**Sources and health risks of polycyclic aromatic hydrocarbons during haze days
in eastern China: a 1-year case study in Nanjing City**

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Manuscript prepared for **Ecotoxicology and Environmental Safety**

February 12, 2017

25 **ABSTRACT**

26 The concentrations of 16 priority polycyclic aromatic hydrocarbons (PAHs) in ambient air were
27 investigated for a 1-year period to assess their sources and health risks during haze days in Nanjing
28 City, eastern China. The highest level of total PAHs (Σ_{16} PAHs) in the gaseous phase during the
29 haze days was $18.0 \pm 13.3 \mu\text{g}/\text{m}^3$. Their sources may be attributable to pyrogenic products (55.2%),
30 petrochemical refining industry (8.7%), and petrol volatilization (36.1%). The incremental lifetime
31 cancer risk during the haze days exceeded or was close to the priority level of risk (10^{-4}), indicating
32 that PAH pollution during the haze days has caused public health problems associated with the
33 respiratory system. The priority PAHs in the particle phase are mainly composed of low-ring
34 components (< 4 rings), accounting for 65.2–96.8% of the Σ_{16} PAHs during haze days. These
35 particles are derived from petroleum hydrocarbons (16.5%), incomplete combustion of gasoline
36 (62.2%), and burning of coal and biomass (21.4%). The priority level of risk fell within an
37 acceptable range (10^{-7} – 10^{-6}). The PAHs in suspended particles can be transported to the surfaces of
38 vegetables by gravitational deposition, causing an increase in PAH concentrations in vegetable
39 leaves. The increased carcinogenic risk associated with human dietary intake was 6.9×10^{-5} for *S.*
40 *oleracea*, 1.7×10^{-5} for *B. pekinensis*, and 6.2×10^{-6} for *B. chinensis*. These levels were close to the
41 critical value (10^{-4}), and the potential health risks from dietary intake of PAHs should be prioritized.

42

43 **Main finding of this study:** The correlation of PAH sources among environmental carriers and the
44 carcinogenic risks via respiratory and dietary intake during haze days

45 **Keywords:** PAH; haze day; risk assessment; dustfall; vegetable

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47 **1. Introduction**

48 Polycyclic aromatic hydrocarbons (PAHs) are highly condensed aromatic compounds. Their
49 natural sources mainly include forest fires, extrusive volcanism, and depositional transformation of
50 biogenic precursors (Hites et al., 1977). Due to the increase in the demand for fossil fuels, PAHs are
51 increasingly released into the urban environment by a series of anthropogenic activities (e.g.,
52 vehicle emissions, coal and fossil fuel combustion, petroleum refining, straw and firewood burning,
53 industrial processing, chemical manufacturing, oil spills, and coal tar) (Kang et al., 2010). These
54 processes cause the deterioration of air quality and result in a variety of public health problems.
55 PAHs produced by human activities have been detected in numerous environmental media, such as
56 the atmosphere, precipitation, urban surface dust, sediment, and soil, and they likely cause
57 significant and long-term damage to the human respiratory system and increase the mutagenic and
58 carcinogenic risks for urban residents (Merlo et al., 1998). Therefore, local administrations and
59 scientists should prioritize examination of PAH sources and potential health risks.

60 Due to rapid economic development, population growth, and urbanization, eastern China has
61 been experiencing severe haze pollution in late autumn and winter (October 15–February 29). One
62 of the notable effects caused by the high-level aerosols is related to the decrease in visibility (Liang
63 et al., 2007). Furthermore, haze days are usually accompanied by severe air pollution. Numerous
64 field studies have provided data on the concentrations, compositions, sources, and optical properties
65 of aerosol particles (Zhang et al., 2012) and have found correlations between the haze season and
66 pollutants in the major cities of eastern China (Chan and Yao, 2008). Several studies have shown
67 that various inorganic salts, such as ammonium sulfate, sodium chloride, ammonium nitrate, and
68 calcium nitrate, constitute an inorganic component of these particles (Wang et al., 2006) and that
69 particles from the burning of agricultural biomass constitute an important organic component (Hays

et al., 2005). The concentrations of PAHs carried by these solid particles are lower but significant. Despite their carcinogenic and mutagenic properties, the gas-to-particle distribution, atmospheric deposition, and long-term health risks of PAHs in haze are not well known.

