Pollution characteristics, sources and lung cancer risk of atmospheric polycyclic aromatic hydrocarbons in a new urban district of Nanjing, China

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ABSTRACT

This paper focused on the pollution characteristics, sources and lung cancer risk of atmospheric polycyclic aromatic hydrocarbons (PAHs) in a new urban district of Nanjing, China. Gaseous and aerosol PM2.5 (particulate matter with aerodynamic diameter smaller than 2.5 μm) samples were collected in spring of 2015. Sixteen PAHs were extracted and analyzed after sampling. Firstly, arithmetic mean concentrations of PAHs and BaPeq (benzo[a]pyrene equivalent) were calculated. The mean concentrations of PAHs were 29.26 ± 14.13, 18.14 ± 5.37 and 48.47 ± 16.03 ng/m3 in gas phase, particle phase and both phases, respectively. The mean concentrations of BaPeq were 0.87 ± 0.51, 2.71 ± 2.17 and 4.06 ± 2.31 ng/m3 in gas phase, particle phase and both phases, respectively. Secondly, diagnostic ratios and principal component analysis were adopted to identify the sources of PAHs and the outcomes were the same: traffic exhaust was the predominant source followed by fuel combustion and industrial process. Finally, incremental lung cancer risk (ILCR) induced by whole year inhalation exposure to PAHs for population groups of different age and gender were estimated based on a Monte Carlo simulation. ILCR values caused by particle phase PAHs were greater than those caused by gas phase PAHs. ILCR values for adults were greater than those for other age groups. ILCR values caused by total (gas + particle) PAHs for diverse groups were all greater than the significant level (10−6), indicating high potential lung cancer risk. Sensitivity analysis results showed that cancer slope factor for BaP inhalation exposure and BaPeq concentration had greater impact than body weight and inhalation rate on the ILCR.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are compounds whose structure consists of two or more fused benzene rings in linear, angular or cluster arrangements (Bortey-Sam et al., 2015). There is an increasing concern about the occurrence of PAHs in the atmospheric environment as they are ubiquitous and some of them are strongly carcinogenic (Ravindra et al.,...
The United States Environmental Protection Agency (USEPA) fixed 16 parent PAHs as priority pollutants and these 16 compounds (16 USEPA priority PAHs) were always main research objects in many reports.

PAHs can be released from both anthropogenic and natural emission sources (Pongpiachan et al., 2015). Many methods have been adopted in the process of PAH source identification. Among these, relative ring abundance (Kong et al., 2015), diagnostic ratios (Chen et al., 2015), principal component analysis (Garrido et al., 2014) and positive matrix factorization (Khan et al., 2015; Y. Wu et al., 2014) are widely used and extremely useful. Results from relevant reports provide important knowledge for effective pollution control measures (Callén et al., 2014). In most regions, main sources of atmospheric PAHs appeared to be traffic exhaust and fossil fuel combustion (Hanedar et al., 2014). Constitution of PAHs in gas phase differs from that in particle phase, indicating different sources (Liu et al., 2014). However, most studies aimed at identifying the sources of particle phase PAHs, but paid little attention to the sources of PAHs in diverse atmospheric phases.

In particular, benzo(a)pyrene (BaP) has been identified as being highly carcinogenic (IARC, 2015). Hence BaP equivalent (BaPeq) concentration was always calculated to evaluate PAH pollution level. Based on this, daily inhalation exposure level (E) and incremental lung cancer risk (ILCR) for human beings caused by atmospheric PAHs can be estimated to assess human health risk. However, studies on ILCR caused by PAHs in diverse phases and for population groups of different age and gender are scarce.

Nanjing, the capital of Jiangsu Province, China, is an industrialized city. With rapid social and economic development, Nanjing has been heavily polluted by air pollutants. Source apportionment showed that vehicle exhaust was the greatest contributor to particle phase PAHs in all seasons (He et al., 2014). In most regions, main sources of atmospheric PAHs appeared to be traffic exhaust and fossil fuel combustion (Hanedar et al., 2014). Constitution of PAHs in gas phase differs from that in particle phase, indicating different sources (Liu et al., 2014). However, most studies aimed at identifying the sources of particle phase PAHs, but paid little attention to the sources of PAHs in diverse atmospheric phases.

The study was performed on the rooftop (20 m above the ground level to avoid airflow obstruction) of a teaching building (32°07’N, 118°54’E) in Nanjing Normal University in spring of the year 2015. The sampling site is located in one of the new urban districts of Nanjing, Jiangsu Province, China (Fig. 1). Around the sampling site are teaching buildings, dwellings and vegetation. A traffic artery is located about 250 m southeast to the site. About 2 km south to the site is a commercial district and about 10 km north to the site (on the other side of Yangtze River) is an industrial district. Therefore, sampling site might receive urban air pollution from nearby streets and industrial process. During sampling, the maximum air temperature was 26.4°C, whereas the minimum value was 18.1°C. The wind through sampling site was mostly southerly or southeasterly in direction, with wind scale in the range of 1 to 4. The weather situation during sampling was mostly sunny or cloudy, without wet deposition.

