

# Dry deposition of atmospheric polycyclic aromatic hydrocarbons (PAHs) in the southeast suburb of Beijing, China

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## Abstract

Dry deposition is an important path for pollutants entering soil and water. In this study, dustfall samples were collected at four representative sampling sites in the southeastern suburb of Beijing from March, 2005 to January, 2006, with a frequency of about once per month, and were analyzed for 16 USEPA priority PAHs using GC/MS. Results showed that the levels of  $\Sigma 16$ PAHs in dustfall samples were 0.72–40.45  $\mu\text{g g}^{-1}$ . The levels of PHE and DahA were the highest and lowest among the 16 PAH compounds, with annual mean values of 2.07  $\mu\text{g g}^{-1}$  and 0.009  $\mu\text{g g}^{-1}$ , respectively. Two and three ring PAH compounds were the dominant ones in dustfall samples. The distribution patterns of PAH compounds in different rings in dustfall were different from those in TSP and gas phase. Annual average fluxes of dustfall and PAHs were 1 296.67  $\text{mg m}^{-2} \text{d}^{-1}$  and 5.14  $\mu\text{g m}^{-2} \text{d}^{-1}$ , respectively. There were about 423 387.6 t dustfall and 1.7 t PAHs depositing onto the surface of Tongzhou District in 2005. Impacts of ground dust, meteorologic parameters, air pollution indexes and deposition velocities on PAHs deposition were discussed. Correlation analysis showed that the fluxes of 2–3 ring PAH compounds had significant positive correlation with the concentrations of 2–3 ring PAH compounds in TSP, and the fluxes of 4 ring PAH compounds had significant positive correlation with those in both TSP and gas phase, while no significant correlation existed between the fluxes of 5–6 ring PAH compounds and the concentrations of 5–6 ring PAH compounds in TSP or gas phase. A regression model was established to estimate the PAH fluxes.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in atmosphere and were detected in many mediums (Wilcke et al., 2002). Most PAH compounds can accumulate in soil, water and sediment, and enter human bodies through food chains (Zufall et al., 1998).

Researches on atmospheric PAH deposition have been carried out widely (Poor et al., 2004; Bae et al., 2002). In China, however, few relevant studies have been made (Wu et al., 2005).

There are two widely used methods in PAH deposition estimation. The first one could be applied based on the monitoring of PAH concentrations in both particle and gas phases. With this method, the deposition rate could be obtained by multiplying the concentration and deposition velocity (Fang et al., 2004). For the second one, gaseous and particulate PAHs are collected directly on an artificial surface, such as water surface

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(Yi et al., 1997; Golomb et al., 1997), and the deposition rate could be calculated based on concentration, sampling period and other information.

Deposition is an important path for PAHs leaving air and could be driven by gravity or washout of snow and rain (Panther et al., 1999). Dustfall samples can be used to analyze the pollution status near the sampling sites. Coarse particles in atmosphere are scavenged mainly by gravity, while pollutants could transport with fine particles for long-distance (Hou et al., 2006). Pollutants in the gas phase may stay in the air for longer time.

Deposition velocity could be affected by meteorological and other parameters such as temperature, wind speed (Lee and Lee, 2004), population, and traffic volume (Otvos et al., 2004). However, most findings of previous studies were achieved based on the bivariate correlation analysis between PAHs and impact factors, and the correlations between the impact factors were frequently ignored.

In this study, concentrations and seasonal variation of PAHs in dry deposition samples in Tongzhou District, Beijing, were studied. Partial correlation analysis was used to analyze the impacts of parameters on PAH deposition. In addition, relationships between PAH deposition and gaseous and particulate PAHs in atmosphere were analyzed.

## 2. Experiments

### 2.1. Site description

Tongzhou District is an important agricultural and industrial area of Beijing, and has a complicated road system. It is located in the southeastern suburb of Beijing City. Dry deposition samples were collected at 4 representing sites, including the Tongzhou Environment Monitor Station (EMS), Zhangxinhuang village (ZX), Beisicun village (BS) and Liuhe village (LH). The longitude and latitude of the 4 sampling sites are 116.66°E, 39.89°N, 116.73°E, 39.86°N, 116.74°E, 39.97°N and 116.70°E, 39.94°N, respectively.

The EMS sampling site is located on the roof of the office building of the Environmental Monitoring Station (three floors building), and the roof is covered with pitch. The EMS site is surrounded by residential buildings and light-traffic roads, and thus could represent the pollution of urban residential area. The ZX site is located on a grass field in ZX village, with a primary school and farmlands surrounding it. An industrial park is to the north of the ZX site, so it could represent the pollution of industry. The BS site is located in BS village, and is surrounded by countryside

houses. Therefore this site could represent the pollution of countryside residential area. The LH site is located in LH village and near the National Road No. 102, which has heavy traffic all year round, so it could represent the pollution of road traffic.

### 2.2. Sample collection

Glass buckets (i.d.  $30 \pm 0.5$  cm, height 30 cm, flat-bottom) were chosen to collect bulk deposition (dry and wet depositions were mixed together) from March 2005 to January 2006. Samples were collected once a month. Due to the weak deposition, an interval of two months was chosen from June to July. The buckets were laid on sites since February 28th, 2005, and samples were collected on April 1st, May 1st, June 2nd, July 29th, September 10th, October 19th, November 19th, December 17th, and January 13th, 2006, respectively. Nine groups of samples were gained in total.