PAHs coexist in gaseous and suspended particulate phases in ambient air and are associated with urban surface dustfall (Esen et al., 2008), owing to the gravitational deposition of PAHs with suspended particles (Martuzevicius et al., 2011). The dustfall not only represents a hazardous carrier of PAHs (Han et al., 2009) but is also the link between particle-phase PAHs and bio-phase PAHs. For instance, some studies have shown that surface dust has become a potentially significant pollution source of PAHs in vegetables in some areas (Kipopoulou et al., 1999). Thus, dustfall should be considered a key pathway of PAH transport in the contamination of vegetables. Several scholars have reported the concentrations and distributions of PAHs in the gaseous phase, particulate phase, and dustfall phase (Ravindra et al., 2006; Wang et al., 2011). However, the relevance of PAHs among different environmental media and their combined health risks are poorly understood.

Since the literature contains few studies that comprehensively assess the levels of PAHs in gases, particles, dustfall, and vegetables in eastern China, it is difficult to determine the relevant sources among the different environmental carriers and to assess the respiratory and dietary risks of PAH exposure during haze days. To the best of our knowledge, no study has focused on the correlation of PAH sources among different environmental carriers. Understanding the sources and pathways of pollutants in the ambient air is important for the accurate assessment of the impacts of pollution. Overall, the major aims of this research are i) to identify PAH sources (e.g., coal, gasoline volatilization, vehicle exhaust, and/or the petrochemical refining industry) in different environmental carriers through a principal component analysis combined with multivariate linear

regression (PCA-MLR); ii) to assess the perceived severity of PAH pollution during haze days; and
iii) to elucidate the transport pathway of PAHs among different environmental carriers and assess
the cancer risk posed by respiratory inhalation and dietary intake.

2. Materials and Methods

2.1. Study site and air, dustfall, and vegetable sampling

A fixed sample point (32°2'6.25"N, 118°50'23.47"W) in Xuanwu District, Nanjing, China was
selected for the entire study. This point is located in an educational and residential area, 40 km from
petrochemical refinery facilities and 300 m from a highway. Air and suspended particles were
collected continuously for 1 year from March 1, 2015 to March 1, 2016, during which the haze
season occurred from October 15, 2015 to February 29, 2016. The sampling setup has been
described in a previous paper (Bidleman, 1988). The suspended particles (>0.3 µm in diameter)
were captured using a fiberglass membrane (Whatman, Maidstone, UK) with a retention rate of >
99%. A downstream hollow tube (8 mm in diameter) was filled with a macroporous resin (XAD-2,
5 g; Sigma, St Louis, USA). The air sample was first routed through the fiberglass membrane to
collect the particle-bound PAHs and then through the filled macroporous resin to capture the
gaseous PAHs. Before the membrane and resin were used, they were pre-dried at 105°C for 12 h to
remove potentially volatile impurities. The system was connected to an air autosampler positioned 1
m above ground level. Continuous sampling was performed for 8 h with an air flow rate of 10
L/min. Then, the membrane and XAD-2 resin were collected for subsequent extraction treatment.
With the exception of rainfall days (which were common during spring and summer), the sample
collection was performed twice a week.

In addition, a group of potted experiments were performed to investigate PAH uptake by
vegetables via surface dustfall. Artificial soil, which contained no PAH contaminants and was

116 composed of vermiculite, perlite, and peat substrates (1:1:2, v:v:v), was used to cultivate the three
117 frigestable vegetables *Spinacia oleracea*, *Brassica pekinensis*, and *Brassica chinensis*. After open
118 cultivation for 70 days, leaves of the vegetables were carefully collected and the surface dustfall
119 was rinsed and collected using Milli-Q water (with an electric conductivity of $18.2 \text{ M}\Omega \times \text{cm}$;
120 Millipore, Bedford, MA, USA). The leaves and aqueous dust were dried in a vacuum freeze drier
121 (Labconco, Kansas City, MO, USA) for 7 days at -65°C , followed by the extraction of PAHs.