1.2. Sample collection

Active air samplers (PUF-PM2.5-300, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China; operating at a constant flow rate of 0.3 m³/min) with polyurethane foam (PUF; Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China) disks and glass fiber filters (GFFs; Nanjing Poly Kang Reagent Company, Nanjing, China) were used to collect gaseous and aerosol PM2.5 samples, respectively. Detailed calibration method and uptake rates of the samplers were confirmed by consulting the Chinese National Standard (HJ 93-2013). The spring of Nanjing was short, ranging from March 24th to May 30th. Collection procedure was performed from April 1st to May 20th, with one gaseous sample and one aerosol PM2.5 sample collected in each week. For each sampling, 24 hr was included from 8:00 to 8:00 in the next day. Totally seven gaseous samples and seven aerosol PM2.5 samples were collected. Among these, six pairs of samples that contained both gas phase and particle phase PAHs collected during the same period can be used as total (gas + particle phase) atmospheric samples. PUF disks were stored at -18°C after each sampling. GFFs were equilibrated in a desiccator (25°C, 40% relative humidity) for 24 hr and weighted before and after each sampling, in accordance with the Chinese National Standard (HJ 656-2013).

1.3. Extraction and analytical procedure

PUF disks were Soxhlet extracted with 180 mL/1:1 n-hexane:acetone at 52°C for 8 hr. GFFs were subjected to microwave extraction (MARS2Xpress, CEM, USA) with 25 mL 1:1 n-hexane:acetone, being heated to 100°C at a rate of 10°C/min and then held for 10 min (Xia et al., 2013). The extracts of GFFs were press filtered prior to concentration, whereas that of PUF disks were concentrated directly, using a vacuum rotary evaporator (R-201, Qiyu, China) at 37°C. After concentration, extracts of gas phase PAHs and particle phase PAHs were transferred to the alumina silica gel column for purification, respectively. The alumina silica gel column consisted of 20 g silica gel and 20 g alumina, and was eluted with 20 mL n-hexane followed by 50 mL 1:1 n-hexane:dichloromethane at a rate of 2 mL/min. The eluted mixture from the column during cleanup was first concentrated to near dryness in the vacuum rotary evaporator (R-201, Qiyu, China) using a 37°C water bath.
The residue was then transferred and diluted with n-hexane and brought to exactly 1.0 mL by nitrogen blowdown (MG-1000, Eyela, Japan) at room temperature (25°C). The samples were sealed in vials and stored at -4°C before being analyzed. Quantitative analysis of the air sample extracts was done by gas chromatography with a mass spectrometer detector (QP2010, Shimadzu, Japan) (Xia et al., 2013; Hassan and Khoder, 2012; Iwegbue et al., 2014). A 30 m × 0.25 mm i.d. × 0.25 μm film thickness capillary column (HP-5MS, Dikma, China) was used. GC temperature was programmed from an initial 50°C (maintain 1 min) at a rate of 15°C/min up to 180°C, and then at a rate of 5°C/min up to 250°C with a final holding time of 20 min. Helium was used as the carrier gas. A 1.0 μL aliquot of the extract was injected while the injector port was held at 280°C and operated in splitless mode at a flow rate of 1.0 mL/min. The head column pressure was 30 kPa. The mass spectrometer was operated in scan mode with an electron impact ionization of 70 eV, an electron multiplier voltage of 1200 V, and an ion source of 230°C. Concentrations were determined for 16 individual PAHs in all samples. They were naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DahA), indeno(1,2,3-cd)pyrene (IcdP) and benzo(g,h,i)perylene (BghiP).

1.4. Quality control

All solvents used were of chromatographic grade (Dikma, China). Before sampling, the PUF disks were cleaned by extracting them in a Soxhlet with 150 mL acetone (72°C), 150 mL dichloromethane (56°C) and 150 mL n-hexane (78°C) for 8 hr, respectively; and the GFFs were cleaned by baking them in a furnace at 450°C for 4 hr. Alumina and silica gel (80–200 mesh, Dikma, China) were heated at 650°C in a muffle furnace (DLII-9, Taisite, China) for 10 hr and kept in a sealed desiccator. Prior to use, the alumina and silica gel were reactivated at 130°C for 4 hr immediately. All glassware was cleaned using an ultrasonic cleaner (KQ-500B, Shumei, China) and heated to 400°C for 6 hr. The analytes were quantified using standard calibration curves constructed with five concentration levels. The field and laboratory blanks were analyzed, and the concentrations of target PAHs in the field blanks were higher than those in the laboratory blanks. Concentrations in both blanks were more than one order of magnitude lower than those of real samples. All the results of samples were field blank corrected. Recovery of individual PAHs ranged from 65% to 96% with a mean value of 85% for PUF disks, whereas that varied from 66% to 103% with a mean value of 84% for GFFs. Data analyzed in the article were not corrected for recoveries. The detection limits were in the range of 0.095–0.76 ng/mL.