According to the data provided by Tongzhou Meteorological Bureau, the annual precipitation in Tongzhou District in 2005 was 412.5 mm, with 261.7 mm in summer. Since the contribution of wet deposition was small for the whole year, no wet deposition samples were collected separately in this study, and all samples were treated as dry deposition (dustfall). Similar methodology was used elsewhere (Wu et al., 2005).

All sampling sites are located in open areas, without trees, buildings or any other sheltering objects near them. To reduce the impacts of ground dust, sampling buckets were placed on platforms about 0.5 m above the ground at all sites. Distilled water was added into the buckets before sampling, and the amount of distilled water was determined according to the evaporation and precipitation situation, generally 50 mL in summer and winter, and 100 mL in other seasons. About 60 mL glycol was also added into each bucket to avoid the freezing of water in winter and reduce the effects of biodegradation. Pilot experiment was conducted to investigate the impact of glycol on deposition through the comparison of two buckets, of which one bucket was added with glycol and water, and the other one was added with water only. Results showed that the impact of glycol is negligible. Leaves and insects were picked out using forceps before sample collection. The samples were kept in a refrigerator ( $-18$  °C) before analysis.

### 2.3. Extraction and analysis

Water in dustfall samples was removed using a freeze drying machine (FD-1A, Beijing Boyikang Apparatus

Company, China) before analysis, and the weight of each sample was measured in order to calculate the dustfall and PAHs fluxes. PAHs in the samples were extracted by acetone and cyclohexane (1:1) for 20 h at 72 °C using soxhlet extraction. The extraction liquid passed through a silica column to separate PAHs fractions from other interfering materials. The elute of the samples was rotary evaporated and concentrated to 2 mL, added with known quantities of internal standard 2-Fluorobiphenyl and *p*-Terphenyl-*d*<sub>14</sub>, and then transferred into vials before analysis using GC–MS (Agilent GC 6890/5973 MSD).

Sixteen USEPA priority PAHs were measured in this study. The 16 PAH compounds are: naphthalene (NAP), acenaphthene (ANE), acenaphthylene (ACY), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DahA), indeno(1,2,3-cd)pyrene (IcdP) and benzo(g,h,i)perylene (BghiP).

#### 2.4. Quality control and quality assurance

A 100 mL solvent blank was concentrated to 200 µL, and then analyzed in order to monitor the solvent background. For each batch of samples, two procedure blank samples were used. All PAH concentrations were blank corrected according to the mean value of two procedure blank samples in the same batch. Duplicate analysis was carried out for half of the dustfall samples, and the relative percentile differences for individual PAH in duplicate samples were less than 15%.

Known quantities of 16 PAH standards were added into the solvent blank to estimate the method recovery, and the recoveries of 16 PAHs ranged from 59.32% (NAP) to 107.24% (PHE). Five PAHs surrogates consisting of naphthalene-D<sub>8</sub>, acenaphthene-D<sub>10</sub>, phenanthrene-D<sub>10</sub>, chrysene-D<sub>12</sub> and perylene-D<sub>12</sub> standards were added to solvent blanks and samples before extraction, and the average recoveries of surrogates were 74.19%–86.85%. The limits of detection (LD, ng) were defined as the mean blank values plus 3 standard deviations, and the LDs for the 16 individual PAH compounds ranged from 0.005 (BbF) to 0.072 (PHE) µg g<sup>-1</sup>.

#### 2.5. Other data

PAHs in total suspended particle (TSP) and gas phase at 3 sites (EMS, ZX and BS) were also collected from March, 2005 to January, 2006 with a frequency of about

once a month. TSP and PAHs in gas phase were captured by glass fibre filters (GFFs) and polyurethane foams (PUFs), respectively. PAHs in GFFs and PUFs were extracted by hexane and cyclohexane (1:1) for 8 h at 90 °C using soxhlet extraction. The extraction liquid of GFFs passed through a silica column to eliminate interfering materials. The elutes of GFFs and PUFs were concentrated, added with known quantities of internal standard, then transferred into vials before PAHs were analyzed using GC–MS. The sampling and experimental details of PAHs in TSP and gas phase were described in another research report.<sup>1</sup>

Daily air pollution indexes (API) of Tongzhou District for the sampling period, including SO<sub>2</sub>, NO<sub>x</sub> and PM<sub>10</sub>, were obtained from the website of Beijing Environment Protection Bureau.<sup>2</sup> Simultaneous meteorological parameters of temperature (*t*), pressure (*p*), relative humidity (RH), wind direction (WD) and wind speed (WS) were provided by Tongzhou Meteorological Bureau.

### 3. Results and discussion

#### 3.1. Descriptions of PAHs in dustfall

##### 3.1.1. Concentration characteristics

Most of 16 PAH compounds were detected in all dustfall samples, and concentrations of DahA were below LDs for all samples. In this study, all values below LDs were replaced by LDs. The maximum and minimum of ∑16PAHs were 40.45 µg g<sup>-1</sup> at EMS site in December and 0.72 µg g<sup>-1</sup> at BS site in June and July, respectively. PHE and DahA were the dominant and lowest compounds among the 16 PAHs, with annual mean values of 2.07 µg g<sup>-1</sup> and 0.009 µg g<sup>-1</sup> (LD), and standard deviations of 2.82 and 0.00, respectively. PHE had the largest range among 16 PAH compounds for the whole sampling period (from 0.20 µg g<sup>-1</sup> to 17.95 µg g<sup>-1</sup>), while IcdP had the smallest range (from 0.008 µg g<sup>-1</sup> to 0.079 µg g<sup>-1</sup>). Among the 4 sampling sites, EMS had the maximum annual mean of ∑16PAHs (9.64 µg g<sup>-1</sup>), while BS had the minimum of 1.62 µg g<sup>-1</sup>. The standard deviations for these two sites were 12.92 and 0.77, respectively.

