

## Diurnal variations of polycyclic aromatic hydrocarbons associated with PM<sub>2.5</sub> in Shanghai, China

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### Abstract

Forty-eight daily time interval PM<sub>2.5</sub> samples were collected from December 2006 to January 2008 in an urban site in Shanghai, China. Concentrations and compositions of polycyclic aromatic hydrocarbons (PAHs) were analyzed with GC-MS to study the diurnal and seasonal variations and to identify the main emitting sources. The diurnal variation of the PAHs concentrations was greater in the late autumn and winter sampling days, and was greatly influenced by meteorological conditions such as wind speed and ambient temperature. The concentration of PAHs in the mornings (6:30–10:00) increased distinctly, and was high in the late autumn and winter sampling days, indicating the contribution from vehicle emissions during rush hours. The diurnal variation of the high molecular weight PAHs did not seem to be controlled by the shift of gas-particle partitioning due to temperature variation, instead, it could be indicative of the variation in the source. Statistical analyses showed that the concentrations of PAHs were negatively correlated with temperature and wind speed, and positively correlated with relative humidity. Diagnostic ratios of PAHs suggested mixed emission sources of petroleum and coal/biomass combustion for PAHs in the PM<sub>2.5</sub> in Shanghai.

**Key words:** PAHs; PM<sub>2.5</sub>; diurnal variation; source identification

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### Introduction

Polycyclic aromatic hydrocarbons (PAHs) are compounds with two to seven aromatic rings derived from the combustion of carbon containing materials (Zhu and Hidetsuru, 1997). They are one of the major toxic air pollutants in urban environments (Yu et al., 2007; Lu et al., 2008). PAHs in the atmosphere of urban areas are nearly all from anthropogenic sources. Most of the airborne PAHs are in PM<sub>2.5</sub>, which can penetrate into the respiratory system of human beings and could cause adverse health effects (Bi et al., 2005).

There are several studies on the characteristics and sources of PAHs in PM<sub>2.5</sub> in large cities in China such as Beijing (Feng et al., 2005; He et al., 2006; Wang et al., 2008), Shanghai (Feng et al., 2006), Nanjing (Wang et al., 2006), Guangzhou (Feng et al., 2006; Tan et al., 2006) and Hong Kong (Zheng and Fang, 2000). All these studies found much higher PAH concentrations in winter and autumn than in summer and spring, and that the higher winter concentration was attributed to higher emissions, lower atmospheric mixing heights, less wet deposition and lower speed of photolytic and radical degradation. These studies were based on integrated 24 hr samples.

In general, the variation of emission sources is not large from day-to-day, especially in the same season. Thus, the compositions of the integrated 24 hr samples collected on different days usually have good correlations, which makes the source identification difficult. However, the variation in emission sources in different time intervals of a day could be more distinct, and the chemical composition of aerosols would change rapidly when there are changes in source and meteorological conditions (Kuhlbusch et al., 2001). Therefore, samples collected in short time intervals are more conducive to source identification (Fine et al., 2004; Russell et al., 2004).

Shanghai is the largest commercial and industrial city in China with a population of over 20 million. The largest steel works and petrochemical complex in China are located in it. Shanghai is also one of the largest seaports in the world. Due to the rapid economic growth in the last three decades, Shanghai is facing serious environmental problems, and air pollution in Shanghai has drawn great concern from all around the world.

Up to now, however, studies on the characteristics and sources of PAHs in PM<sub>2.5</sub> in Shanghai are limited (Feng et al., 2006) and the diurnal variation of PAHs not clear. The objectives of the present study are: (1) to analyze the diurnal variation of the PAHs in PM<sub>2.5</sub>; (2) to investigate

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the influence of meteorological conditions on PAHs; and (3) to identify the main emission sources of PAHs by diagnostic PAHs ratios.

## 1 Experimental

### 1.1 Sampling site

The sampling site is located on the rooftop of nine-storey building (about 30 m above ground) at the Yan-chang campus of Shanghai University in Zha-bei District of Shanghai. The site is surrounded by low rise office and residential buildings. A road with moderate traffic is about 200 m north of the site, and another road with heavy traffic lies about 600 m in the west. Previous studies conducted in Beijing and Shanghai showed little spatial variation of the concentration and composition of fine particles in central urban areas (He et al., 2001; Ye et al., 2003). Our sampling site is a representative of the urban atmospheric environment in Shanghai.