1.5. BaPeq concentration estimates

BaPeq concentration is often used in the estimation of inhalation exposure to PAHs and was calculated according to Eq. (1) (Pongpiachan et al., 2015):

\[
\text{BEC} = \sum_{i=1}^{n} C_i \times \text{TEF}_i
\]

where BEC (ng/m³) is the BaPeq concentration of PAHs; \( C_i \) (ng/m³) is the concentration of PAH congener \( i \); TEF \( i \) is the toxicity equivalency factor of PAH congener \( i \) (Nisbet and LaGoy, 1992). We treated \( C \), which approximately followed lognormal distribution, in Eq. (1) probabilistically. Detailed information on BaPeq concentration calculation was presented in Supporting Materials (S.2, Table S3).

1.6. Source identification

Diagnostic ratios and principal component analysis (PCA) were used to identify the primary sources of PAHs in diverse phases. Some authors have pointed out that PAH compounds differing in relative molecular mass can be used as tracers to distinguish main sources (Bourotte et al., 2005;...
1.7. Daily inhalation exposure level (E) estimates

Citizens in Nanjing were divided into eight population groups according to age and gender: children (4–10 years), adolescents (11–17 years), adults (18–60 years), and seniors (61–70 years) of both males and females. Daily inhalation exposure level (E) for each population group was calculated based on Eq. (2) (USEPA, 1992):

\[
E = BEC \times \text{IR}
\]

where, \(E\) (ng/day) is the daily inhalation exposure level; \(BEC\) (ng/m\(^3\)) is the BaPeq concentration in the sampling site; \(\text{IR}\) (m\(^3\)/day) is the inhalation rate. We treated BEC and IR, which followed lognormal and normal distribution, respectively, in Eq. (2) probabilistically. Detailed information on daily inhalation exposure level calculation was presented in Supporting Materials (S.3, Table S4).

1.8. Incremental lung cancer risk (ILCR) estimates

The incremental lung cancer risk (ILCR) of diverse population groups induced by inhalation exposure to PAHs was calculated based on Eq. (3) (USEPA, 1992):

\[
\text{ILCR} = \frac{\text{SF} \times E \times \text{EF} \times \text{ED} \times \text{CF}}{\text{BW} \times \text{AT}}
\]

where, ILCR (dimensionless) is the incremental lung cancer risk induced by inhalation exposure; SF ((kg·day)/mg) is the cancer slope factor for BaP inhalation exposure (a lognormal distribution with a geometric mean of 3.14 and a geometric standard deviation of 1.80) (Chen and Liao, 2006; Y.H. Wang, 2006); \(E\) (ng/day) is the daily inhalation exposure level; \(\text{EF}\) (day/year) is the exposure frequency (350 days per year) (Jamhari et al., 2014); \(\text{ED}\) (year) is the exposure duration (for children: \(\text{ED} = 7\); for adolescents: \(\text{ED} = 7\); for adults: \(\text{ED} = 43\); for seniors: \(\text{ED} = 10\)) (Xia et al., 2013); \(\text{CF}\) (mg/ng) is the conversion factor \(10^{-6}\); \(\text{BW}\) (kg) is the body weight; \(\text{AT}\) (day) is the average lifespan for carcinogens (25,550 days). We treated SF, E and BW, which followed lognormal, lognormal and normal distribution, respectively, in Eq. (3) probabilistically. Detailed information on ILCR calculation was presented in Supporting Materials (S.4, Table S5).

1.9. Uncertainty analysis

A Monte Carlo simulation was used to deal with the uncertainties in the E and ILCR assessment. According to previous reports, 5000 iterations with each parameter independently from the appropriate distribution are sufficient to ensure the stability of results (Chen and Liao, 2006; Xia et al., 2013). Based on these, sensitivity analysis can be done to distinguish the influence degrees of various variables by the help of SPSS21.0 software. Rank correlation coefficients between each input variable and output (risk) were calculated, and then by normalizing the output variance to 100% (Chen and Liao, 2006), the contribution of each input variable to the output (risk) variable was assessed, and the sensitivity of each input variable relative to one another was evaluated.

2. Results and discussion

2.1. Pollution characteristics

2.1.1. Pollution level

The mean concentrations of PAHs were 29.26 ± 14.13, 18.14 ± 5.37 and 48.47 ± 16.03 ng/m\(^3\) in gas phase, particle phase and both phases, respectively (Fig. 2). The mean concentrations of BaPeq were 0.87 ± 0.51, 2.71 ± 2.17 and 4.06 ± 2.31 ng/m\(^3\) in gas phase, particle phase and both phases, respectively (Fig. 2). The BaPeq concentration of total PAHs was much higher than 2.5 ng/m\(^3\), the daily limited standard of atmospheric BaP in the newest ambient air quality standard of China (GB 3095-2012), indicating atmospheric PAH pollution in the study area. It is worth noting that, although the mean concentration of gas phase PAHs was higher than that of particle phase PAHs (\(p < 0.1\)), the mean BaPeq concentration of particle phase PAHs was higher than that of gas phase PAHs (\(p < 0.1\)), in accordance with results from other reports (Lai et al., 2013; Wang et al., 2015). The TEFs of high molecular weight (HMW) PAHs, which primarily existed in particulate were much greater than those of low molecular weight (LMW) PAHs, which primarily existed in gas.