122 2.2. Extraction and analysis of PAHs

123 The samples, i.e., the fiberglass membrane, XAD-2 resin, dried dustfall, and dried leaves, were
124 treated using a solvent extraction method in 60-mL brown glass vials fitted with Teflon-lined butyl
125 rubber stoppers. Chromatographic-grade dichloromethane (20 mL; Sigma-Aldrich Co., St Louis,
126 MO., USA) was added to each of the vials, and they were exposed to ultrasonic treatment for 30
127 min at 70 W. The supernatant was collected after centrifugation at $2500 \times g$ for 10 min. Each pellet
128 was re-suspended in the vial using 20 mL dichloromethane, and centrifugation was used again to
129 settle the suspended solids. This extraction-centrifugation process was performed three times to
130 obtain a final extraction liquid of 60 mL. After extraction, liquid was filtered through a $0.22\text{-}\mu\text{m}$
131 fiberglass membrane and evaporated to 0.5 mL using a nitrogen blowing process at 25°C , followed
132 by a dilution with acetonitrile to 2.0 mL. The 16 priority PAHs, listed as major pollutants by the US
133 Environmental Protection Agency (EPA), were naphthalene (NAP), acenaphthylene (ANY),
134 acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA),
135 pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF),
136 benzo[k]fluorathene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DiahA),
137 benzo[ghi]perylene (BghiP), and indeno(1,2,3-cd)pyrene (IcdP). These PAHs were measured
138 simultaneously using a high-performance liquid chromatograph (LC-20AT; Shimadzu, Kyoto,

Japan) equipped with an ultraviolet (UV) detector and a $\Phi 4.6 \times 150$ -mm Intertsil ODS-SP column (5 μm , 4.0×250 mm; Shimadzu). The wavelengths were set at 254 nm and 280 nm, respectively. The mobile phase was spectrum-pure acetonitrile with a flow rate of 1.0 mL/min, and the column temperature was 30°C. A gradient elution method was used to measure the PAHs: 0–35 min, acetonitrile/water = 65/35; 35–40 min, acetonitrile/water = 100/0; and 40–50 min, acetonitrile/water = 65/35 (v/v). The concentrations of the 16 PAHs were determined on the basis of the calibration curve obtained from the PAH calibration mix (TraceCERT®, Sigma-Aldrich, St Louis, MO, USA). The standard recovery rates of the PAHs extracted from the fiberglass membrane, XAD-2 resin, dried dustfall, and dried leaves (107.7–68.8%) are listed in **Table S1**. These rates confirmed that the analysis methods could be applied in the present study.

2.3. PCA-MLR

Principal component analysis (PCA) was performed to obtain correlation matrices using Canoco software for Windows (ver. 4.5; Microcomputer Power, Ithaca, NY) (Ter Braak and Smilauer, 2002). The matrices were used to elucidate the linear combinations of PAHs to distinguish among sources (Dickhut et al., 2000; Næs and Oug, 1998). The possible sources included automotive exhaust, crankcase oil, wood burning, coal-fired power plant, coal tar, creosote, and petroleum oil spills (Harrison et al., 1996; Ma et al., 2010). The factor loading values and score matrices were calculated using the concentrations of the PAHs as inputs according to the following equation:

$$X = T \times L \quad (1),$$

where X is the concentration matrix, T is the factor score matrix, and L is the factor loading matrix. The possible source categories could be identified from the factor loading matrix.

Principal component analysis combined with multivariate linear regression (PCA-MLR) was performed to determine the percentage contributions of different PAH sources in a given sample of ambient air. The basic equation for a multiple linear model is as follows:

$$y = \sum_1^p m_i X_i + b \quad (2),$$

where y and X_i are the total PAHs ($\sum_{16}$ PAHs) as the dependent variables, and the PCA factor scores are the independent variables. The effects of the dependent variables on the independent variable can be compared directly using the regression coefficients if the independent and dependent variables are “normally standardized”:

$$\text{standardized normal deviate of } x = (x - \bar{x})/\delta_x \quad (3),$$

where x is the variable, $\bar{x}$ is the mean of x , and σ_x is the standard deviation of x . This new variable represents the distance, in standard deviation units, of a given sample from the mean. When the variables of Equation 1 are normalized and the regression coefficients are represented as B , the equation may be expressed as follows:

$$Z = \sum_1^p B_i X_i \quad (4),$$

where z is the standardized normal deviation of $\sum$ PAHs and B_i is the multivariate regression coefficient:

$$t_i(\%) = (B_i / \sum B_i) \times 100\% \quad (5)$$

where t_i is the contribution level of pollution source i .

2.4. Risk assessment

The individual PAH potency equivalency factors relative to BaP developed by (Chiang et al., 2009) were used to estimate the multi-component PAH exposure:

$$\text{BEC} = \sum_{i=1}^n C_i \times \text{TEF}_i \quad (6),$$

182 where C_i is the concentration of the PAH congener and TEF_i is the toxicity equivalency factor of
 183 the PAH congener.