### 1.2 Sampling

Samples were collected on glass fiber filters (GM-A 20.3 cm  $\times$  25.4 cm, baked at 450°C for 4 hr before use) with a high-volume PM<sub>2.5</sub> sampler (GUV-15HBL1, Thermo, USA) and the flow rate was 1.13 m<sup>3</sup>/min. Before and after sampling, the filters were weighed under constant temperature (20°C) and relative humidity (45%). The sampled filters were wrapped with annealed aluminum foil and stored in a refrigerator at -20°C till analysis.

Sampling was conducted during December 18 to 19 in 2006, February 9 to 10, March 4 to 5, May 30 to 31, August 23 to 24, November 8 to 9 and November 20 to 21 in 2007 and January 22 to 23 in 2008. Samples were collected during six daily time intervals: afternoon (13:30–16:00), night fall (16:30–19:30), overnight (20:00–23:40) and early morning (0:00–6:20), morning (6:30–10:00) and midday (10:15–13:20). The time intervals were designed to capture the variation in emission sources such as the increased traffic emissions in rush hours. Except the early morning sampling, the sampling time was 3–4 hr. Hourly meteorological parameters such as temperature, wind speed and relative humidity were cited from the website <http://www.wunderground.com>.

### 1.3 PAHs analysis

Prior to extraction, a surrogate mixture consisting of anthracene-d<sub>10</sub>, chrysene-d<sub>12</sub>, perylene-d<sub>12</sub> was spiked onto the filters. Then, the filter was cut into pieces and extracted with three aliquots of 60 mL dichloromethane/methanol (2:1, V/V) under ultrasonic agitation. The combined extracts were filtered and concentrated by rotary evaporation under vacuum. Prior to GC-MS analysis, hexamethylbenzene was added as internal standard, and to check the recovery of the surrogates. PAHs were quantified using the corresponding deuterated internal standards. MS was operated in EI mode at 70 eV and the scan range was 50–550 amu. GC was equipped with a DB-5MS capillary column (30 m  $\times$  0.25 mm

$\times$  0.25  $\mu$ m), with helium as carrier gas (at a flow rate of 1.0 mL/min). Relative response factors for PAHs to the internal standard were calculated with the 5-point calibration curve method.

### 1.4 Acronyms and classification of PAHs

Twenty one PAHs, including phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU), acephenanthrene (ACE), pyrene (PYR), benzo[ghi]fluoranthene (BgF), cyclopenta[cd]pyrene (CPP), benz[a]anthracene (BaA), chrysene/triphenylene (CHR), retene (RET), benzo[b+k]-fluoranthene (BbkF), benzo[a]fluoranthene (BaF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (PER), indeno[cd]fluoranthene (IcF), indeno[cd]pyrene (IcP), dibenzo[ah]anthracene (DahA), benzo[ghi]perylene (BgP) and coronene (COR) were identified and quantified. These PAHs can be classified into two sub groups of low molecular weight (LMW, molecular weight  $\leq$  228, from PHE to CHR) and high molecular weight (HMW, molecular weight  $\geq$  252, from BeP to COR).

### 1.5 Quality control

Solvent blanks, filter blanks and field blanks were analyzed to check the background. Trace amount of low molecular weight PAHs was found in the field blanks and the concentrations were less than 5% when compared to the samples. Therefore, the results were not corrected for field blanks. The mean recoveries for the surrogates in all samples were 70% for anthracene-d<sub>10</sub>, 74% for chrysene-d<sub>12</sub> and 72% for perylene-d<sub>12</sub>. Reported PAH concentrations were recovery corrected.

## 2 Results and discussion

### 2.1 Meteorological conditions in Shanghai

Shanghai is in the northern subtropical zone and influenced by the East Asian Monsoon. The prevailing wind in winter is from northwest, and is from southeast in summer. The seasons in Shanghai are defined as follows: spring (March–May), summer (June–August), autumn (September–November) and winter (December–February). The mean values of the meteorological parameters of the sampling days are summarized in Table 1. It can be seen that the wind speed in spring and summer was higher than that in autumn and winter (Ge, 1997).