Fig. 2 – Concentrations of PAHs and BaPeq in diverse phases. PAHs: atmospheric polycyclic aromatic hydrocarbons; BaPeq: Benzo[a]pyrene equivalent.
Comparisons of PAHs and BaPeq concentrations among Nanjing and other regions are presented in Supporting Materials (S.5, Table S6). Compared with data in similar studies, the mean concentration of particle phase PAHs in this study was higher than that in East China Sea (background site) in spring, whereas lower than that in Zhengzhou, China (an industrial city) in spring (S.5, Table S6). The sampling site is located in a new urban district, where industrial production is relatively far away and transport was not so well-developed, leading to relatively lower PAH pollution level compared with industrial regions.

2.1.2. Ring distribution
Summary situations of ring distribution and PAH constitution are depicted in Figs. 3 and 4, respectively. Detailed information was presented in Supporting Materials (S.5, Table S7). Gas phase PAHs was dominated by 3-ring PAHs (59.35%), followed by 4-ring (22.21%), 2-ring (15.03%), 5-ring (2.32%) and 6-ring (1.07%) compounds, while particle phase PAHs was dominated by 4-ring PAHs (40.21%), followed by 3-ring (22.24%), 2-ring (21.27%), 5-ring (11.93%) and 6-ring (4.35%) compounds. In general, total PAHs was dominated by 3-ring (43.59%) and 4-ring (30.02%) PAHs, followed by 2-ring (17.45%), 5-ring (6.49%) and 6-ring (2.45%) compounds. PAHs with 3 or 4 rings are all semi-volatile and usually occupy significantly in both phases (Kong et al., 2015). The share percentage of PAHs with 5 or 6 rings was higher in particle phase than in gas phase, for the reason that HMW PAHs are mostly non-volatile and exist mainly in particulate (Huang et al., 2006; Wang et al., 2015). The ratio of PAHs (3-ring and 4-ring)/PAHs (5-ring and 6-ring) was widely used in evaluating the source direction of atmospheric PAHs: higher values imply regional transport while lower ones indicate local emissions (Kong et al., 2015; Wang et al., 2011). The specific value of gas phase PAHs was 24.00, whereas that of particle phase PAHs was 3.84, being much less. Therefore, more gas phase PAHs than particle phase PAHs originated from outside regions. The specific value of total PAHs was 8.24, much greater than the value (2.46) obtained in winter in Nanjing (Kong et al., 2015), indicating a long distance transport, which was probably associated with the frequent sandstorm weather in spring.

For PAH compounds with contributors, PHE, PYR and FLA were major PAH compounds in both phases (Fig. 4). The predominant compounds were NAP, ACE and ACY in Kandy, Sri Lanka (Wickramasinghe et al., 2011) in the whole year, BbF, CHR and BghiP in a suburban site of Nanjing, China in spring (He et al., 2014), BbF, BkF and CHR in an industry site of Zhengzhou, China in spring (J. Wang et al., 2014), BbF, BaA and BghiP in a residential site of Zhengzhou, China in spring (J. Wang et al., 2014). Different constitutions probably resulted from various sources.

2.2. Source identification

2.2.1. Diagnostic ratios
Diagnostic ratios were calculated in this study to identify the sources of PAHs. Table 1 lists typical diagnostic ratios and corresponding judge criterions taken from previous literature while Fig. 5 depicts the general situation of ratio calculations. Comparison results among Nanjing and other regions are presented in Supporting Materials (S.6, Table S8).

For the ratio of ANT/(ANT + PHE) (Fig. 5A), the values of gas phase PAHs were mostly less than 0.10, indicating petroleum sources, whereas those of particle phase PAHs were all greater than 0.10, indicating typical combustion sources (Table 1). The values of total PAHs ranged from 0.08 to 0.36 with a mean value of 0.15, mainly indicating combustion sources. For the ratio of BaA/(BaA + CHR) (Fig. 5A), the values of gas phase PAHs were mostly less than 0.10, indicating petroleum sources, whereas those of particle phase PAHs were all greater than 0.10, indicating typical combustion sources (Table 1). The values of total PAHs ranged from 0.08 to 0.36 with a mean value of 0.15, mainly indicating combustion sources. For the ratio of BaA/(BaA + CHR) (Fig. 5A), the values of gas phase PAHs were mostly less than 0.10, indicating petroleum sources, whereas those of particle phase PAHs were all greater than 0.10, indicating typical combustion sources (Table 1). The
above ratios primarily indicated combustion sources, along with some petroleum sources to gas phase PAHs. For the ratio of FLA/(FLA + PYR) (Fig. 5B), the mean values of PAHs in gas phase, particle phase and both phases were 0.47, 0.40 and 0.43, respectively, mainly indicating petroleum combustion (Table 1). For the ratio of IcdP/(IcdP + BghiP) (Fig. 5B), the values of gas phase PAHs ranged from 0.30 to 0.56 with a mean value of 0.49, mainly indicating petroleum combustion with biomass and coal combustion attached (Table 1). The values of PAHs in particle phase and both phases were all greater than 0.5 (except one of particle phase PAHs) with mean values of 0.54 and 0.52, respectively, indicating biomass and coal combustion (Table 1). The above ratios indicated fuel combustion sources as a whole.