184 The incremental individual lifetime cancer risk ($ILCR_1$) in ambient air was calculated using the
 185 model proposed by (Chen and Liao, 2006), which can be defined as follows:

$$186 \quad ILCR_1 = \left[\frac{C_a \left(CSF_{B[a]P} (BW/70)^{\frac{1}{3}} \times IR_{air} \times EF \times ED \right)}{BW} \times AT \right] \times cf \quad (7),$$

187 where $CSF_{B[a]P}$ is the inhalation cancer slope factor $1/[(mg/kg \cdot day)^{-1}]$, C_a is the $B[a]P_{eq}$
 188 concentration (ng/m^3), IR_{air} is the inhalation rate (m^3/h) = $20 m^3/day$ (USEPA, 1991), cf is the
 189 conversion factor = 10^{-6} , EF is the exposure frequency = $250 days/year$, ED is the exposure duration
 190 = $70 years$ (EPA, 1989), BW is the body weight = $57 kg$ (average body weight of an Asian adult;
 191 (Walpole et al., 2012), and AT is the average life span of the carcinogen = $70 years \times 365 days/year$
 192 = $25,550 days$ (EPA, 1989).

193 3. Results and Discussion

194 3.1. Concentrations of PAHs in the gaseous phase and as suspended particles

195 **Fig. 1** summarizes the concentrations of the 16 PAHs in the gaseous and particulate phases
 196 during one year. **Fig. 1a** showed that the $\sum_{16}$ PAH concentrations in the gaseous phase ranged from
 197 0.8 to $43.2 \mu g/m^3$ in the spring and from 11.3 to $22.2 \mu g/m^3$ in the summer, with corresponding
 198 average concentrations of $9.6 \pm 14.4 \mu g/m^3$ and $8.7 \pm 8.4 \mu g/m^3$, respectively. The $\sum_{16}$ PAH
 199 concentrations ranged from 2.1 to $37.5 \mu g/m^3$ in the autumn and from 4.6 to $40.3 \mu g/m^3$ in the
 200 winter, with average concentrations of $7.4 \pm 8.3 \mu g/m^3$ and $18.0 \pm 13.3 \mu g/m^3$, respectively. The
 201 average concentrations for the $\sum_{16}$ PAHs followed the decreasing order of winter > spring >
 202 summer > autumn. In the winter, when the total PAH concentrations were highest, the major
 203 low-ring (2–3 rings) PAH pollutants, including FLU ($12.0 \pm 13.4 \mu g/m^3$), NAP ($1.8 \pm 0.5 \mu g/m^3$),

204 and ACE ($0.5 \pm 0.3 \mu\text{g}/\text{m}^3$), accounted for more than 90% of the Σ_{16} PAHs ($18.0 \pm 13.3 \mu\text{g}/\text{m}^3$). In
 205 the spring, summer, and autumn, the FLU, NAP, and ACE were still dominant in the Σ_{16} PAHs,
 206 but their concentrations followed a distinctly decreasing order: FLU ($6.5 \pm 12.3 \mu\text{g}/\text{m}^3$) > ANY (1.3
 207 $\pm 1.1 \mu\text{g}/\text{m}^3$) > NAP ($1.2 \pm 1.9 \mu\text{g}/\text{m}^3$) in spring, ANY ($3.5 \pm 6.6 \mu\text{g}/\text{m}^3$) > FLU ($2.9 \pm 5.4 \mu\text{g}/\text{m}^3$) >
 208 NAP ($1.9 \pm 1.7 \mu\text{g}/\text{m}^3$) in summer, and NAP ($3.7 \pm 6.9 \mu\text{g}/\text{m}^3$) > FLU ($1.7 \pm 1.9 \mu\text{g}/\text{m}^3$) > ANY
 209 ($1.3 \pm 3.3 \mu\text{g}/\text{m}^3$) in autumn. The three compounds accounted for 93.2%, 94.8%, and 89.1% of the
 210 Σ_{16} PAHs in spring, autumn, and winter, respectively. These results indicate that low-ring PAHs
 211 were dominant in these gaseous-phase priority PAHs.

