Polycyclic aromatic hydrocarbons (PAHs) associated with fine particulate matters in Nanjing, China: Distributions, sources and meteorological influences

Jiabao He\textsuperscript{a,b}, Shuxian Fan\textsuperscript{a,b,*}, Qingzi Meng\textsuperscript{b}, Yu Sun\textsuperscript{b}, Jian Zhang\textsuperscript{b}, Fan Zu\textsuperscript{c}

\textsuperscript{a} Key Laboratory for Aerosol-Cloud-Precipitation of China Meteorological Administration, Nanjing University of Information Science and Technology, Nanjing 210044, China
\textsuperscript{b} Department of Atmospheric Physics, Nanjing University of Information Science and Technology, Nanjing 210044, China
\textsuperscript{c} Jiangsu Institute of Meteorological Sciences, Nanjing 210008, China

**Highlights**
- This is the first-ever analysis of PAHs based on four-season data sets in East China.
- PAH sources and their contributions show seasonal variability.
- Biomass burning is the extra source of PAHs in autumn in East China.
- PAHs concentration correlates with visibility most remarkably under high RH.
- Contributions of regional transport and local emission in each season are evaluated.

**Abstract**
A study of 16 polycyclic aromatic hydrocarbons (PAHs) associated with fine particulate matters at suburban and urban sites in Nanjing was carried out each season from November 2009 to July 2010. At the suburban and urban sites, the concentrations of total PAHs (T-PAHs) were in the ranges of 30.76–102.26 ng/m\textsuperscript{3} and 25.92–90.80 ng/m\textsuperscript{3}, respectively. This paper elucidates the distributions, sources of PAHs and meteorological influences: 1) PAHs concentrations at the two sites were close to each other and similarity between PAHs profiles of the two sites indicated they had common sources, which were attributed to the combined effect of regional transport and local emission. 2) At both sites, the profiles displayed obvious seasonal variations, as a result of the seasonality of sources and meteorological influences. The T-PAHs concentrations were in the order of winter > spring > autumn > summer. 3) Source apportionment showed vehicle exhaust (72.93–87.24%) was the greatest contributor in all seasons. The coal combustion and coke production (coal/coke) (10.02–18.63%) were identified in all but summer seasons, because of the low collection efficiency of PAHs markers of coal/coke under high temperature. For autumn, biomass burning (10.58%) was an extra contributor. 4) Regarding meteorological parameters, a negative effect of temperature over PAHs was confirmed, with a correlation coefficient of $-0.51$ ($p < 0.05$). Precipitation could remove PAHs to some extent. Both positive and negative correlations between PAHs concentration and wind speed in each season were analyzed in combination with air mass back-trajectories so as to evaluate the effects of regional air transport. The results showed that polluted air from ENE-S and NNW-NE brought in outside sources to the study area and played a major role in the accumulation of fine-particulate PAHs in spring and winter respectively, while clean air from southwest contributed to the dilution in summer.

**1. Introduction**
Atmospheric fine particulates play a major role in air pollution. Fine particles deposit slowly from the atmosphere and may be airborne for days or even weeks, being transported from region to region (Harrison et al., 1996). They are the major culprits in
visibility degradation (Watson, 2002) and effective loadings of toxic chemicals (NRC, 1998). Previous studies have estimated the contributions of various sources to atmospheric fine particulates using inorganic or organic species as markers. Among these chemical species, polycyclic aromatic hydrocarbons (PAHs) are a class of ubiquitous organic compounds (WHO, 2003), absorbed predominantly on fine particulate matters (Baek et al., 1991; Fan et al., 2009). With potential toxic, carcinogenic and mutagenic effects, they possess a fairly high health risk, and thus raise much attention (Ames et al., 1975).

