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OCCURRENCE AND HUMAN EXPOSURE TO PHTHALATE DIESTERS AND POLYCYCLIC AROMATIC HYDROCARBONS IN INDOOR WINDOW FILMS IN HARBIN, NORTHEAST CHINA

C.Y. Huo¹, L.Y. Liu¹, W.L. Ma¹, Z.F. Zhang¹, W.W. Song¹, H.L. Li¹, W.L. Li¹, Y.F. Li¹

¹*International Joint Research Center for Persistent Toxic Substances (IJRC-PTS), State Key Laboratory of Urban Water Resource and Environment, School of municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, P. R. China*

Introduction

Phthalate diesters (PAEs) were reported to possess endocrine disrupting potential, and have been classified as priority organic pollutants by the U. S. Environmental Protection Agency (USEPA) and by the Chinese National Environmental Monitoring Center. Due to their wide application in consumer products, PAEs have been detected in various environmental media worldwide. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants listed as priority pollutants in many countries. They have been of concern for several decades due to their ubiquity in the environment and adverse effects on human beings. Semi volatile organics (SVOCs) can be adsorbed onto and absorbed into the organic film on glass windows as well as human skin. It is important to measure the levels of PAEs and PAHs in indoor window film because dermal uptake directly from air has been suggested to be a largely overlooked and potentially important pathway for the indoor human exposure.

The objectives of this study are: (1) to examine the growth characteristics of both mass and thickness of window films as functions of time (days), (2) to investigate the occurrence and growth behavior of PAEs and PAHs in indoor window films, (3) to understand the differences in the concentrations and profiles of PAEs and PAHs in summer and winter, and (4) to evaluate potential human health risk from exposure to indoor air and dust for people working inside the buildings.

Materials and methods

Sample collection. Indoor window film samples (n=64) were collected in 2 buildings of a university in Harbin, China in winter of 2014 and summer of 2015. In Building A, samples were collected from indoor window glasses (upper samples at 1.5-2.0 m above the ground, lower samples at 2.0-2.5 m above the ground) on the west side In Building B, samples were collected in south and north sides of the same floor. The samples were collected every 7 days at the same time. All the indoor window film samples were pre-cleaned with ethanol soaked Kimwipes (Kimberly Clark, Roswell, Georgia, USA) prior to the sampling campaign.

Sample preparation. The indoor window film samples were analyzed for 6 PAEs and 1 PAHs. Prior to extraction, surrogate standards were spiked into all samples. Samples were extracted with 40 mL of acetone:dichloromethane mixture (1:1, V:V) for 60 min using an agitator. The extraction were repeated twice using 30 mL of the solvent mixture, then combined the extract and passed through anhydrous sodium sulfate to remove moisture. The extract was solvent exchanged to isoctane using the rotary evaporator, then blown down to a volume of 0.8 mL in isoctane under a gentle nitrogen stream, and the final volume was adjusted to 1.0 mL for instrumental analysis.

Instrumental analysis. Total 6 PAEs were analyzed with Agilent 6890 gas chromatography/5975B mass spectrometry in electron capture negative ionization mode equipped with a DB-5 column (60 m×0.25 mm×0.25 μm), using following temperature program: held at 80 °C for 1 min, 25 °C /min to 230 °C, and held for 3 min, 20 °C /min to 270 °C, and held for 2 min, 15 °C /min to 300 °C, and held for 3 min. The temperatures were 150 °C, 230 °C, and 250 °C for the quadrupole, ion source, and interface, respectively. A 16 PAHs were analyzed with Agilent 6890 gas chromatography/5973 mass spectrometer in selected ion monitoring (SIM) mode equipped with HP-5MS capillary (column 60 m×0.25 mm×0.25 μm). The column temperature programs were used as follows: held at 90 °C for 1 min, then raised from 90 to 180 °C with 10 °C /min, held for 1 min, from 180 to 280 °C at 3 °C /min, held for 20 min.