**Table 1** Daily mean values of meteorological parameters

Date	Temperature (°C)	Relative humidity (%)	Wind speed (m/sec)
18–19/12/2006	6.8	70	1.2
09–10/02/2007	7.4	83	1.9
04–05/03/2007	7.3	66	7.3
30–31/05/2007	23.3	65	4.9
23–24/08/2007	30.7	70	5.3
08–09/11/2007	17.6	65	3.3
20–21/11/2007	12.2	53	1.7
22–23/01/2008	1.3	73	4.7

## 2.2 General characteristics of PAHs in PM<sub>2.5</sub> during the sampling periods

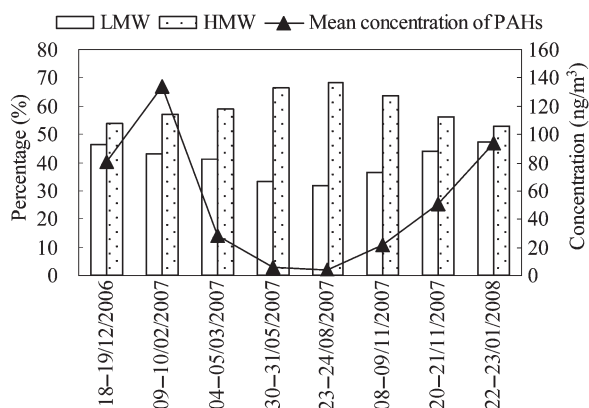
Figure 1 shows the concentrations of PAHs in PM<sub>2.5</sub> in different seasons. The concentration of PAHs in 23–24/08/2007 was the lowest (3.6 ng/m<sup>3</sup>), and the concentration in 09–10/02/2007 was the highest (133.6 ng/m<sup>3</sup>). Although samples were collected only in short periods in each season, the temporal variations of PAHs agreed with the reported seasonal variations (Guo et al., 2003; He et al., 2006). Our PAH concentrations (averaged at 38.8 ng/m<sup>3</sup>) were comparable to the published results for Shanghai (Feng et al., 2006; Xiong et al., 2009), and was lower than other large cities in China such as Beijing (112.7 ng/m<sup>3</sup> in 2003, He et al., 2006), Qingdao (87.5 ng/m<sup>3</sup>, Guo et al., 2003) and Guangzhou (117.4 ng/m<sup>3</sup>, Li et al., 2005), but was obviously higher than that in the developed countries/regions such as London (17.23 ng/m<sup>3</sup>, Baek et al., 1992), Hong Kong (7.42 ng/m<sup>3</sup>, Zheng and Fang, 2000) and Los Angeles (2.46 ng/m<sup>3</sup>, Fraser et al., 1998), indicating that the atmospheric PAHs pollution is still a problem in Shanghai.

Much of PAH species are semi-volatile and occur in both gaseous and particulate phases in the atmosphere (Simcik et al., 1998). It can be seen from Fig. 1 that contribution of HMW PAHs was the highest in 23–24/08/2007 (68.4%) and was the lowest in 22–23/01/2008 (52.7%), and vice versa for LMW PAHs. Such results were similar to those found in other cities (Guo et al., 2003; Feng et al., 2005, 2006), and in accordance with the shift of gas-particle partitioning of the semi-volatile species under different ambient temperatures.

## 2.3 Influence of meteorology on PAHs concentrations

It has been well recognized that the concentration and distribution of air pollutants are influenced by meteorological conditions (Pankow et al., 1993; Cortes et al., 2000; Zheng and Fang, 2000). In order to investigate the influence of meteorological conditions on the distribution of PAHs, correlations between the concentrations of individual PAHs and the meteorological parameters were calculated and are listed in Table 2.