In Beijing, summer and winter are longer than spring and autumn. Therefore, samples collected during

<sup>1</sup> Zhang, S. C., Zhang, W., Wang, K. Y., Shen, Y. T., Hu, L. W., Wang, X. J., 2006. Atmospheric polycyclic aromatic hydrocarbons in the southeast suburb of Beijing, China. Beijing: College of Urban and Environmental Sciences, Peking University, 1–17.

<sup>2</sup> <http://www.bjepb.gov.cn>.

Table 1  
Seasonal concentrations of 16 PAH compounds in dustfall ( $\mu\text{g g}^{-1}$ )

		NAP	ACE	ACY	FLO	PHE	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	IcdP	DahA <sup>a</sup>	BghiP
EMS	Spring	0.49	0.09	0.02	0.24	1.48	0.09	0.82	0.35	0.02	0.13	0.04	0.02	0.01	0.01	0.01	0.01
	Summer	0.26	0.03	0.01	0.10	0.57	0.06	0.39	0.23	0.02	0.15	0.04	0.04	0.01	0.02	0.01	0.01
	Autumn	0.30	0.08	0.02	0.21	1.85	0.11	1.87	0.90	0.10	0.55	0.13	0.11	0.03	0.03	0.01	0.01
	Winter	1.06	0.65	0.05	1.49	11.53	0.70	6.11	3.40	0.24	0.57	0.17	0.11	0.06	0.02	0.01	0.02
ZX	Spring	0.34	0.04	0.01	0.16	0.90	0.11	0.56	0.29	0.03	0.06	0.04	0.02	0.01	0.01	0.01	0.01
	Summer	0.35	0.05	0.01	0.17	0.83	0.07	0.51	0.36	0.04	0.20	0.09	0.06	0.04	0.04	0.01	0.02
	Autumn	1.34	0.29	0.04	0.55	4.54	0.37	4.19	2.39	0.33	1.08	0.30	0.29	0.21	0.07	0.01	0.04
	Winter	0.80	0.24	0.03	0.49	4.07	0.45	3.64	2.13	0.27	0.65	0.25	0.20	0.12	0.05	0.01	0.04
LH	Spring	0.45	0.08	0.04	0.21	1.33	0.14	0.94	0.54	0.05	0.13	0.05	0.04	0.03	0.02	0.01	0.01
	Summer	0.19	0.02	0.01	0.10	0.51	0.05	0.33	0.25	0.03	0.12	0.04	0.04	0.03	0.02	0.01	0.01
	Autumn	0.24	0.07	0.03	0.14	1.16	0.13	1.23	0.84	0.16	0.38	0.11	0.11	0.11	0.03	0.01	0.02
	Winter	0.18	0.10	0.01	0.24	2.57	0.20	1.93	1.09	0.15	0.32	0.14	0.12	0.08	0.04	0.01	0.03
BS	Spring	0.19	0.02	0.01	0.09	0.39	0.04	0.23	0.13	0.02	0.04	0.02	0.01	0.01	0.01	0.01	0.01
	Summer	0.07	0.01	0.00	0.05	0.31	0.03	0.20	0.14	0.02	0.09	0.03	0.03	0.01	0.01	0.01	0.01
	Autumn	0.15	0.04	0.01	0.09	0.55	0.06	0.55	0.37	0.09	0.26	0.09	0.08	0.06	0.03	0.01	0.01
	Winter	0.09	0.04	0.00	0.08	0.61	0.06	0.43	0.25	0.04	0.08	0.05	0.03	0.02	0.01	0.01	0.01

<sup>a</sup> Values in this line were the LDs of DahA.

February 28th–May 1st (61 d), May 1st–September 10th (131 d), September 10th–November 19th (70 d) and November 19th–January 13th, 2006 (55 d) were treated as representative samples of spring, summer, autumn and winter, respectively. PAH concentrations of the 4 seasons were calculated and listed in Table 1.

### 3.1.2. Temporal and spatial variation

The mean seasonal concentrations of  $\sum 16\text{PAH}$  at all sampling sites were 2.93, 1.90, 7.39 and  $12.16 \mu\text{g g}^{-1}$  in spring, summer, autumn and winter, with standard deviations of 1.31, 0.75, 5.98 and 10.49, respectively. They followed the order of winter > autumn > spring > summer.

Monthly total concentrations of 16 PAHs at 4 sampling sites were shown in Fig. 1(a). In general, they followed the order of EMS > ZX > LH > BS. Compared with the other 2 sites, concentrations of  $\sum 16\text{PAHs}$  at BS and LH sites were relatively steady among seasons, while at the other 2 sites, concentrations of  $\sum 16\text{PAHs}$  from October to December were much higher than in other months. Seasonal PAH sources might exist near EMS and ZX sites from October to December.