For the ratio of BaP/BghiP (Fig. 5C), the values were all greater than 0.6 (except one of particle phase PAHs) with mean values of 1.21, 1.17 and 1.30 for PAHs in gas phase, particle phase and both phases, respectively, indicating traffic exhaust (Table 1). The outcome may be explained by results of FLA/(FLA + PYR) as traffic exhaust originates mainly from petroleum combustion process. Compared with results from other regions, the mean value of particle phase PAHs (1.17) was much greater than those in both São Paulo, Brazil and Kuala Lumpur, Malaysia in spring (S.6, Table S8), suggesting traffic exhaust an outstanding contributor to atmospheric PAHs in study area. For the ratio of FLO/(FLO + PYR) (Fig. 5C), the values were all less than 0.50 (except one of gas phase PAHs) with mean values of 0.37, 0.32 and 0.34 for PAHs in gas phase, particle phase and both phases, respectively, indicating gasoline vehicle emissions among traffic exhaust. The above ratios indicated traffic exhaust sources, especially gasoline vehicle emissions.

Overall, atmospheric PAHs in the new urban district of Nanjing originated mainly from combustion processes. Among these, vehicle emissions were outstanding, especially those from gasoline powered vehicles.

2.2.2. PCA

PCA was performed to get further insight of the sources. PCA results of PAHs in diverse phases are presented in Table 2 with four, two and four factors totally explaining 92.91%, 95.94% and 98.46% of the data variance, respectively. Variables higher than 0.8 in this study were considered relevant in the interpretation of each factor.

For gas phase PAHs, four factors explain 42.08%, 19.66%, 15.76% and 15.41% of the total variance, respectively, indicating traffic exhaust originates mainly from petroleum combustion process. Compared with results from other regions, the mean value of particle phase PAHs (1.17) was much greater than those in both São Paulo, Brazil and Kuala Lumpur, Malaysia in spring (S.6, Table S8), suggesting traffic exhaust an outstanding contributor to atmospheric PAHs in study area. For the ratio of FLO/(FLO + PYR) (Fig. 5C), the values were all less than 0.50 (except one of gas phase PAHs) with mean values of 0.37, 0.32 and 0.34 for PAHs in gas phase, particle phase and both phases, respectively, indicating gasoline vehicle emissions among traffic exhaust. The above ratios indicated traffic exhaust sources, especially gasoline vehicle emissions.

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For gas phase PAHs, four factors explain 42.08%, 19.66%, 15.76% and 15.41% of the total variance, respectively (Table 2). Factor 1 is highly associated with set of PYR, BghiP, CHR, BaP, FLA, BaA, PHE and ANT, where PYR, BghiP, BaP, FLA, BaA, PHE and ANT, where PYR, BghiP, BaP, FLA and BaA

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**Table 1 – Typical diagnostic ratios and corresponding judge criterions.**

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Specific value</th>
<th>Source</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANT/(ANT + PHE)</td>
<td>&lt;0.10</td>
<td>Petroleum</td>
<td>Yunker et al. (2002)</td>
</tr>
<tr>
<td></td>
<td>&gt;0.10</td>
<td>Combustion</td>
<td></td>
</tr>
<tr>
<td>BaA/(BaA + CHR)</td>
<td>&lt;0.20</td>
<td>Petroleum</td>
<td>Yunker et al. (2002)</td>
</tr>
<tr>
<td></td>
<td>0.20–0.35</td>
<td>Mixed sources</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;0.35</td>
<td>Petroleum combustion</td>
<td></td>
</tr>
<tr>
<td>FLA/(FLA + PYR)</td>
<td>&lt;0.40</td>
<td>Petroleum</td>
<td>Yunker et al. (2002)</td>
</tr>
<tr>
<td></td>
<td>0.40–0.50</td>
<td>Petroleum combustion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;0.50</td>
<td>Grass, wood and coal combustion</td>
<td></td>
</tr>
<tr>
<td>IcdP/(IcdP + BghiP)</td>
<td>&lt;0.20</td>
<td>Petroleum</td>
<td>Yunker et al. (2002)</td>
</tr>
<tr>
<td></td>
<td>0.20–0.50</td>
<td>Petroleum combustion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;0.50</td>
<td>Grass, wood and coal combustion</td>
<td></td>
</tr>
<tr>
<td>BaP/BghiP</td>
<td>&lt;0.60</td>
<td>Non-traffic exhaust</td>
<td>Katsoyiannis et al. (2007);</td>
</tr>
<tr>
<td></td>
<td>&gt;0.60</td>
<td>Traffic exhaust</td>
<td>Brändli et al. (2007)</td>
</tr>
<tr>
<td>FLO/(FLO + PYR)</td>
<td>&lt;0.50</td>
<td>Gasoline vehicle emissions</td>
<td>Ravindra et al. (2006)</td>
</tr>
</tbody>
</table>