Moderate negative linear relationship with temperature



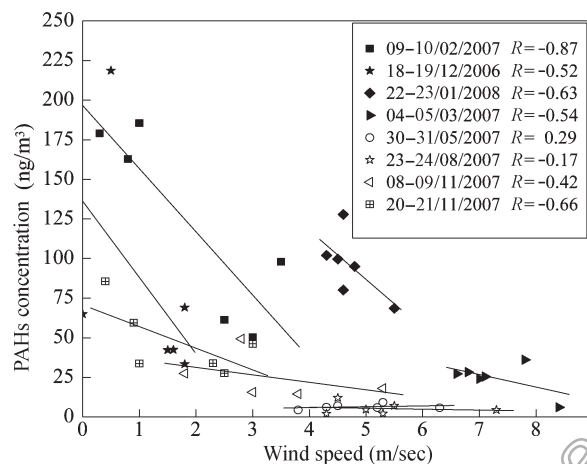
**Fig. 1** Mean concentration and compositions of PAHs in PM<sub>2.5</sub> in Shanghai during different sampling periods. LMW: low molecular weight; HMW: high molecular weight.

**Table 2** Beta weighting for correlation between concentrations of PAHs and meteorological parameters

BETA	All samples ( <i>n</i> = 48)		
	Temperature	Wind speed	Relative humidity
PHE	-0.71	-0.08	0.04
ANT	-0.59	-0.18	0.15
FLU	-0.64	-0.17	0.15
PYR	-0.61	-0.22	0.21
CPP	-0.29	-0.38	0.37
BaA	-0.37	-0.35	0.34
CHR	-0.45	-0.36	0.27
RET	-0.43	-0.39	0.22
Bb <sub>k</sub> F	-0.46	-0.34	0.31
BaF	-0.31	-0.38	0.36
BeP	-0.44	-0.37	0.31
PaP	-0.39	-0.37	0.36
PER	-0.34	-0.39	0.37
QP	-0.38	-0.24	0.18
IcF	-0.40	-0.36	0.33
IcP	-0.42	-0.36	0.34
DahA	-0.39	-0.37	0.32
BgP	-0.40	-0.39	0.33
COR	-0.36	-0.41	0.32
ΣPAHs	-0.47	-0.34	0.30

was observed for all target compounds. This can be ascribed to three causes. First, the mixing height is usually higher at higher ambient temperatures resulting in lower PAHs concentrations. Second, under high temperature and strong solar radiation, the degradation rate of PAHs is usually faster. Third, the wind from the sea in the warmer seasons (late spring and summer) in Shanghai, will dilute local pollutants in air. The negative correlations of the low molecular weight PAHs such as PHE, ANT, FLU and PYR with the ambient temperature were more significant than other compounds. This phenomenon is expectable because these compounds are more volatile, and the temperature variation would have a greater influence on the gas-particle partitioning of these compounds besides the effect of changing mixing layer height.

A negative correlation between the individual PAHs with wind speed was also found because the high wind speed is known to disperse the pollutants. Figure 2 shows the correlation between PAHs concentrations and wind speed. More significant negative correlations (a higher *R* value) were found in days with lower ambient temperatures



**Fig. 2** Plot of PAHs concentrations in PM<sub>2.5</sub> vs. wind speed.

such as in winter, late autumn and early spring, while no significant correlation was found in late spring (30–31/05/2007) and summer (23–24/08/2007). High wind speed and high ambient temperature caused the low concentrations of PAHs in the warmer seasons (late spring and summer, Table 1 and Fig. 2).

Moderate positive correlations between the PAHs concentrations and relative humidity were found (Table 2). Li et al. (2009) also found positive correlation between  $PM_{2.5}$  concentration and relative humidity in Beijing in winter. As increasing relative humidity can suppress the adsorption of gas phase organic species onto particle surfaces (Pankow et al., 1993), the change of gas-particle partitioning under different relative humidity should not be the reason for the positive correlation observed in this study. Analysis on the hourly meteorological parameters showed that relative humidity had negative correlation with temperature and wind speed in the sampling days, suggesting that the positive correlation between relative humidity and PAHs concentrations might be the result of the mutual correlation between meteorological parameters. In addition, relative humidity and wind speed had less influence on PHE, ANT, FLU and PYR than other PAHs. Further study on the effect of relative humidity is needed.