PAHs concentration in particulates is mainly determined by two factors: contribution of emission sources and meteorological influences (Wild and Jones, 1995; Dimashki et al., 2001; Vestreng and Klein, 2002). Firstly, PAHs are mainly derived from incomplete combustion or pyrolysis of fossil fuels and other organic materials (Harrison et al., 1996). The emission sources include coal combustion (Galarneau et al., 2008); vehicle exhaust (Sklorz et al., 2007); straw burning (Zhang et al., 2009); wood combustion (Sienna et al., 2005); waste incineration (Peltonen and Kuljukka, 1995); cigarette smoking (Zhang et al., 2009); and industrial production (Kume et al., 2005) such as metal production (Mantis et al., 2005); coke production (Mantis et al., 2005); iron production (Wang et al., 2008), etc. Among these identified sources, vehicle exhaust and certain industrial processes are the main contributors (Mantis et al., 2005; Hien et al., 2007). Recently, vehicle exhaust was reported to be the most predominant PAHs source, especially in regions where coal and coke were replaced by gas or oil (Guo et al., 2003; Hong et al., 2007; Lee and Kim, 2007). As for meteorological influences, significant correlations were reported between PAHs concentration and temperature (Fang et al., 2004); relative humidity (RH) (Chetwittayachan et al., 2002; Hien et al., 2007); wind speed (WS) (Tan et al., 2006); total solar radiation (Chetwittayachan et al., 2002); rainfall and sunshine hours (Hien et al., 2007). Sometimes, PAHs concentration displays no relationship with WS, RH and atmospheric pressure (Fang et al., 2004). Wind with diverse speed/direction is accompanied by air mass transport, influencing the accumulation, diffusion, and elimination of air pollutants. In view of the management of regional air quality, the contributions of regional transport and local emission to air pollutants were also analyzed. Harrison et al. (1996) found that urban PAHs concentration was about 4-folds higher than rural concentration in Birmingham, indicating local emission was the main influence. Lee et al. (2001) and Guo et al. (2003) suggested the higher PAHs concentration in Hong Kong resulted from the long-range transport of air pollutants from Mainland China.

On the whole, any of these factors mentioned above could be responsible for the occurrence of particulate PAHs. However, one paper taking all these factors into account is scarce. PAHs as well as these influencing factors vary with seasons. To our knowledge, relevant and all-sided analysis for different seasons is generally missing in the literatures except that Lee and Kim (2007) apportioned the major sources of particulate PAHs and quantified the impact of regional transport to the air quality in each season in Seoul, Korea. In this study, particulate matter (PM) samples were collected in four seasons in the urban and suburban areas to comparatively investigate fine-particulate PAHs in terms of the seasonality of sources and meteorological influences.

Nanjing is located in the Yangtze Delta Region (YDR) of East China. The YDR is a core economic development zone in China, and is becoming one of the world’s major manufacturing bases. Since the 21st century, this region has experienced serious economic transformation and rapid urbanization development, accompanied by deterioration of atmospheric environment. Unfortunately, research on PAHs is lacking for this crucial region during this special era. Only one survey conducted by Wang et al. (2007) roughly evaluated PAHs sources in two seasons at an urban area in Nanjing. In view of these concerns, PM sampling campaigns were conducted in Nanjing, a representative metropolis in the YDR. The aims of this study are to (1) investigate fine particulates in terms of PAHs levels and their distributions; (2) identify various PAHs sources in each season; (3) elucidate potential relationships between meteorological parameters and PAHs concentration, clarify the effects of local emission and regional transport on Nanjing air quality in each season; to evaluate as many processes or factors responsible for the abundance of fine-particulate PAHs as possible.

2. Materials and methods

2.1. Site characterization and sampling strategy

Aerosol sampling was performed seasonally day and night at two sites in Nanjing (Fig. 1). One site was on the old campus of Nanjing University (NJU) in the urban setting, surrounded by commercial centers, residential areas, and roads with heavy traffic. The other site was located in the Nanjing University of Information Science and Technology (NJUST), representing a suburban setting; it was 17 km away from downtown, situated next to a busy road and near a large-scale industrial park including thermal power plants, iron-works, petrochemical engineering plants, chemical plants, etc. Synchronized sampling at the two sites was carried out for about 10 days each season in November 2009 (autumn), January 2010 (winter), April 2010 (spring), and July 2010 (summer). And an extra 22-day sampling campaign was conducted at the suburban site only in December 2009 (winter). There were 60 samples (n = 60) for the suburban site, and 38 samples (n = 38) for the urban site. The sampling time includes two periods each day:

![Fig. 1. Locations of sampling sites.](image-url)
daytime from 08:00 to 20:00 LST (LST = GMT+8:00) and nighttime from 20:00 to 08:00 LST.