Concentrations of PAHs in summer were the lowest at all sampling sites based on paired-samples *t* test ( $\alpha=0.05$ ). Some PAH compounds, especially the light molecular weight compounds, tend to stay in gas phase due to the high air temperature in summer (Lee and Lee, 2004). Photolysis and rain washout effects are also strong in summer, and they could lower the concentrations of PAHs in particles in atmosphere (Re-poppi and Santiago-Silva, 2005). All these could help explain the

low PAH concentrations in summer. Concentrations of PAHs in winter samples were significantly higher than those in the other 3 seasons at EMS site. This could be

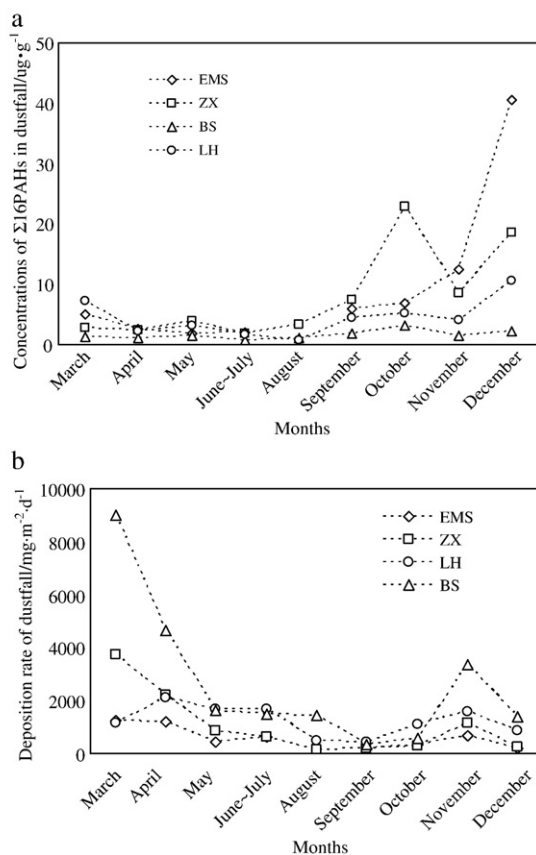


Fig. 1. Concentrations (a) and deposition rates (b) of  $\sum 16\text{PAHs}$  in different months.

explained by the deposition of particles produced by central heating in winter (burning of coal). There was no significant difference between the concentrations of PAHs in spring, autumn and winter at LH site. This may be attributed to the steady traffic volume all year round near this site.

### 3.1.3. Fluxes of dustfall and PAHs

The inner diameter of the buckets used in this study is  $30 \pm 0.5$  cm, and its area is  $0.0707$  m<sup>2</sup>. The September dustfall sample at EMS site had the minimum deposition rate of  $199.61$  mg m<sup>-2</sup> d<sup>-1</sup>, and the March one at BS site had the maximum deposition rate of  $9017.65$  mg m<sup>-2</sup> d<sup>-1</sup>. The annual average deposition rates at EMS, ZX, LH and BS sites were  $559.23$ ,  $845.07$ ,  $1221.20$  and  $2458.02$  mg m<sup>-2</sup> d<sup>-1</sup> with standard deviations of  $420.34$ ,  $1201.45$ ,  $579.57$  and  $2741.99$ , respectively. The high standard deviations could be attributed to the significant monthly variations of dustfall fluxes. Deposition rates of the 4 sites followed the order of BS > LH > ZX > EMS, and were opposite to the order of PAHs concentrations presented in Section 3.1.2. The variations of deposition rates were shown in Fig. 1(b).

Seasonal deposition rates were calculated, and were listed in Fig. 2(a). Fig. 2(a) showed that the highest and lowest dustfall deposition rates could be seen in spring

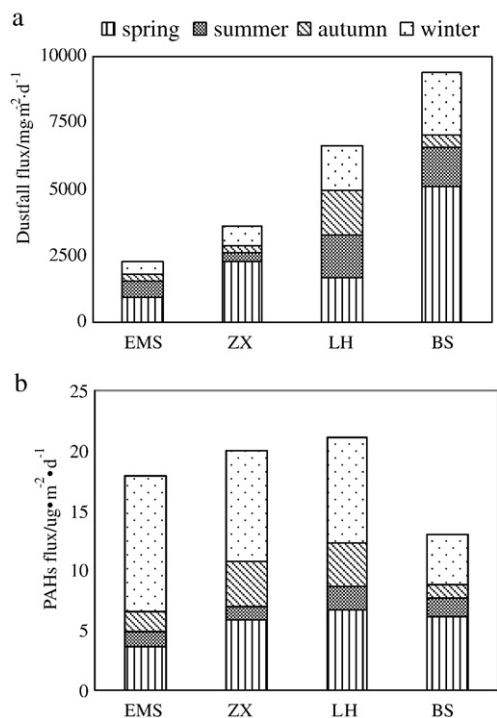


Fig. 2. Fluxes of dustfall and PAHs.

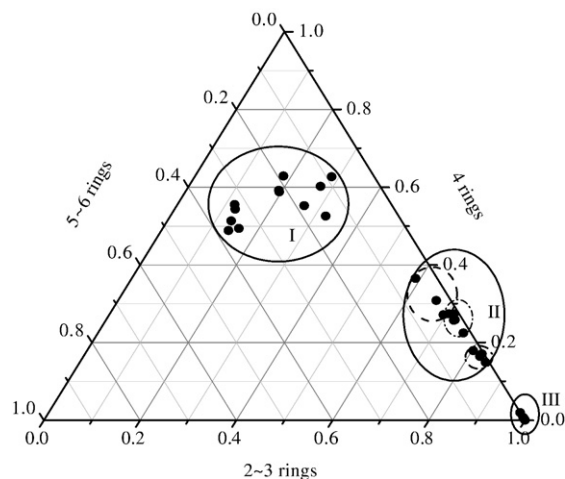


Fig. 3. Percentage of different PAH compounds in TSP, dustfall and gas phase.

and autumn, respectively. Summer deposition rate at EMS site was a little bit higher than winter, while at the other 3 sites, summer deposition rates were lower than winter.