#### 2.4 Diurnal variations of PAHs in different sampling periods

Figure 3 shows the diurnal variation of PAHs in  $PM_{2.5}$  in different sampling periods. The significant diurnal vari-

ations of PAHs concentrations were observed in some sampling days, for example, the highest concentrations was  $218.6 \text{ ng/m}^3$  during 6:30–10:00 and the lowest was  $33.4 \text{ ng/m}^3$  during 20:00–23:40 in 18–19/12/2006. While in 22–23/01/2008 and 04–05/03/2007, the diurnal variations were quite small. We found that the wind speed was high and constant in days with small diurnal variations of PAHs concentrations, while the wind speed had strong diurnal variation and was very low in the night and early morning hours for days with strong diurnal variations of PAHs concentrations. Mixing layer height ( $H$ ), determined by the meteorological conditions, is considered a main factor controlling the pollutant concentrations. In this study, the atmospheric mixing heights were estimated with Eqs. (1)–(3) following the GB/T 13201-91 method of China, and are listed in Fig. 3 together with the PAHs concentrations.

$$H = \frac{a_s u_{10}}{f} \quad (1)$$

$$H = \frac{b_s}{(u_{10}/f)^{1/2}} \quad (2)$$

$$f = 2\omega \sin\varphi \quad (3)$$

Equation (1) is used for unstable or neutral conditions while Eq. (2) for stable conditions. In equations,  $a_s$ ,  $b_s$  are the mixing layer coefficients,  $u_{10}$  represents the wind speed at the height of 10 m,  $\omega$  represents earth's rotation angular velocity and  $\varphi$  is the geographic latitude.

It can be seen from Fig. 3 that the diurnal variation of

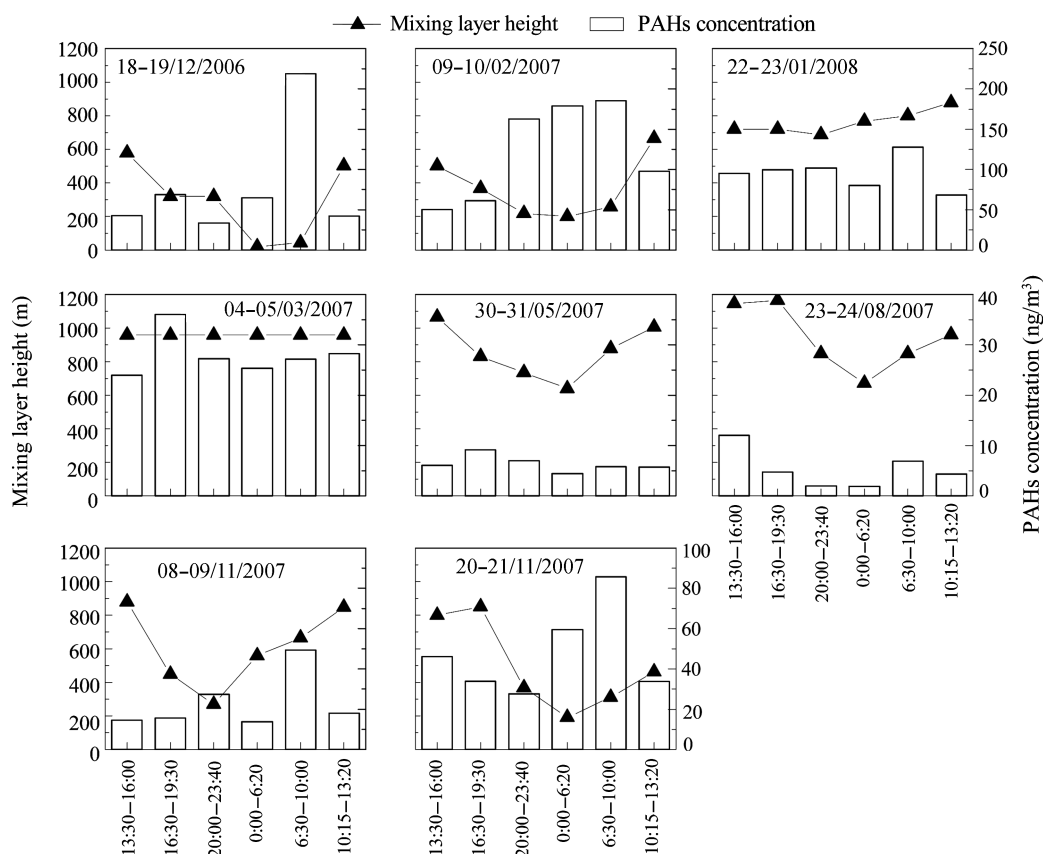


Fig. 3 Diurnal variations of PAHs concentrations in  $PM_{2.5}$  and the mixing layer height in different sampling days.

the mixing layer height explains well the variation of the PAHs concentrations in the winter, early spring and late autumn, but not as well for the late spring and summer. This suggests that the atmospheric mixing height was not the sole controlling factor of the diurnal variation of PAHs, other factors such as emission sources and chemical degradation can also influence the diurnal variation of PAHs.

