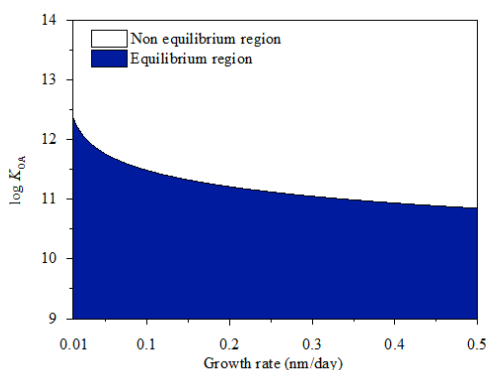


Figure 3. Modeling equilibrium regions for  $\log K_{OA}$  as a function of film growth rate.

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