Airborne particles were collected on 80-mm diameter quartz-fiber filters (Shanghaixingya, China) using a cascade impactor (Liaoningkangjie, China) at a flow rate of 28.3 L/min. PM particles were separated into nine fractions according to the size ranges of 10–9.0, 9.0–5.8, 5.8–4.7, 4.7–3.3, 3.3–2.1, 2.1–1.1, 1.1–0.68, 0.68–0.43, and 0.43–0 µm. The fine particulates in this study is referred to as PM$_{2.5}$. Prior to sampling, the filters were calcined at 550 °C for 4–5 h to remove any organic compounds on them. Before and after sample collection, the filters were equilibrated in a desiccator at room temperature for 48 h and then weighed. They were then folded in half and stored at −20 °C in a freezer until extraction and analysis. Additionally, filter blanks were prepared and handled the same way as the samples.

2.2. Extraction and analysis

Detailed procedures of extraction and analysis were described in a previous study (Fan et al., 2010). Briefly, half of each filter was cut into pieces and put into a 150-mL flat bottom flask with 90-ml dichloromethane. PAHs were removed from the filter using Soxhlet extraction for 18 h in 55 °C water bath. Subsequently, the extracts were condensed to 5 mL using a Kuderno–Danish (K–D) concentrator and further adjusted to 1 mL by nitrogen blow-down. Then, they were stored at −20 °C until analysis. Gas chromatography coupled to mass spectrometry (GC–MS) was used for the separation and quantification of the target PAHs according to the U.S. EPA Method TO-13A (U.S. EPA, 1999; Wang et al., 2007; Shi et al., 2010).

In this study, 17 PAHs were detected including naphthalene (Nap), acenaphthylene (Ace), fluorone (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), Benzo[e]pyrene (BeP), indeno[1,2,3-cd]pyrene (InP), dibenz[a,h]anthracene (DaA), and benzo[ghi]perylene (BghiP). Detailed description of quality control can be found in Fan et al. (2010). Nap was excluded in data analytics due to its low recovery. Therefore, the objects in our study are actually 16 PAHs species. They can also be classified into lower molecular weight (LMW) containing 2- and 3-ring PAHs (Nap, Ace, Flu, Phe, and Ant), middle molecular weight (MMW) containing 4-ring PAHs (Fla, Pyr, BaA, and Chr) and higher molecular weight PAHs (HMW) containing 5-, 6- and 7-ring PAHs (BbF, BkF, BaP, BeP, InP, DaA, and BghiP).

3. Results and discussion

3.1. General characteristics of PM$_{2.5}$-bound PAHs

3.1.1. Spatial and temporal distribution

Table 1 lists the mean PAHs concentrations in different seasons. The concentrations of total PAHs (T-PAHs) at the suburban and urban sites were in the ranges of 30.76–102.26 ng/m$^3$ and 25.92–90.80 ng/m$^3$, respectively. In general, T-PAHs were relatively more abundant in winter and spring. The suburban PM$_{2.5}$ concentrations (102.26 ng/m$^3$) was found at the suburban site in winter, and the minimum (25.92 ng/m$^3$) occurred at the urban site in summer. Additionally, the concentrations of most PAH species were higher in nighttime than in daytime in all but autumn seasons, because of the accumulation of pollutants caused by the inversion layer at night (Wang et al., 2006). The higher concentrations during the daytime in autumn may be caused by enhanced biomass burning in the daytime of the harvest period. The concentrations of 16 species at the two sites were close to each other (Fig. 2). Even the majority of PAHs were a little more abundant at the suburban site, contrary to a popular belief that pollution degree is lighter in suburban areas relative to urban areas. The causes are as follows. First, the suburban site was located near an industrial district and may receive more pollutants from industrial sources. Second, with a rapid increase of vehicle numbers in the suburbs in recent years, the gap of vehicle numbers in the suburbs in recent years, the gap
Table 1  
Mean PAHs concentrations (ng/m³) in PM2.1 at the two sites in Nanjing during the sampling period.