There are three months each quarter. However, in Beijing, spring and autumn are much shorter than summer and winter. Therefore, in our study, 60 days were designated for spring and autumn, and 120 days were designated for summer and winter. With this designation, the calculated annual average dustfall flux for Tongzhou District was  $1296.67$  mg m<sup>-2</sup> d<sup>-1</sup>, with a standard deviation of  $772.33$ . Since Tongzhou District has an area<sup>3</sup> of  $907$  km<sup>2</sup>, in average, about  $423,387.6$  t dustfall deposited on the surface of this area in 2005.

Using data in Table 1 and Fig. 2(a), seasonal PAH deposition fluxes were calculated, and they followed the order of winter > spring > autumn > summer. Winter PAH deposition flux contributed nearly half of the annual flux. Coal combustion in heating season might be the major reason (Golomb et al., 1997). The annual average fluxes of PAHs were  $5.06$  µg m<sup>-2</sup> d<sup>-1</sup> at EMS site,  $5.05$  µg m<sup>-2</sup> d<sup>-1</sup> at ZX site,  $5.31$  µg m<sup>-2</sup> d<sup>-1</sup> at LH site and  $3.10$  µg m<sup>-2</sup> d<sup>-1</sup> at BS site, respectively. The average flux of the four sites was  $5.14$  µg m<sup>-2</sup> d<sup>-1</sup>. PAH deposition flux in the study area was very close to that in Tianjin City ( $4.88$  µg m<sup>-2</sup> d<sup>-1</sup>, 15 PAHs except NAP) (Wu et al., 2005), much higher than that in Paris ( $5.3$ – $63$  µg m<sup>-2</sup> month<sup>-1</sup>) (Ollivon et al., 2002), and lower than that in Taichung ( $38.6$ – $58.5$  µg m<sup>-2</sup> d<sup>-1</sup>) (Fang et al., 2004). In total,  $1.7$  t PAHs were deposited onto the surface of Tongzhou District for the year of 2005.

<sup>3</sup> <http://www.bjtz.gov.cn>.

Compared with fluxes of dustfall, there is no significant difference between the 4 sampling sites except the case that winter PAH flux at BS site was much lower than the other 3 sites. Fluxes of PAHs were shown in Fig. 2(b).

### 3.2. Distribution of PAH compounds in different rings in dustfall and atmosphere

A triangular map (Fig. 3) was made to describe the percentage of PAH compounds in dustfall, TSP and gas phase. Data of PAH concentrations in TSP and gas phase could be seen in the research report mentioned in Section 2.5. TSP, dustfall and gas phase samples fell into three groups (I, II and III). For PAHs in TSP samples, percentages of 2–3 ring compounds were almost equal to those of 5–6 ring compounds, and were both less than 40%. Four ring compounds dominated with the percentage ranged from 48.85% to 62.89%. The sum percentage of 2–3 and 5–6 ring compounds was steady all year round. 2–3 ring compounds dominated in summer and autumn, and 5–6 ring ones dominated in winter and spring. For PAHs in gas phase, 2–3 ring compounds dominated all year round with percentage exceeded 97%. Previous study showed that most high molecular weight PAH compounds absorb in fine particles in the atmosphere (Yang et al., 2005), and dustfall originated mainly from the deposition of coarse particles. Therefore, the percentage of 5–6 ring compounds was lower in dustfall samples than that in TSP samples.

PAH distribution among different rings for all dustfall samples was studied. As shown in Fig. 3, all the dustfall samples aggregated into a few groups, and the proportion of 5–6 ring compounds was steady, accounted for less than 5% in all samples. 2–3 ring compounds dominated with percentage ranged from 60% to 90%. The proportion of 4 ring compounds was from 10% to 40%. According to the proportion of 4 ring

compounds, 3 groups of samples were identified. Four spring samples and EMS site winter sample were in the first group. The proportion of 4 ring compounds at this group was around 20%. After the heating period, the high ring proportion decreased sharply. The involvement of EMS site winter sample in this group could be explained by the fact that central heating contributes much less PAHs to the air than villagers' heating ovens. The summer and autumn samples at BS site and the autumn sample at LH site were identified in the second group. The proportion of 4 ring compounds at this group was higher than 30%. The other 8 samples were included in the third group. The proportion of 4 ring compounds at this group was around 30%, and the proportions of 4 ring compounds in summer and autumn were both higher than those in winter.

Relative percentages of 16 PAH compounds in TSP, gas phase and dustfall were shown in Fig. 4. The units used in Fig. 4 are  $\text{ng m}^{-3}$  for PAHs in TSP and gas phase, and  $\text{ng m}^{-2} \text{d}^{-1}$  for those in dustfall. In this way, the longitudinal axes represent the relative percentages of PAHs in the 3 phases. As seen in Fig. 4, high molecular weight compounds tended to stay in TSP, while more low and medium molecular weight ones could be found in gas phase and dustfall.