212 The concentrations of Σ_{16} PAHs in the particulate phase were $2.98\text{--}14.4 \times 10^{-2} \mu\text{g}/\text{m}^3$ in spring,
 213 $3.2\text{--}12.2 \times 10^{-2} \mu\text{g}/\text{m}^3$ in summer, $11.5\text{--}23.7 \times 10^{-2} \mu\text{g}/\text{m}^3$ in autumn, and $2.9\text{--}25.3 \times 10^{-2} \mu\text{g}/\text{m}^3$ in
 214 winter (**Fig. 1b**). It is apparent that the Σ_{16} PAH concentrations in autumn and winter were higher
 215 than those in spring and summer. This suggests that serious particulate-phase PAH pollution
 216 occurred during haze days in autumn and winter. In addition, in all seasons, the PAHs in the
 217 particulate phase were dominated by low-ring aromatics, including NAP, ANY, ACE, FLU, PHE,
 218 and ANT. These low-ring aromatics comprised 71.8–96.8% of the measured Σ_{16} PAHs in spring,
 219 62.3–81.3% in summer, 44.5–92.8% in autumn, and 65.2–96.8% in winter. Four-ring PAHs,
 220 including FLA, PYR, BaA, and CHR, made a small contribution to the Σ_{16} PAHs and were minor
 221 components of the Σ_{16} PAHs in spring (0.7–8.4%), summer (3.3–26.5%), autumn (8.3–23.0%),
 222 and winter (0.0–13.2%). PAHs with condensed rings, including BbF, BkF, BaP, DiaH, BghiP, and
 223 IcdP, were moderate contributors to the Σ_{16} PAHs, accounting for 2.5–13.6% in spring, 8.4–34.7%
 224 in summer, 1.1–35.2% in autumn, and 2.4–27.0% in winter. Compared with the gaseous-phase
 225 PAHs, the PAHs containing 4–6 aromatic rings were important among the particulate-phase Σ_{16}
 226 PAHs, which indicates that fused PAHs tended to exist in the particulate phase.

227 3.2. Sources of PAHs

228 We investigated the PAH sources in the gaseous and particulate phases using PCA. The
229 calculated factor loadings are presented in **Table S2**. The principal components were designated
230 PC1–PC3. For PAHs in the gaseous state, three cumulative variances for PC1, PC2, and PC3
231 accounted for 80.5%, 12.5%, and 6.9% of the total variance, respectively (**Table S2**). PC1 consisted
232 of major condensed rings (BkF, DiahA, BghiP, and BbF) and secondary three-ring aromatics (ACE
233 and PHE). These results are consistent with the emission profiles of PAHs from a primary source of
234 coal combustion in a residential area (Liu et al., 2009) and a secondary source of vehicle exhaust
235 (Harrison et al., 1996; Simcik et al., 1998), suggesting that PC1 represents pyrogenic sources.

236 PC2 was enriched in NAP and CHR, which are tracers of petroleum hydrocarbons from oil
237 refineries (**Table S2**) (Short et al., 2008). This result is not unexpected, as the sampling site was
238 located in an educational zone and residential area 40 km from a petrochemical refining area. This
239 finding is consistent with the results of a previous study that suggested that volatile low-ring PAHs
240 are easily transferred through long-distance transport (Ma et al., 2010). Thus, PC2 appears to have
241 been associated with traces of oil transported from a petrochemical refinery. PC3, accounting for
242 6.9% of the total variance, was highly loaded with low-molecular-weight PAHs, including ANY
243 and ANT. Based on the emission characteristics of the PAHs (Ma et al., 2010), this result may be
244 attributed to emissions from the volatilization of gasoline from vehicle exhaust in the gaseous
245 phase.

246 For PAHs in suspended particles, the principal components were assigned to PC1–PC3. The
247 three factors accounted for 50.0%, 32.2%, and 11.8%, of the total variance, respectively (**Table S2**).
248 Together, these three factors accounted for 94% of the total variance and could explain the major
249 sources of PAHs in suspended particles. PC1 was composed primarily of NAP, BkF, BaP, and FLU.

250 The condensed BkF and BaP could be attributed to pyrogenic sources, including coal burning (for
251 power plants and space heating) and vehicle emissions. The low-ring NAP and FLU may be
252 attributed to traces of petroleum hydrocarbons from oil refineries and coke ovens (Khalili et al.,
253 1995).