<table>
<thead>
<tr>
<th>PAHs</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suburban</td>
<td>Urban</td>
<td>Suburban</td>
<td>Urban</td>
<td>Suburban</td>
<td>Urban</td>
</tr>
<tr>
<td>Acy</td>
<td>1.13</td>
<td>1.07</td>
<td>1.27</td>
<td>1.20</td>
<td>1.30</td>
</tr>
<tr>
<td>Flu</td>
<td>0.88</td>
<td>0.80</td>
<td>1.02</td>
<td>0.96</td>
<td>0.76</td>
</tr>
<tr>
<td>PhE</td>
<td>1.30</td>
<td>1.25</td>
<td>1.55</td>
<td>1.51</td>
<td>1.11</td>
</tr>
<tr>
<td>Ant</td>
<td>2.44</td>
<td>2.76</td>
<td>3.12</td>
<td>2.98</td>
<td>1.52</td>
</tr>
<tr>
<td>Flu</td>
<td>3.75</td>
<td>5.47</td>
<td>4.89</td>
<td>4.31</td>
<td>1.94</td>
</tr>
<tr>
<td>Pyr</td>
<td>2.95</td>
<td>4.44</td>
<td>3.96</td>
<td>3.65</td>
<td>1.85</td>
</tr>
<tr>
<td>BaA</td>
<td>2.39</td>
<td>4.08</td>
<td>2.74</td>
<td>3.16</td>
<td>1.85</td>
</tr>
<tr>
<td>Chr</td>
<td>3.83</td>
<td>7.11</td>
<td>4.98</td>
<td>5.12</td>
<td>2.62</td>
</tr>
<tr>
<td>BbF</td>
<td>4.86</td>
<td>10.02</td>
<td>6.82</td>
<td>6.84</td>
<td>2.89</td>
</tr>
<tr>
<td>BkF</td>
<td>3.26</td>
<td>5.70</td>
<td>4.41</td>
<td>4.27</td>
<td>2.03</td>
</tr>
<tr>
<td>BeP</td>
<td>3.62</td>
<td>7.24</td>
<td>4.88</td>
<td>4.79</td>
<td>2.37</td>
</tr>
<tr>
<td>BaP</td>
<td>2.79</td>
<td>5.97</td>
<td>3.52</td>
<td>3.71</td>
<td>1.94</td>
</tr>
<tr>
<td>InP</td>
<td>3.45</td>
<td>6.64</td>
<td>4.89</td>
<td>4.85</td>
<td>2.78</td>
</tr>
<tr>
<td>DaA</td>
<td>1.59</td>
<td>2.16</td>
<td>1.86</td>
<td>1.83</td>
<td>1.70</td>
</tr>
<tr>
<td>BghiP</td>
<td>3.54</td>
<td>6.62</td>
<td>5.08</td>
<td>4.92</td>
<td>2.52</td>
</tr>
<tr>
<td>T-PAHs</td>
<td>43.49</td>
<td>73.03</td>
<td>56.92</td>
<td>55.95</td>
<td>30.76</td>
</tr>
<tr>
<td>LMW</td>
<td>7.46</td>
<td>7.58</td>
<td>8.89</td>
<td>8.50</td>
<td>6.27</td>
</tr>
<tr>
<td>HMM</td>
<td>23.11</td>
<td>44.35</td>
<td>31.46</td>
<td>31.21</td>
<td>16.23</td>
</tr>
<tr>
<td>COMPANHS (%)</td>
<td>70.87</td>
<td>76.75</td>
<td>72.54</td>
<td>72.98</td>
<td>66.38</td>
</tr>
<tr>
<td>CANPAHs (%)</td>
<td>50.98</td>
<td>57.07</td>
<td>51.34</td>
<td>53.23</td>
<td>51.40</td>
</tr>
</tbody>
</table>

* D: Daytime, N: Nighttime.
* COMPAHs: combustion derived PAHs including Fla, Pyr, Chr, BbF, BkF, BaA, BaP, InP, and BghiP.
* CANPAHs: carcinogenic PAHs including BaA, Chr, BbF, BkF, BaP, InP, and DaA.
leading contribution of combustion sources. The LMW/HMW ratio is often used for distinguishing pyrogenic from petrogenic sources. Higher LMW concentration means more non-combusted petroleum products, while HMW is related to typical pyrogenic products derived mainly from fossil fuel combustions (Hassanien and Abdel-Latif, 2008). This result is confirmed by the negative correlation between LMW/HMW ratio and COMPAHs concentration in Fig. 4. In this study, the LMW/HMW ratio was generally low (between 0.15 and 0.45). The positive correlation between COMPAHs and T-PAHs ($R = 0.99$ at both site; Fig. 4) further confirms the major role of combustion sources.