The PAHs concentration increased from early morning (0:00–6:20) to morning (6:30–10:00) in all sampling days (Fig. 3). Moreover, in the autumn and winter sampling days, the highest PAHs levels occurred in the morning hours (6:30–10:00). Similar phenomena had also been found in Los Angeles in winter (Fine et al., 2004). The occurrence of the high concentration of PAHs in the morning rush hours indicated the important contribution from vehicle emissions. Besides emissions from vehicles, stagnant atmospheric condition was another reason for high PAHs levels in the morning during autumn and winter (Fine et al., 2004). Calm wind and low temperature in the early morning especially in late autumn and winter would cause low atmospheric mixing height and the formation of thermal inversion, thus high PAHs.

Besides the absolute PAHs concentrations, the mass fraction of PAHs in PM<sub>2.5</sub> also exhibited noticeable diurnal variations as shown in Fig. 4. The mass fraction of PAHs showed a more significant diurnal variation in the sampling days when the diurnal variations of wind speed and ambient temperature were strong. Samples taken in the time intervals with low wind speed and low temperature had a higher mass fraction of PAHs. One possible reason for this should be that under low wind speed and low temperature condition, locally emitted pollutants, such as emissions from heavy-duty diesel trucks as they are only allowed to enter the urban area during the night, would

accumulate, thus the fine particles would be relatively fresh and the mass fraction of secondary components would be small. While PM<sub>2.5</sub> in the time intervals with high wind speed would contain more transported particles, secondary components such as sulfate, nitrate and secondary organic aerosols (SOA) formed during the transport would lower the mass fraction of PAHs. PM<sub>2.5</sub> samples taken in midday and afternoon usually had smaller mass fraction of PAHs, high degradation rate of PAHs under high temperature and strong solar radiation would be another reason besides the higher formation rate of secondary components. It can also be seen from Fig. 4 that the mean mass fraction of PAHs was higher in the samples taken in the cold days than that in warm days, showing that the composition of fine particles in different times of the year was different due to the differences in emission sources and chemical reaction rates.

As shown in Fig. 4, the LMW/HMW ratios varied in different time intervals. To study the diurnal variation of the PAHs composition with respect to meteorological conditions, the ratios (%) of LMW or HMW PAHs to total PAHs were calculated and are shown in Fig. 5. It can be seen that the contribution of HMW PAHs (also true for LMW PAHs) had noticeable diurnal variations and the highest contribution of HMW PAHs usually occurred in the early morning (0:00–6:20) or morning time (6:30–10:00). The contribution of HMW PAHs showed negative correlation with the ambient temperature (Fig. 5). This trend is in contradiction with the seasonal variation of the contribution of HMW PAHs as discussed earlier. Thus, gas-particle partitioning of the LMW PAHs under different temperatures should not be the reason for the diurnal variation observed. From the diurnal variation of wind speed (Fig. 5) we could find that the contribution of HMW PAHs showed good negative correlation with wind speed,