ANT: Anthracene; PHE: phenanthrene; BaA: benz[a]anthracene; CHR: chrysene; FLA: fluoranthene; PYR: pyrene; IcdP: indeno(1,2,3-cd)pyrene; BghiP: benzo(g,h,i)perylene; BaP: benzo[a]pyrene equivalent; FLO: fluorene.
are all tracers for gasoline vehicle emissions (Hong et al., 2007; Ravindra et al., 2008). Therefore, factor 1 represents traffic exhaust. Factor 2 is mostly associated with FLO, which is the probable tracer for fuel combustion, coke production or diesel vehicle emissions (Kong et al., 2010; Lai et al., 2013). So factor 2 could be explained as mixed sources. Factor 3 is strongly related with IcdP, which is a signature for vehicle emissions, especially gasoline powered vehicles (D. Wu et al., 2014). With high loading of ACY, which mainly stems from power plants or coke ovens, factor 4 could be due to industrial process (D. Wu et al., 2014). In general, gas phase PAHs originated primarily from traffic exhaust, along with fuel combustion and industrial production.

For particle phase PAHs, two factors explain 62.96% and 32.99% of the total variance, respectively (Table 2). Factor 1 groups BkF, BaA, BaP, ACE, ANT, ACY, BbF, IcdP and CHR. Among these, BkF, BaP, ACE and IcdP are tracers for vehicle emissions (Kong et al., 2010), whereas BaA, ANT and BbF are indicators for coal combustion (Kong et al., 2010). Therefore, factor 1 represents mixed sources. Associated with DahA, PYR, FLA and PHE, which are indicators for gasoline vehicle emissions, factor 2 could be due to traffic exhaust (Hong et al., 2007; Ravindra et al., 2008). In general, particle phase PAHs originated primarily from traffic exhaust (especially gasoline vehicle emissions) and coal combustion.

For total PAHs, four factors explain 43.22%, 28.40%, 13.99% and 12.86% of the total variance, respectively (Table 2). Factor 1 is highly loaded with PYR, BghiP, CHR, FLA and BaP. Among these, PYR, BghiP, FLA and BaP are tracers for gasoline vehicle emissions (Lai et al., 2013; Ravindra et al., 2008), whereas PYR, CHR and FLA are indicators for coal and wood combustion (Tian et al., 2009; D. Wu et al., 2014). Therefore, factor 1 could be explained as mixed sources. Factor 2 is highly loaded with DahA, FLO, ACE and NAP. Among these, DahA, FLO and ACE are tracers for vehicle emissions (Hong et al., 2007; Kong et al., 2010) while NAP represents wood combustion (Kong et al., 2010). Moreover, FLO indicates fossil fuel combustion and industrial process, such as coke production (Lai et al., 2013; Ravindra et al., 2008). Therefore, factor 2 could be explained as mixed sources. Related with ACY, which is an indicator for industrial production (D. Wu et al., 2014), factor 3 could be due to industrial process. Related with IcdP and BkF, which are tracers for vehicle emissions (especially diesel vehicle emissions), factor 4 could be due to traffic exhaust (Hong et al., 2007; Jamhari et al., 2014; Simcik et al., 1999). In general, traffic exhaust, fuel combustion and industrial process were three main sources for total PAHs.

It can be inferred from the above analysis that, for PAHs in diverse phases, traffic exhaust was the prominent source followed by fuel combustion and industrial process. Beyond these, gasoline vehicle emissions occupied a great share in traffic exhaust. The traffic artery, commercial district and industrial district around the sampling site significantly affected the source types. Results from PCA strongly reinforced those from diagnostic ratios.

### 2.3. Human health risk assessment

#### 2.3.1. Daily inhalation exposure level

The general situation of daily inhalation exposure level estimates is presented in Table 3. The exposure levels of particle phase PAHs were higher than those of gas phase PAHs for all population groups, due to the fact that the BaP eq concentrations of particle phase PAHs were higher than those of gas phase PAHs. To PAHs in diverse phases, the rankings of exposure levels according to age and gender were adults > adolescents > seniors > children and males > females, respectively, in accordance with the rankings of inhalation rate for all age and gender groups, respectively. Diverse inhalation rates for population groups vary with their different basal metabolic rates and energy requirements.