QA/QC. For each batch of 10 samples, a method blank and a spiked blank were processed. The mean recoveries of PAEs in the spiked samples and recovery standard in real samples ranged from 96-116% and 70-86%, respectively. All concentrations of phthalates in indoor glass samples were corrected with

blank values and recoveries. The mean recoveries of PAHs in the spiked samples and recovery standard in real samples ranged from 76-87% and 71-85%, respectively.

Results and discussion

The Growth of Indoor Window Film. The film mass (in mg/m² film) was plotted against time (in days) of growth of the window film (Figure 1). Linear regression analysis suggested that the film mass was positively and significantly correlated with the days of film growth days for all cases (from 7 to 77 days, $p < 0.05$). This nearlinear accumulation of window film suggested that the film did not reach a saturable condition. It has been reported that the window film continued to grow even after 273 days or upto two years.

Occurrence and Profiles of PAEs and PAHs. PAEs were detected in all window film samples. The median concentrations of $\Sigma 6$ PAEs in winter samples were 9900 ng/m² film or 2000 $\mu\text{g/g}$ film, approximately 2 times higher than that in summer samples (the median were 4700 ng/m² film or 650 $\mu\text{g/g}$ film). Among 6 PAEs compounds determined, di-(2-ethylhexyl) phthalate (DEHP) was the dominant compound in both winter and summer, followed by dibutyl phthalate (DBP).

PAHs were 100 % detected in window film samples ($n = 64$). For all the samples, the median concentrations of total PAHs ($\Sigma 16$ PAHs) in winter (1277 ng/m² film or 321 $\mu\text{g/g}$ film) were two orders of magnitude higher than that found in summer (44 ng/m² film or 8.80 $\mu\text{g/g}$ film). In winter, 4 rings PAHs accounted for 47.5 ± 5.43 % of $\Sigma 16$ PAHs concentrations, followed by 5 rings PAHs (22.8 ± 4.0 %). However, 2 and 3 rings PAHs accounted for the largest proportion of $\Sigma 16$ PAHs concentrations in summer.

Factors Affecting Concentrations of PAEs and PAHs in Window Films. The number of days of film growth is the most important factor that influence the concentrations of PAEs (in ng/m²) in window film. The concentrations of DBP, butyl benzyl phthalate (BBP), DEHP and $\Sigma 6$ PAEs (in ng/m²) significantly increased with the number of days exposed ($p < 0.05$, Figure 2a and 2b). However, no such trend was observed for dimethyl phthalate (DMP), diethyl phthalate (DEP) and di-iso-butyl phthalate (DiBP) ($p > 0.05$). The proportion (%) of low molecular weight PAEs such as DMP and DiBP significantly and negatively correlated with the number of days of film growth ($p < 0.05$) and a positive correlation was observed for high molecular weight compounds such as BBP (Figure 2c).

Significant and positive correlations among PAHs were found for the samples (Figure 3). Significant higher concentrations of PAHs in winter suggested that serious pollution of PAHs in cold winter, which were due to the biomass burning and the poor ventilation during cold winter season. Source apportionment confirmed that the source of PAHs in winter was from biomass burning.

Derivation of Air Concentrations and Human Exposure to PAHs. The ambient air concentration of PAEs and PAHs was derived from the concentrations measured in window films, on the basis of the assumption that gasphase and film-phase (window film) concentrations are at equilibrium. The predicted median air concentrations of DiBP and DBP in winter season were lower than that of summer season.

On the basis of the air and window film PAE and PAH concentrations, the estimated daily exposure dose and health risks posed to teenagers and adults who lived in these building were calculated. For PAEs, the exposure risk generally followed the order of DBP > DEHP > DiBP. In winter, the median HQ values for teenagers and adults were 0.11 and 0.095, respectively, and these values were similar to that calculated for summer, suggesting a similar exposure risk.

The median toxic equivalent quantity (TEQ) of PAHs were 14 and 2.0 ng/m³ for winter and summer samples, respectively. The median cancer risk for exposure to PAHs for teenagers were 4.7×10^{-4} and 6.5×10^{-6} in winter and summer, respectively, suggesting that the low cancer risk of PAHs.