### 3.3. Effects of ground dust, meteorological parameters and deposition velocity

#### 3.3.1. Ground dust

Dustfall fluxes could be influenced by the height of samplers (Shannigrahi et al., 2005). Ground dust could increase the dustfall fluxes. The effects of ground dust on PAHs deposition are complicated. Ground dust from "clean" area may bring a dilution effect on the PAH concentrations in dustfall. Although measures have been taken at the sampling sites in this study to reduce the effects of ground dust, it is impossible to eliminate such

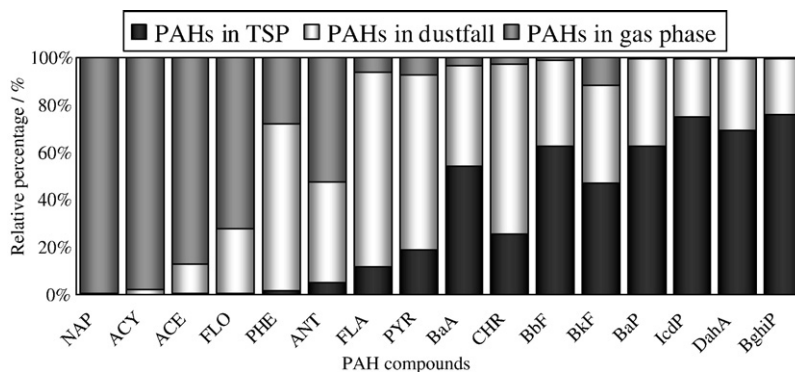


Fig. 4. Relative percentage of 16 PAH compounds in 3 mediums.

effects 100%. In this study, uncovered ground was identified around BS site, and thus BS site might receive more ground dust effects among these 4 sites. The dilution effect caused by ground dust might be one of the reasons why BS site had high dustfall flux but low PAH concentrations than the other 3 sites. EMS site is located on the roof of a three floor building (covered with pitch), and received the lowest ground dust effects. It might contribute to the high PAH concentrations at this site.

3.3.2. Meteorological parameters and APIs

Meteorological conditions and other pollutants in atmosphere may influence the dustfall deposition rates and PAH concentrations in dustfall. Therefore, in this study, meteorological parameters (*p*, *t*, RH, WS) and APIs (SO<sub>2</sub>, NO<sub>x</sub>, PM<sub>10</sub>) were used to analyze the impacts of these parameters using partial correlation analysis. As shown in Table 2, dustfall deposition rates had significant positive correlation with WSs (*p*=0.019). Strong dustfall deposition may happen at high WS situation. PAH concentrations had significant positive correlation with SO<sub>2</sub> APIs (*p*=0.048). This may be attributed to the fact that PAHs and atmospheric SO<sub>2</sub> have similar sources such as coal burning in heating season.

Dustfall deposition had no significant correlation with other parameters (*p*, *t*, RH and all APIs). This could be explained partly by the colinearity of these parameters with WS. The relationships between these parameters and PAH concentrations are complicated. For example, PAH concentrations in air might increase with the reduction of *t* because of the heating in winter, while simultaneously, high WS in winter might bring a dilution effect for PAH concentrations.

Correlation coefficients between frequencies of 16 WDs of each season and dustfall deposition rates and

Table 2  
Partial correlation analysis of deposition rates and PAH concentrations with impacting parameters

	Dustfall deposition rates		PAH concentrations	
	Correlation coefficients	<i>p</i> -values	Correlation coefficients	<i>p</i> -values
<i>p</i>	-0.570	0.238	-0.518	0.292
<i>t</i>	-0.649	0.164	-0.696	0.125
RH	-0.535	0.275	0.445	0.377
WS	0.886**	0.019	-0.107	0.840
PM <sub>10</sub>	0.061	0.896	-0.278	0.545
SO <sub>2</sub>	0.076	0.872	0.760**	0.048
NO <sub>x</sub>	-0.548	0.203	0.443	0.319

\*\*Significant at α=0.05.

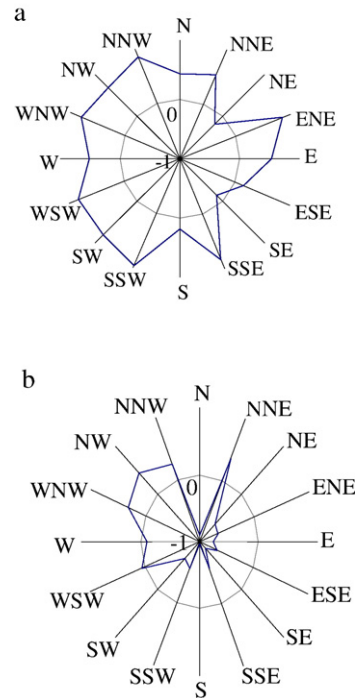


Fig. 5. Correlation coefficients of wind frequencies with deposition velocities (a) and PAHs (b).

PAH concentrations in dustfall were calculated (Lang et al., 2002), in order to identify the effects of wind conditions. As shown in Fig. 5, significant positive correlations existed between deposition rates and most WD frequencies. The annual average WSs in each direction were shown in Fig. 6. Significant positive correlation (*p*=0.044) existed between deposition rates and frequencies of SSW wind direction. The average WS in SSW direction was below 4 m s<sup>-1</sup>. Correlation coefficients with frequencies of NNW, NNE, E, SW and WSW directions were above 0.5, and all WSs in these directions were below 4 m s<sup>-1</sup>. In SE and NE directions, significant negative correlation existed between deposition rates and frequencies in these two directions, while

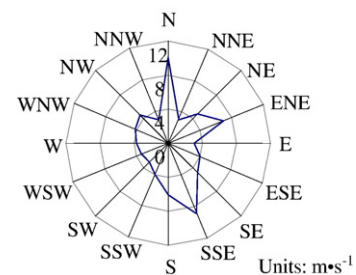


Fig. 6. Wind Rose Maps of the sampling period (m s<sup>-1</sup>).

the WSs in these two directions were higher than  $5 \text{ m s}^{-1}$ . The correlation coefficients with frequencies of calm winds were also above 0.5. All these results showed that the relationships between WSs and deposition rates were not simple positive or negative correlations. A critical speed existed. When the WS was higher than the critical speed, the deposition rates increased with the increase of WS. When the WS was lower than the critical speed, the deposition rates decreased with the increase of WS. The critical speed in this study was around  $4\text{--}5 \text{ m s}^{-1}$ .