Generally, carcinogenic PAHs (CANPAHs) include BaA, Chr, BbF, BkF, BaP, InP, and DaA, whose concentrations were in the range of 15.81–50.35 ng/m$^3$, accounting for 49.24–64.51% of the T-PAHs (Table 1). Among these CANPAHs, BaP was considered the primary representative and was regarded by the World Health Organization (WHO) as a good index for the whole PAHs carcinogenicity (Shi et al., 2010). Ambient Air Quality Standards (AAQS) with proposals and guidelines have been set for BaP in many countries. In this study, BaP concentration of two sites varied from 1.09 to 12.51 ng/m$^3$ during the whole sampling period, with a mean value of 3.73 ng/m$^3$ and median value of 4.19 ng/m$^3$. The daily concentration of BaP in 72% of our sampling days exceeded the upper limit (2.5 ng/m$^3$) of the Chinese AAQS issued in 2012 (GB 3095-2012), and the mean value was nearly three times higher than the annual standard (1.0 ng/m$^3$). A high level of human health risk existed, which should alarm the public of the pollution risks.

3.2. Source apportionment

3.2.1. Coefficient of divergence analysis

Similarities between PAHs profiles at the two sites can be further identified by coefficient of divergence (CD), which is a self-normalizing parameter used to evaluate the divergence degree of two sets of data (Kong et al., 2012). CD is determined as follows:

$$CD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^{p} \left( \frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2}$$

where $j$ and $k$ represent PAHs profiles from different sampling sites, $p$ is the number of target components, and $x_{ij}$ and $x_{ik}$ stand for the average concentrations of component $i$ at sites $j$ and $k$, respectively. Wongphatarakul et al., 1998 thought the CD value of 0.269 could reflect the divergence between particles from two cities. The value less than 0.2 means that $j$ and $k$ are influenced by common sources (Kong et al., 2012). In this study, CD of PAHs profiles from the two sites is 0.16, which suggests the PAHs from these two districts in Nanjing had common sources, confirming to the findings in Section 3.1.1. This is a result of either local emissions mixed evenly across the two sites, or regional transport brought in outside air masses affecting the whole Nanjing area.

3.2.2. Principal component analysis

Principal component analysis (PCA) is a widely used multivariate statistical tool to identify the major sources for air pollutants (Harrison et al., 1996; Guo et al., 2003). Under the prerequisite of retaining the original information as much as possible, PCA transforms the original set of variables into a smaller set of linear combinations (Ho et al., 2002). The factor loadings obtained for each variable within the factors generated by PCA are a type of correlation coefficient, and a higher value means greater significance. Figure 5 shows the factor loadings of two retained factors that accounted for annual PAHs at the two sites. Principal component 1 (PC1) and PC2, respectively, explained 74% and 20% of the total variance for the suburban site, 77% and 12% for the urban site. Both PC1s had high loadings for BkF, BbF, BaP, BaA, InP, BghiP, and Chr, which were characteristic of vehicular exhaust. Because data in literatures showed that BbF, BkF, BaP, InP, BghiP, and OR marked diesel and gasoline combustion sources (Harrison et al., 1996; Fang et al., 2004), Li et al. (2012) concluded species...
including BaA, Chr, BkF, BbF, and BaP were associated with petroleum combustion sources. Both PC2s were interpreted as sources of coal combustion and coke production (coal/coal) with high loadings for Acy, Ace, Ant, DaA, and Flu, for the reason that Nap, Acy Ace, Flu Phe and Ant were associated with coal tar/coal combustion sources (Sofowote et al., 2008); Ant had been identified in coal combustion and coke production (Guo et al., 2003; Akyüz and Çabuk, 2008); DaA was related to thermal power plant that used coal as fuel (Fang et al., 2004). Consequently, the suburban and urban sites indeed had the same source types. For all seasons, PM$_{2.1}$-bound PAHs in Nanjing were mainly affected by vehicular exhaust and coal/coal sources.