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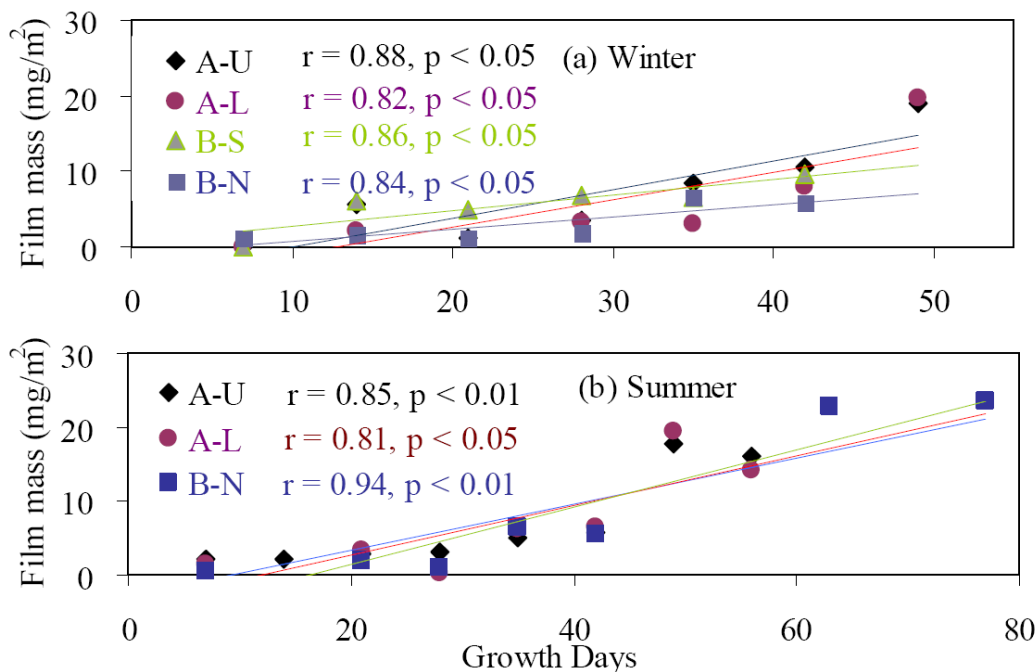


Figure 1. The growth of film mass (mg/m^2) as a function of days. (A: Building A; B: Building B; U: upper window glass; L: lower window glass; N: north orientation; S: south orientation.)