Although there were no significant positive correlations between PAH concentrations and WSs, PAH concentrations had significant negative correlation with frequencies of N ( $p=0.092$ ) and S ( $p=0.037$ ) WDs. The average WS in N direction was about  $12 \text{ m s}^{-1}$ . With this WS, significant dilution effect from ground dust may exist. In Beijing, south wind dominates in summer. PAH concentrations were low in summer because of the photo-degradation and rain washout effects.

### 3.3.3. Deposition velocity

The deposition velocity function is:

$$V_{d,PAH} = K(F_T)/(C_g + C_p).$$

In this function,  $V_{d,PAH}$  represents deposition velocities of different PAH compounds ( $\text{cm s}^{-1}$ ),  $F_T$  is the

dry deposition fluxes of PAHs ( $\text{ng m}^{-2} \text{ month}^{-1}$ ),  $C_g$  and  $C_p$  represent concentrations of PAHs in gas and particle phases, respectively ( $\text{ng m}^{-3}$ ), and  $K$  is a coefficient to adjust the units (Terzi and Samara, 2005). Suppose there are 30 days in a month,  $K$  is  $3.86 \times 10^{-5}$ . Since there was no TSP and gas phase data for LH site, the following discussion focused on the other 3 sampling sites (EMS, ZX and BS). Deposition velocities of 16 PAH compounds for 3 sampling sites and 4 seasons were shown in Fig. 7.

As shown in Fig. 7, compounds with molecular weights between PHE and BkF had relatively high deposition velocities, and most of them were 3–4 ring PAHs. In comparison, deposition velocities of 2 ring and 5–6 ring compounds were low. These results could help to explain the composition pattern of PAH compounds in dustfall. Deposition velocities at different sampling sites followed the order of  $\text{EMS} > \text{ZX} > \text{BS}$ , which suggested that PAH dry deposition in urban area was stronger than in suburb and countryside areas. Previous studies showed that PAH deposition fluxes decreased with the increase of distance from large cities (Garban et al., 2002), and this might result from the differences of ground roughness between urban area and countryside (Cousins et al., 1999). High building in urban area could help slow down the wind speed and deposit the dustfall.

Compounds with molecular weights higher than PHE had higher deposition velocities in summer and autumn

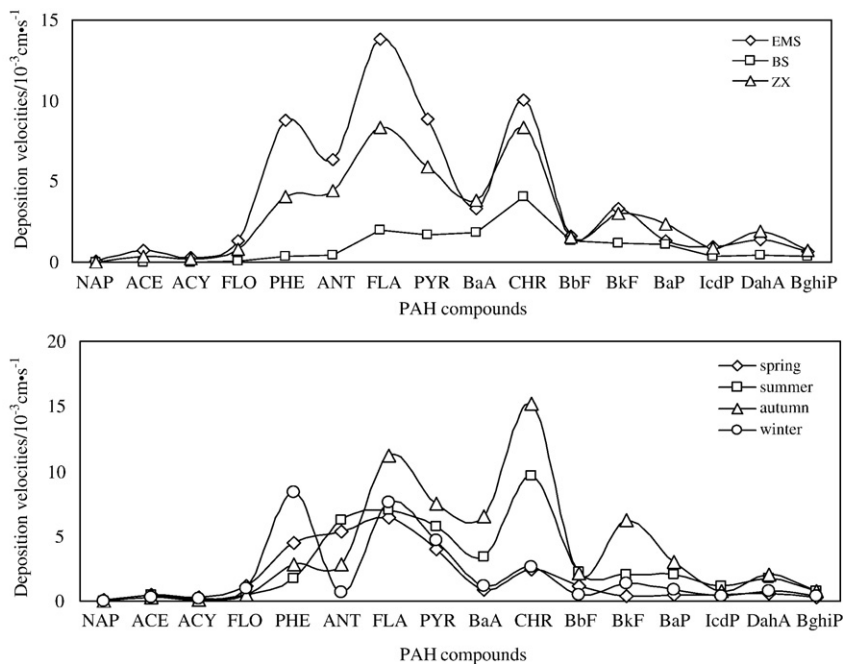


Fig. 7. Average deposition velocities ( $10^{-3} \text{ cm s}^{-1}$ ) at 3 sampling sites (a) and in 4 seasons (b).



Table 3  
Correlation analysis of monthly PAH fluxes with PAHs in gas phase and TSP

			Logarithmic transformed values of monthly fluxes			
			$\sum\text{PAHs}_{2-3\text{rings}}$	$\sum\text{PAHs}_{4\text{rings}}$	$\sum\text{PAHs}_{5-6\text{rings}}$	$\sum\text{PAHs}$
Logarithmic transformed PAH concentrations in gas phase	$\sum\text{PAHs}_{2-3\text{rings}}$	Correlation coefficients	-0.349			
		<i>p</i> -values	0.357			
	$\sum\text{PAHs}_{4\text{rings}}$	Correlation coefficients		0.592*		
		<i>p</i> -values		0.093		
	$\sum\text{PAHs}_{5-6\text{rings}}$	Correlation coefficients			-0.443	
		<i>p</i> -values			0.455	
	$\sum\text{PAHs}$	Correlation coefficients				-0.306
		<i>p</i> -values				0.424
Logarithmic transformed PAH concentrations in TSP	$\sum\text{PAHs}_{2-3\text{rings}}$	Correlation coefficients	0.919***			
		<i>p</i> -values	0.000			
	$\sum\text{PAHs}_{4\text{rings}}$	Correlation coefficients		0.695**		
		<i>p</i> -values		0.038		
	$\sum\text{PAHs}_{5-6\text{rings}}$	Correlation coefficients			0.378	
		<i>p</i> -values			0.316	
	$\sum\text{PAHs}$	Correlation coefficients				0.861***
		<i>p</i> -values				0.003