We used the average concentrations of the two sites to identify specific sources for each season. Source apportionment for spring and winter both identified two same sources, the same as those mentioned above: vehicle exhaust and coal/coal (78.23% and 15.64% for spring; 74.09% and 18.63% for winter). In Table 2, the factor loadings for summer and autumn are displayed. Only one PC (87.24%) was extracted in summer, representative of vehicle source. The likely causes are that vehicle emission was enhanced because of automobile air-condition, and that the tracers of coal/coal sources (Sofowote et al., 2008); Ant had been identified in coal combustion and coke production (Guo et al., 2003; Akyüz and Çabuk, 2008); DaA was related to thermal power plant that used coal as fuel (Fang et al., 2004). Consequently, the suburban and urban sites indeed had the same source types. For all seasons, PM$_{2.1}$-bound PAHs in Nanjing were mainly affected by vehicular exhaust and coal/coal sources.

We used the average concentrations of the two sites to identify specific sources for each season. Source apportionment for spring and winter both identified two same sources, the same as those mentioned above: vehicle exhaust and coal/coal (78.23% and 15.64% for spring; 74.09% and 18.63% for winter). In Table 2, the factor loadings for summer and autumn are displayed. Only one PC (87.24%) was extracted in summer, representative of vehicle source. The likely causes are that vehicle emission was enhanced because of automobile air-condition, and that the tracers of coal/coal sources (Sofowote et al., 2008); Ant had been identified in coal combustion and coke production (Guo et al., 2003; Akyüz and Çabuk, 2008); DaA was related to thermal power plant that used coal as fuel (Fang et al., 2004). Consequently, the suburban and urban sites indeed had the same source types. For all seasons, PM$_{2.1}$-bound PAHs in Nanjing were mainly affected by vehicular exhaust and coal/coal sources.

The likely causes are that vehicle emission was enhanced because of automobile air-condition, and that the tracers of coal/coal sources (Sofowote et al., 2008); Ant had been identified in coal combustion and coke production (Guo et al., 2003; Akyüz and Çabuk, 2008); DaA was related to thermal power plant that used coal as fuel (Fang et al., 2004). Consequently, the suburban and urban sites indeed had the same source types. For all seasons, PM$_{2.1}$-bound PAHs in Nanjing were mainly affected by vehicular exhaust and coal/coal sources.

### Table 2

The loadings of 16 individual PAHs in summer and autumn based on PCA.

<table>
<thead>
<tr>
<th></th>
<th>Summer</th>
<th></th>
<th>Autumn</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PC 1</td>
<td>PC 2</td>
<td>PC 3</td>
<td></td>
</tr>
<tr>
<td>Acy</td>
<td>0.731</td>
<td>0.557</td>
<td>0.597</td>
<td></td>
</tr>
<tr>
<td>Ace</td>
<td>0.722</td>
<td>0.634</td>
<td>0.681</td>
<td></td>
</tr>
<tr>
<td>Flu</td>
<td>0.597</td>
<td>0.618</td>
<td>0.742</td>
<td></td>
</tr>
<tr>
<td>Phe</td>
<td>0.608</td>
<td>0.681</td>
<td>0.742</td>
<td></td>
</tr>
<tr>
<td>Ant</td>
<td>0.634$^d$</td>
<td>0.681</td>
<td>0.618</td>
<td></td>
</tr>
<tr>
<td>Fla</td>
<td>0.597</td>
<td>0.618</td>
<td>0.742</td>
<td></td>
</tr>
<tr>
<td>Pyr</td>
<td>0.742</td>
<td>0.597</td>
<td>0.618</td>
<td></td>
</tr>
<tr>
<td>BaA</td>
<td>0.853</td>
<td>0.597</td>
<td>0.618</td>
<td></td>
</tr>
<tr>
<td>Chr</td>
<td>0.873</td>
<td>0.618</td>
<td>0.742</td>
<td></td>
</tr>
<tr>
<td>BbF</td>
<td>0.947</td>
<td>0.597</td>
<td>0.618</td>
<td></td>
</tr>
<tr>
<td>BkF</td>
<td>0.981</td>
<td>0.597</td>
<td>0.618</td>
<td></td>
</tr>
<tr>
<td>BeP</td>
<td>0.962</td>
<td>0.597</td>
<td>0.618</td>
<td></td>
</tr>
<tr>
<td>BaP</td>
<td>0.893</td>
<td>0.597</td>
<td>0.618</td>
<td></td>
</tr>
<tr>
<td>InP</td>
<td>0.809</td>
<td>0.597</td>
<td>0.618</td>
<td></td>
</tr>
<tr>
<td>DaA</td>
<td>0.814</td>
<td>0.597</td>
<td>0.618</td>
<td></td>
</tr>
<tr>
<td>BghiP</td>
<td>0.754</td>
<td>0.597</td>
<td>0.618</td>
<td></td>
</tr>
<tr>
<td>% Variance &amp; Source</td>
<td>87.24 &amp; 72.93 &amp; 10.58 &amp; 10.02</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^d$ Only high factor loadings listed.