254 The component loadings of PAHs in suspended particles (**Table S2**) indicated that PC2 was
255 composed of low-ring NAP, PYR, and ANT. These low-ring aromatics can be ascribed mainly to
256 the incomplete combustion of gasoline from vehicle exhaust (Lu et al., 2009). Condensed PAHs,
257 including InPy, DiahA, BaP, BbF, BkF, BaA, PYR, and FLA, were the major components of PC3.
258 A study of data from Sweden, Britain, and Finland showed that condensed PAHs from coal and
259 wood were readily enriched in particles in winter (Prevedouros et al., 2004), suggesting that in the
260 present study, the PAHs in particles were dominated by coal and biomass burning.

261 From Equations 2–4, a pair of multiple linear equations to calculate the source contributions to
262 the PAHs can be written as follows:

263 gaseous phase: $Z = (0.818 \times PC1) + (0.129 \times PC2) + (0.534 \times PC3), (R^2 = 0.98)$ (8),

264 particulate phase: $Z = (0.256 \times PC1) + (0.966 \times PC2) + (0.332 \times PC3), (R^2 = 0.96)$ (9),

265 On the basis of analyses from **Table S2**, we have attributed PC1, PC2, and PC3 of PAHs in
266 gaseous phase to pyrogenic sources, petrochemical refining industry, and petrol volatilization,
267 respectively. The contribution rates for these sources can be calculated according to Equations 5
268 and 8. The contributions to PAHs in the gaseous phase were 55.2% pyrogenic sources, 8.7%
269 petrochemical refining industry, and 36.1% petrol volatilization. From Equation 9, the
270 contributions to PAHs in the particulate phase were 16.5% petroleum hydrocarbons, 62.2%
271 incomplete combustion of gasoline, and 21.4% coal and biomass burning.

272 3.3. Seasonal changes in PAH sources

273 The relationships between the seasonal changes in PAHs in the gaseous phase and the sources
274 are further displayed in **Fig. 2a and b**. The red arrows represent the relationships between PAHs
275 and the coordinate axis, illustrating the PCA results shown in **Table S2**. **Table S2** shows that PC1
276 (explaining 80.5% of the variance) and PC2 (explaining 12.5% of the variance) had gradients
277 characteristic of pyrogenic sources from coal combustion and transported oils from the
278 petrochemical refining industry, respectively. In **Fig. 2a**, the values of PAHs in spring (black open
279 circles) and winter (yellow open triangles) are very close to the FLU, ANT, DiahA, and BghiP
280 arrows, indicating that these PAHs in the gaseous phase were derived from pyrogenic sources in
281 spring and winter; the primary source was coal combustion and the secondary source was vehicle
282 exhaust. The data from summer (purple squares) and autumn (green rhombuses) were close to the
283 PC2 components NAP and CHR, which are derived from transported oils from the petrochemical
284 refining industry. These results indicate that PAHs in the gaseous phase in summer and autumn
285 were derived mainly from transported oils from the petrochemical refining industry. Similarly, the
286 data from summer (purple squares) and autumn (green rhombuses) were close to PC3 components
287 ANY and ANT (**Fig. 2b**), which are associated with the volatilization of gasoline from vehicle
288 exhaust. These results suggest that PAHs in the gaseous phase in summer and autumn were derived
289 from the combined sources of transported oils from the petrochemical refining industry and
290 volatilization of gasoline from vehicle exhaust.

291 The relationships between the seasonal changes in PAHs in suspended particles and their
292 sources are shown in **Fig. 2c and d**. The values of PAHs in spring (black circles) and winter (yellow
293 triangles) generally coincided with NAP, BkF, BaP, and FLU in PC1. These results indicate that
294 petroleum hydrocarbons from oil refineries can be carried by suspended particles in spring and
295 winter. The values of PAHs in summer and autumn were generally close to the low-ring NAP, PYR,

296 and ANT in PC2, indicating that PAH pollution in summer and autumn was influenced by the
297 incomplete combustion of gasoline from vehicle exhaust. A few PAH values obtained in autumn
298 and winter were adjacent to the PC3 components InPy, DiahA, BaP, BbF, BkF, BaA, PYR, and
299 FLA, which were related to coal and biomass burning. These results indicate that small proportions
300 of PAH sources in suspended particles in autumn and winter were associated mainly with coal and
301 biomass burning.