\*Significant at  $\alpha=0.1$ ; \*\*Significant at  $\alpha=0.05$ ; \*\*\*Significant at  $\alpha=0.01$ .

than in spring and winter, while other compounds showed the opposite trends. For high molecular weight PAH compounds, this trend might result from the distribution of PAH compounds in particles with different size. The high ring PAH compounds tend to accumulate in fine particles (Wu et al., 2006). In spring and winter, strong wind prevents the deposition of fine particles. In summer and autumn, however, more fine particles deposit due to the rain washout and light wind. For the light molecular weight PAHs, the deposition velocities were low in summer and autumn because they tend to stay in gas phase due to the high temperature (Tsapakis and Stephanou, 2005). Deposition velocity of PHE in winter was significantly higher than those in other 3 seasons. PHE is one of the diagnostic PAH compounds of coal combustion (Simcik et al., 1999). More coal was used in winter than in other seasons.

#### 3.4. Relationship between PAHs in dustfall and atmosphere

Normal distribution test was applied for monthly average PAH deposition fluxes and concentrations of PAHs in gas and TSP phases. Results showed that all the data followed logarithmic normal distribution. We assume that PAHs in dustfall samples came from the atmospheric deposition, and the monthly deposition fluxes had close relationships with atmospheric PAH concentrations. Correlation analysis was applied for the logarithmic transformed data of monthly fluxes and corresponding average concentrations of  $\sum\text{PAHs}$ ,  $\sum\text{PAHs}_{2-3\text{rings}}$ ,  $\sum\text{PAHs}_{4\text{rings}}$  and  $\sum\text{PAHs}_{5-6\text{rings}}$ . The

number of samples was all 9. Results were listed in Table 3.

As shown in Table 3, monthly  $\sum\text{PAHs}$  fluxes had significantly positive correlation ( $\alpha=0.01$ ) with  $\sum\text{PAHs}$  concentrations in TSP, but had no significant correlation with those in gas phase. The fluxes of 2–3 ring PAHs had significantly positive correlation ( $\alpha=0.01$ ) with concentrations of 2–3 ring PAHs in TSP. Four ring fluxes had significant positive correlation ( $\alpha=0.1$ ) with PAH concentrations in both TSP and gas phase. 5–6 ring fluxes had no significant correlation with atmospheric PAHs. 2–3 ring compounds in gas phase are relatively steady (Ravindra et al., 2006). 5–6 ring compounds exist mainly in fine particles, and hard to deposit.

Although no significant correlation between 5–6 ring fluxes and concentrations in TSP was observed, PAH concentrations in TSP were still a good indicator in estimating the monthly fluxes of total PAH. A regression equation was established. The equation is  $y=0.550x+7.652$ , where  $y$  and  $x$  represent the logarithmic transformed values of PAH monthly fluxes and PAH concentrations in TSP. The units are  $\ln(\text{ng m}^{-2} \text{ month}^{-1})$  and  $\ln(\text{ng m}^{-3})$ , respectively. The *p*-values of intercept and slope are 0.000 and 0.003, respectively. *F* value of the equation is 20.000 with a *p*-value of 0.003. In this study, the measured and estimated values for average monthly PAH deposition fluxes were 32.35 and 29.44  $\mu\text{g m}^{-2} \text{ month}^{-1}$ , respectively, with a relative error of -9%. With this equation, monthly PAH deposition fluxes could be estimated roughly based on the total PAH concentrations in TSP.

#### 4. Conclusions

Dustfall samples were collected from March, 2005 to January, 2006 at 4 sampling sites in the southeastern suburb of Beijing. Concentrations of  $\Sigma 16\text{PAHs}$  ranged from 0.72 to 40.45  $\mu\text{g g}^{-1}$ . 2–3 ring PAH compounds were the dominant ones in dustfall samples. The distribution pattern of PAH compounds in different rings in dustfall was different from that in TSP and gas phase.

Annual fluxes of dustfall at EMS, ZX, LH and BS sites were 1296.67  $\text{mg m}^{-2} \text{d}^{-1}$  and 5.14  $\text{g m}^{-2} \text{d}^{-1}$ , respectively, while annual fluxes of PAHs at the 4 sites were 5.06, 5.05, 5.31 and 3.10  $\mu\text{g m}^{-2} \text{d}^{-1}$ , respectively. About 423 387.6 t dustfall and 1.7 t PAHs deposited on the surface of Tongzhou District in 2005.

The deposition of dustfall and PAHs was influenced by factors such as dilution caused by ground dust and deposition velocities of PAH compounds. Wind speed had a complex effect on the deposition velocity.

2–3 ring PAH compounds fluxes had positive correlation with 2–3 ring PAH concentrations in TSP. Four ring PAH compounds fluxes had positive correlation with those in both TSP and gas phase, while no significantly correlation existed between 5–6 ring fluxes and 5–6 ring PAH concentrations in atmosphere. A regression model was established, and could be used to estimate the PAH fluxes.

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