### 3.3. Meteorological influences

#### 3.3.1. Relation between PAHs in PM$_{2.1}$ and meteorological parameters

Meteorological conditions can affect PAHs in terms of their generation, phase partition, accumulation, diffusion, removal, etc. Li et al. (2006) indicated the typical subtropical monsoon climate in Guangzhou, being cool and dry in winter while hot and humid in summer, played a key role in controlling the seasonality of sources and PAHs concentrations. Fig. 6 reveals the diurnal variations of PAHs concentrations and meteorological parameters. The PAHs concentrations from the two sites showed similar variation trend. The low concentrations in summer changed smoothly while the high levels in winter fluctuated. Tan et al. (2006) suggested the fluctuation in winter was related to periodic cold snaps.

The relationship between PM$_{2.1}$-bound PAHs and relevant parameters can be analyzed using SPSS packages and the Spearman rank correlation coefficients (Hong et al., 2007). Negative correlation was found between mean PAHs concentration of the two sites and temperature, with a correlation coefficient of $-0.51$ ($p < 0.05$). Higher temperature would not only increase the participation of PAHs in the vapor phase but also cause more degradation. Fig. 6 indicates that precipitation could remove some PAHs. Chetwittayachan et al. (2002) and Hien et al. (2007) found PAHs concentration negatively correlated with RH remarkably; but in this study, the correlation between the two was not so significant ($R = -0.18$). On the whole, the visibility increased as the PAHs concentration reduced ($R = -0.34$, $p < 0.05$). Additionally, more complex relationships among concentration, RH and visibility can be found in Fig. 7. Under the same PAHs concentration, the higher the RH was, the lower the visibility became. Previous studies found the days with lower visibility were associated with higher RH (Sequeira and Lai, 1998; Malm and Day, 2001). The RH values were
divided into five ranges here. We found the PAHs concentration was significantly and exponentially associated with visibility within each RH range. Under the high RH of 80–90%, the PAHs concentration correlated with visibility most remarkably ($R = 0.82$). Besides, the influences of wind speed/direction (WS/WD) on PAHs will be discussed next in section 3.3.2.

### 3.3.2. Roles of regional transport and local emission

Air mass transport can bring in pollutants or clean air from distant areas, thus influencing local PAHs concentration. Apart from local emission, regional transport was reported as an important mechanism to explain PAHs concentration in the atmospheric environment (Ravindra et al., 2006). To some extent, the impact of regional transport or local emission can be reflected by the aging degree of air masses. The isomer ratio of a more reactive PAH to a stable PAH, such as BaA/Chr and BaP/BeP, can be employed to illustrate whether the air masses collected are fresh or aged (Ding et al., 2007). During the process of air transport, BaA and BaP are expected to degrade more easily than their isomers, so the ratios will be modified by their strong reactivity. Naturally, a higher value indicates relatively little photochemical reaction and a major impact from local sources, and a lower ratio means more degradation happened in situ or during the process of air transport. The ratio larger than 1.0 was reported for typical local sources (Khalili et al., 1995). Fig. 8 reveals the relationship between BaA/Chr ratio and T-PAHs concentration. Apart from a few particular values representing autumn, the majority showed a negative correlation between T-PAHs and BaA/Chr ratio ($R = 0.69$), and most ratios were smaller than 1.0, revealing the severity of degradation. The aging degree was in the order of autumn < summer < spring < winter.