### Table 2 – Factor loadings of PCA analysis for PAHs in diverse phases.

<table>
<thead>
<tr>
<th>PAHs</th>
<th>Gas phase (n = 7)</th>
<th>Particle phase (n = 7)</th>
<th>Gas + particle phase (n = 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Factor 1</td>
<td>Factor 2</td>
<td>Factor 3</td>
</tr>
<tr>
<td>NAP</td>
<td>0.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACE</td>
<td>0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACY</td>
<td>0.95</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>FLO</td>
<td>0.86</td>
<td>0.75</td>
<td>0.82</td>
</tr>
<tr>
<td>PHE</td>
<td>0.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ANT</td>
<td>0.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FLA</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PYR</td>
<td>0.97</td>
<td>0.82</td>
<td>0.73</td>
</tr>
<tr>
<td>BaA</td>
<td>0.80</td>
<td>0.95</td>
<td>0.92</td>
</tr>
<tr>
<td>CHR</td>
<td>0.92</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>BbF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BkF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaP</td>
<td>0.88</td>
<td>0.95</td>
<td>0.86</td>
</tr>
<tr>
<td>IcdP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DahA</td>
<td>0.93</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>BghiP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total variance (%)</td>
<td>42.08%</td>
<td>19.66%</td>
<td>15.76%</td>
</tr>
<tr>
<td>Cumulative variance (%)</td>
<td>42.08%</td>
<td>61.74%</td>
<td>77.50%</td>
</tr>
</tbody>
</table>

Factors with loadings higher than 0.6 were shown in the table and with loadings higher than 0.8 were shown in bold. PCA: principal component analysis; PAHs: atmospheric polycyclic aromatic hydrocarbons.
Research concerning daily PAH inhalation exposure level is quite limited. The mean BaPeq concentrations of inhalation exposure to total atmospheric PAHs in outdoor environments of Tianjin, China were found to be 321.6 and 519.0 ng/day for children and adults, respectively, which were much higher than the corresponding values in this study (Table 3), resulting from PAH pollution (Bai et al., 2009). The median BaPeq concentrations of inhalation exposure to total atmospheric PAHs in Taiwan, China were estimated to be 1590 and 1628 ng/day for children and adults, respectively, which were much higher than the corresponding values in this study (Table 3), due to the fact that the samples in Taiwan contained 21 PAH compounds and the concentrations of them were extremely high (Chen and Liao, 2006). The median BaPeq concentrations (81.7–265 ng/day) of inhalation exposure to total atmospheric PAHs in Taiyuan, China for different groups were found to be higher than corresponding values in this study (Table 3). Compared with available results, the daily inhalation exposure levels in the new urban district of Nanjing were relatively low.

2.3.2. ILCR assessment
The general situation of ILCR values for diverse population groups caused by PAHs in diverse phases is presented in Table 4. ILCR values caused by particle phase PAHs were greater than the corresponding ones caused by gas phase PAHs, because of the higher BaPeq concentrations of inhalation exposure to particle phase PAHs (Table 3). For PAHs in diverse phases, according to age, ILCR values for adults were the greatest, followed by those for children (Table 4). The greatest ILCR values for adults resulted from the greatest daily inhalation exposure levels and exposure duration, despite their highest body weight. Consequently, adults might be the main objects in the process of lung cancer risk control. It is worth noting that, although the daily inhalation exposure levels and exposure duration of children were the lowest, the lowest body weight of children made ILCR values greater than those for both adolescents and seniors. Reports worldwide showed the same result that children are sensitive to health risks of environmental pollution (Wang et al., 2011). There is no explicit gap between ILCR values for males and females. Although daily inhalation exposure levels were greater for males than for females, the lower body weight of females made ILCR values greater (Table 3). It was different from results obtained in Taiyuan, China, where females showed greater ILCR values than males except adults (Xia et al., 2013). According to the risk assessment guidance from USEPA, ILCR less than $1 \times 10^{-6}$ is considered insignificant, while that greater than $1 \times 10^{-4}$ is always considered significant (Callén et al., 2014; J. Wang et al., 2014). All kinds of ILCR values caused by total PAHs for diverse population groups were greater than $1 \times 10^{-6}$ (Table 4), suggesting that protection measures should be taken. For inhalation exposure to total PAHs, the ILCR values at 67.54th, 72.43th, 39.28th, 72.23th, 66.24th, 71.60th, 41.36th and 71.09th percentile for boys, male adolescents, male adults, male seniors, girls, female adolescents, female adults and female seniors were greater than $10^{-4}$, indicating high potential lung cancer risk; the ILCR values at 99.43th, 99.58th, 97.00th, 99.70th, 99.55th, 99.66th, 96.72th and 99.71th percentile for above groups were greater than $10^{-4}$, indicating significant cancer risk.

<table>
<thead>
<tr>
<th>Table 3 – Daily inhalation exposure levels (ng/day) of PAHs in diverse phases for diverse population groups.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas phase</strong></td>
</tr>
<tr>
<td>Mean</td>
</tr>
<tr>
<td>Boys</td>
</tr>
<tr>
<td>Male adolescents</td>
</tr>
<tr>
<td>Male adults</td>
</tr>
<tr>
<td>Male seniors</td>
</tr>
<tr>
<td>Girls</td>
</tr>
<tr>
<td>Female adolescents</td>
</tr>
<tr>
<td>Female adults</td>
</tr>
<tr>
<td>Female seniors</td>
</tr>
</tbody>
</table>

PAHs: atmospheric polycyclic aromatic hydrocarbons.