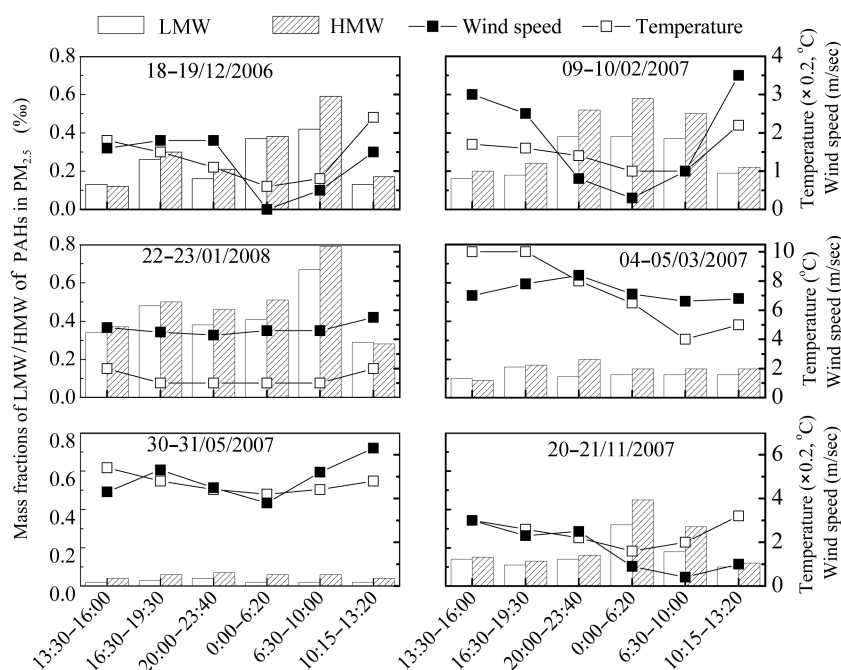


Fig. 4 Diurnal variations of the mass fractions of LMW and HMW PAHs in PM<sub>2.5</sub> in Shanghai.

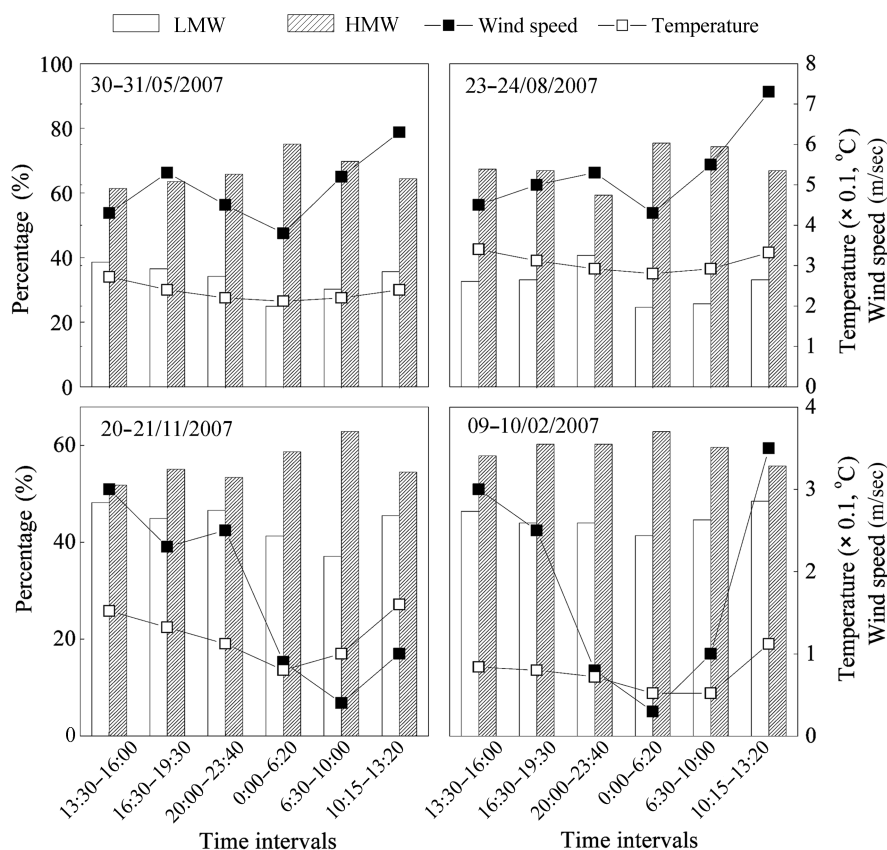


Fig. 5 Diurnal variations of the percentage of LMW and HMW PAHs in total PAHs, and wind speed and temperature.

the highest contribution of HMW PAHs occurred at the same time interval when the wind speed was the lowest. Therefore, the accumulation or enhanced contribution of locally emitted pollutants should be the major reason for the observed diurnal variations of the HMW and LMW PAHs. Our urban sampling site is expected to experience the accumulation of engine exhaust under calm or low wind speed conditions. With the increase of wind speed, transported particles would contribute more to the total fine particles. Studies showed that HMW species such as BgP and COR dominated the PAHs from engine exhaust (Nielsen, 1996), while lighter components such as PHE, ANT and FLU dominated in PAHs from coal burning (Khalili et al., 1995; Kuhlbusch et al., 2001). The diurnal variation of the HMW (LMW) PAHs contribution found in this study was thus in accordance with the suggested variation of emission sources.