---

**Fig. 6.** Diurnal variation of observed PAHs concentrations and meteorological parameters.

**Fig. 7.** Relationship between PAHs concentration and visibility within different RH ranges.

**Fig. 8.** Relationship between BaA/Chr ratio and T-PAHs concentration.
In autumn, most ratios were higher than 1.0, with a positive correlation with the T-PAHs, indicating the major role of local emission. A further explanation could be obtained by the relationship between WS and PAHs concentration. An inverse relationship between the concentration and WS suggests the predominance of local sources, because strong wind brings pollutants out of the study area whereas weak wind allows pollutants to accumulate in time (Hong et al., 2007). Fig. 9a shows the distribution of WS/WD-concentration for autumn, while Fig. 9b shows the air mass back-trajectories reflecting the direction of the predominant air mass. Corresponding to Section 4 (38%) and Section 2 (38%) of trajectories in Fig. 9b, the predominant air masses in Fig. 9a were estimated to be from SSW-SSE and NW-N, respectively. In these directions, the spiral shape means the concentration was positively correlated with WS when WS was less than ~2 m/s while a negative correlation was found when WS exceeded a certain value. Therefore, the sources in autumn mainly came from local or adjacent southeast areas as well as dilution by clean air masses from farther areas did not contribute to the accumulation of PM$_{2.1}$-bound PAHs.

In summer, the weather conditions, such as high temperature, high humidity and intense radiation, promote photochemical reactions. Hence, whether local emission or regional transport contributed to the aged air masses in summer needed further analysis. Cluster analysis of back-trajectories was applied. The trajectories were categorized into five sectors (Fig. 9d). Three typical air mass trajectories accounted for 26% from local (section 4), 24% from southwest (Section 1) and 23% from southeast (Section 5). Combined with Fig. 9c, in the southeast the WS was low and the concentration showed a relatively high level; in the southwest, the concentration reduced as WS increased. Therefore, sources from local or adjacent southeast areas as well as dilution by clean air from southwest dominated PM$_{2.1}$-bound PAHs in summer.

In spring and winter, when weather conditions were not sufficient for photochemical reaction compared to summer, the serious aging degree likely signified the important role of regional transport. Fig. 9e indicates a positive correlation between the concentration and WS in the direction of ENE-S. These directions were found to be the predominant air mass directions in spring, as they were assumed to be corresponding to Section 4 (37%), Section 1 (28%) and Section 3 (23%) of trajectories in Fig. 9f. On the whole, regional transport from ENE-S brought in outside sources and dominated the abundance of PM$_{2.1}$-bound PAHs in spring. In winter, the concentration peak occurred when air masses came from NNW-NE (Fig. 9g), mainly corresponding to Section 2 (48%) of trajectories in Fig. 9h. In consideration of the positive correlation between the PAHs concentration and WS in these directions, we could conclude the polluted air masses from North China contributed to the accumulation of PM$_{2.1}$-bound PAHs in Nanjing. Additionally, Section 1 (41%) in Fig. 9h was related to local air masses in the southwest in Fig. 9g. In short, local emission accompanied by regional transport from North China was responsible for the PM$_{2.1}$-bound PAHs in winter.

4. Conclusions

In this study, the concentrations of PM$_{2.1}$-bound PAHs at the urban and suburban sites in Nanjing were monitored each season from November 2009 to July 2010. The average concentrations of T-PAHs were in the order of winter > spring > autumn > summer at both sites. Relative to the urban site, the PAHs concentration in the suburban was slightly higher, mainly due to the surroundings of the two sites and the combined effect of regional transport and local emission. The coefficient of divergence of 0.16 indicated the source commonality of the two sites, and the PAHs profiles of the two sites varied with seasons. Potential sources and meteorological influences were investigated for the four seasons. On the whole, regional transport from ENE-S bringing in vehicle exhaust and coal/coke emissions played a major role in the accumulation of PM$_{2.1}$-bound PAHs in spring; local vehicle emissions, dilution by clean air from southwest as well as some weather conditions including high air temperature and RH were responsible for the low concentration in summer; the abundance in autumn was related to local and adjacent sources, including vehicle exhaust, biomass burning and coal/coke; the highest level in winter resulted from vehicle exhaust and coal/coke emissions, with equally important contributions of local emission and regional transport from North China, under the meteorological conditions of low temperature and RH, weak radiation, and decreased boundary layer.
Acknowledgments
This work was supported by the National Natural Science Foundation of China (No. 41275151, No. 71101029, No. 41375138) and by a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References

US Environmental Protection Agency (EPA), 1999. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS) [5], second ed. Compendium Method TO-13A.