<table>
<thead>
<tr>
<th>Table 4 – ILCR for diverse population groups caused by PAHs in diverse phases.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas phase</strong></td>
</tr>
<tr>
<td>Mean</td>
</tr>
<tr>
<td>Boys</td>
</tr>
<tr>
<td>Male adolescents</td>
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<tr>
<td>Male adults</td>
</tr>
<tr>
<td>Male seniors</td>
</tr>
<tr>
<td>Girls</td>
</tr>
<tr>
<td>Female adolescents</td>
</tr>
<tr>
<td>Female adults</td>
</tr>
<tr>
<td>Female seniors</td>
</tr>
</tbody>
</table>

ILCR: incremental lung cancer risk; PAHs: atmospheric polycyclic aromatic hydrocarbons.
The mean values of ILCR caused by PM$_{2.5}$-bound PAHs were found to be $8.9 \times 10^{-7}$ and $6.3 \times 10^{-7}$ for adults (≥18 years) living in industry districts and residential districts of Zhengzhou, China, respectively (J. Wang et al., 2014). The ILCR in Zhengzhou was less than the corresponding values in this study (Table 4). It is worth noting that, the inhalation rate used for ILCR estimates in Zhengzhou was much less than those adopted in this study, which made the calculated ILCR values less. The mean values of ILCR caused by PM$_{10}$-bound PAHs in Kandy, Sri Lanka were almost 2 to 3 orders of magnitude greater than the corresponding values in this study (Table 4), resulting from severe PAH pollution, which significantly elevated daily inhalation exposure levels (Wickramasinghe et al., 2011). The mean value of ILCR caused by PM$_{10}$-bound PAHs was estimated to be $3.01 \times 10^{-7}$ for general citizens in an urban area of Kuala Lumpur, Malaysia (Jamhari et al., 2014), which was less than the mean values caused by PM$_{2.5}$-bound PAHs for all groups in this study (Table 4). The mean values of ILCR caused by total PAHs were found to be in the range of $4.7 \times 10^{-4}$ to $2.41 \times 10^{-3}$ for general citizens in several power plants of Huainan, China, which were much greater than the corresponding values in this study (Table 4), due to the high atmospheric PAH pollution level in industrial districts (Wang et al., 2015). Research in industrial plants of Taiwan, China reflected the same high risk values (Lin et al., 2008). The median values of ILCR caused by total PAHs in urban districts of Taiyuan, China, an industrial city, were estimated to be $2.08 \times 10^{-6}$ (boys), $1.56 \times 10^{-6}$ (male adolescents), $1.03 \times 10^{-5}$ (male adults), $1.60 \times 10^{-6}$ (male seniors), $2.14 \times 10^{-6}$ (girls), $1.58 \times 10^{-6}$ (female adolescents), $9.26 \times 10^{-6}$ (female adults) and $1.67 \times 10^{-6}$ (female seniors), respectively (Xia et al., 2013), being totally greater than the corresponding values in this study (Table 4). In general, ILCR in the new urban district of Nanjing was in a middle level among results from regions worldwide.

2.3.3. Sensitivity analysis on ILCR

The sensitivity analysis results on the ILCR values for all population groups are depicted in the form of the percentile contribution to variance (5.7, Fig. S2). The two most influential variables that contributed most to the total variance of risk for all population groups were the same: the cancer slope factor for BaP inhalation exposure (SF) and BaPeq concentration. Average contributions for SF and BaPeq concentration counted about 73.38% and 26.63%, respectively. Result here is in accordance with that in Tianjin, China (Bai et al., 2009). Based on results above, we can improve the accuracy of the risk assessment by improving the accuracy of SF and BaPeq concentration, especially the accuracy of SF. Besides these, body weight (BW) and inhalation rate (IR) averagely contributed −4.05% and 4.05% to the total variance, respectively, less than contributions of SF and BaPeq concentration.

3. Conclusions

The mean BaPeq concentration of total atmospheric PAHs was higher than the Chinese National Standard, indicating PAH pollution. PHE, PYR and FLA were major PAH compounds in diverse phases. LMW PAH compounds existed mainly in gas, whereas HMW ones appeared mainly in particulate. Two source identification methods showed the same outcomes: traffic exhaust (especially gasoline vehicle emissions) was the predominant source of atmospheric PAHs in diverse phases, along with fuel combustion and industrial process. Apart from this, petroleum volatilization made great contribution to gas phase PAHs. ILCR values caused by particle phase PAHs were greater than those caused by gas phase PAHs. ILCR values for adults were greater than those for other age groups. SF and BaPeq concentration had the greater impact than BW and IR on the ILCR.

Conflict of interest statement

The authors declare that there are no conflicts of interest.

Submission declaration

The authors declare that this work described has not been published previously, and that it is not under consideration for publication elsewhere, and its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere including electronically in the same form, in English or in any other language, without the written consent of the copyright-holder.

Acknowledgments

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Appendix A. Supplementary data

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REFERENCES