## 2.5 Source identification by diagnostic ratios of PAHs

Diagnostic ratios for PAHs can be used to investigate their origins or as an indication of the aging of the air samples. As shown in Table 3, BeP/(BaP+BeP) ratio in PM<sub>2.5</sub> ranged from 0.49 to 0.78, and it followed the order of summer > spring > autumn > winter, which was in accordance with the seasonal variation of ambient temperature, confirming the influence of temperature and solar radiation on the degradation rate of BaP (Nielsen, 1988).

ANT/(ANT + PHE) ratio in this study ranged from 0.06

Table 3 Diagnostic ratios of PAHs in PM<sub>2.5</sub> during sampling periods in Shanghai

PAH ratio	Mean	Min.	Max.
BeP/(BaP+BeP)	0.63	0.49	0.78
ANT/(ANT+PHE)	0.13	0.06	0.36
BaA/(BaA+CHR)	0.27	0.18	0.40
FLU/(FLU+PYR)	0.52	0.40	0.58
IcP/(IcP+BgP)	0.45	0.35	0.47

to 0.36 and BaA/(BaA +CHR) from 0.18 to 0.40, indicating that the PAHs were mainly from combustion sources (Budzinski et al., 1997; Yunker et al., 2002). It was found that PAHs from petroleum source had FLU/(FLU+PYR) ratio < 0.2, while 0.4–0.5 for combustion of fuel (tail gas from vehicles) and > 0.5 for grass, wood and coal combustion (Miguel and Pereira, 1989). PAHs from the burning of rice straw in Asia has FLU/(FLU+PYR) ratios of 0.51 (Sheesley and Schauer, 2003). Research conducted in a Chinese tunnel (He et al., 2008) also showed that the mean ratio of FLU/(FLU+PYR) was about 0.4. And FLU/(FLU+PYR) ratio of the particles from burning of bituminous coal from China was about 0.53 (Liu et al., 2009), which was in agreement with the results from other countries, such as USA, Canada, and Brazil (Miguel and Pereira, 1989; Yunker et al., 2002). Thus, the FLU/(FLU+PYR) ratios of 0.40 to 0.58 suggested that PAHs in PM<sub>2.5</sub> in urban Shanghai were from mixed sources of coal/biomass burning and vehicle emissions. The detection of retene in nearly all samples with concentrations

ranged from 0.05 to 6.65 ng/m<sup>3</sup> confirmed the contribution from biomass burning (Ramdahl, 1983).

The IcP/(IcP + BgP) ratio of PAHs from vehicles has been reported to be < 0.4, and coal combustion > 0.5 (Miguel and Pereira, 1989; Yunker et al., 2002). Research by He et al. (2008) showed a mean IcP/(IcP + BgP) ratio of 0.22 in the Zhujiang tunnels of China, and the ratio from burning of Chinese bituminous coal was about 0.59 (Liu et al., 2009). The IcP/(IcP+BgP) ratio of 0.35–0.47 in Shanghai (Table 3) also indicated mixed sources for PAHs.

### 3 Conclusions

Significant diurnal variations of PAHs concentrations in PM<sub>2.5</sub> were found in urban Shanghai. The PAHs concentration increased from the early morning (0:00–6:20) to morning (6:30–10:00), indicating the contribution of vehicle emissions in the rush hours. The highest PAHs level in the late autumn and winter sampling days was usually found in the morning. The variation of mixing layer height was a main factor influencing the diurnal variation of PAHs concentrations besides the change of emission sources. The variation of the relative contribution of LMW and HMW PAHs in different sampling days could be the result of the shift of gas-particle partitioning under different ambient temperatures. While the diurnal variation of the contributions of the LMW and HMW PAHs did not agree with the change of ambient temperature, but was in accordance with the variation of the contribution from vehicle emissions and thus could be an indicator of emission source change. The diagnostic ratios of PAHs indicated that PAHs in PM<sub>2.5</sub> in urban Shanghai was from mixed sources of petroleum and coal/biomass combustion.

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