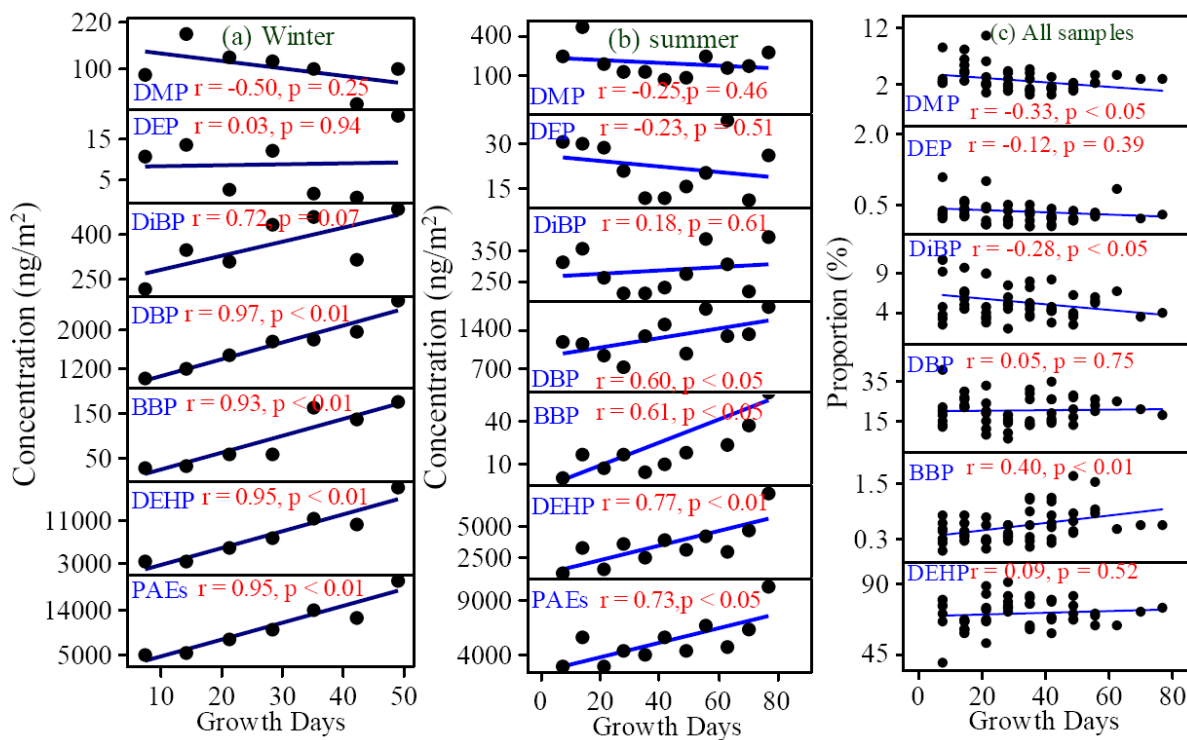


Figure 2. The concentrations of PAE compounds (ng/m^2) and their proportion (%) in glass window films as a function of film growth with time

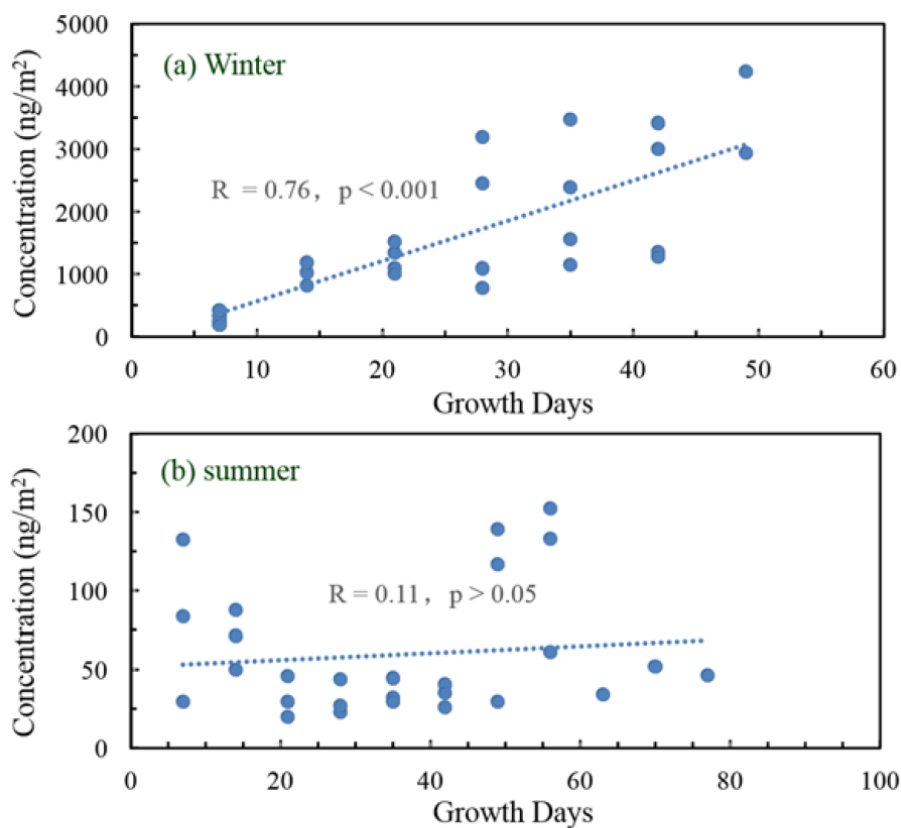


Figure 3. The concentrations of PAHs (ng/m²) in glass window films as a function of film growth with time