302 Based on the above analyses, the PAH pollution can be associated with haze days in autumn and
303 winter (almost Dec. to March). On haze days, the PAHs (FLU, ANT, DiahA, and BghiP) in the
304 gaseous phase were derived from pyrogenic sources (primary coal combustion and secondary
305 vehicle exhaust). Those in the suspended particles (NAP, BkF, BaP, and FLU) were likely
306 associated with petroleum hydrocarbons primarily from oil refineries and secondarily from coal and
307 biomass burning. The sampling site is located in an educational and residential area and far from a
308 petrochemical refinery (40 km) and highway (300 m). Thus, the PAHs (FLU, ANT, DiahA, and
309 BghiP) in the gaseous phase are attributed to short-distance transport associated with coal burning
310 in nearby residential heating systems and nearby traffic-related sources. The PAHs in the suspended
311 particles (NAP, BkF, BaP, and FLU) exhibit a distinct source that indicates long-distance transport
312 of PAHs attached to particle surfaces because of the association with petroleum hydrocarbons from
313 oil refineries.

314 *3.4. Association of PAH phases*

315 PAHs can fall onto the surfaces of vegetable leaves with suspended particles to form surface
316 dust. Mathematical analysis of dependent variables and independent variables has often been used
317 to determine correlations in intricate natural environments (Valipour, 2015a; Valipour, 2015b;
318 Valipour and Eslamian, 2014). The relationships of the Σ_{16} PAHs between the gaseous and

319 particulate phases were determined to examine their interdependency. A linear correlation can be
320 seen in **Fig. 3a**, which shows that the Σ_{16} PAHs in the surface dustfall increase with particulate Σ_{16}
321 PAHs. The slope, correlation coefficient (R^2), and confidence level (p) were 1865.8, 0.87, and
322 less than 0.01, respectively. These results suggest that the Σ_{16} PAHs in the surface dustfall on
323 vegetable leaves were derived mainly from particulate PAHs in ambient air. Notably, the data for
324 spring and autumn were correlated linearly with those for autumn and winter, indicating that the
325 relationship between the particulate Σ_{16} PAHs and those in dustfall was not affected by the
326 seasonal variation in PAH species in particulate PAHs. Other studies from the Shanghai and Beijing
327 regions showed that PAHs in dustfall were mainly derived from vehicle emissions and crankcase oil
328 (Lian et al., 2009) and that PAHs in dustfall were attributed to gravitational deposition of particulate
329 PAHs in ambient air (Zhang et al., 2007). Our results are consistent with those of previous studies.
330 Based on the analyses in Fig. 2, it is noteworthy that the long-distance transport of PAHs attached
331 to particle surfaces from oil refineries in the present study was considered a primary source. Thus,
332 PAHs in dustfall on vegetable surfaces comes from the long-distance transport of volatile
333 petroleum.

334 In addition, because the PAHs in dustfall remain in contact with vegetable leaves, the leaves can
335 absorb these pollutants. We investigated the relationship between the total PAHs in dustfall and
336 those in vegetable leaves to elucidate this relationship. **Fig. 3b** shows a linear correlation between
337 the concentrations of each PAH species in the dustfall and those in the vegetable leaves. Condensed
338 PAHs (not marked in **Fig. 3b**) were distributed in a low-concentration region at the bottom left of
339 the x - y coordinate matrix. The six low-ring PAHs (BaA, FLU, PYR, BaP, ACE, and NAP)
340 displayed three linear distributions in different vegetable leaves. Here, it should be noted that most
341 low-ring PAHs in dustfall exhibit a linear correlation with those absorbed by vegetables, whereas a

poor linear correlation between vegetables and dustfall was observed for high-ring PAHs. A previous study reported that low-ring PAHs are easily absorbed by vegetables (Tao et al., 2009), suggesting the selective absorption of PAHs in the environment-plant system. Hence, in combination with the analysis of **Fig. 3a**, this result indicates that PAHs in suspended particles can be transferred to dustfall via a dry deposition process and can be selectively absorbed continuously into the leaves of vegetables.

3.5. Potential risks related to respiratory inhalation and dietary intake

According to the US EPA, the level of acceptable risk comparable to normal daily exposure (e.g., diagnostic X-ray) corresponds to a 1 in 1 million chance of the occurrence of additional human cancer over a 70-year lifetime ($ILCR_1 = 10^{-6}$) (Asante-Duah, 2002). An additional lifetime cancer risk of at least 1 in 10,000 ($ILCR = 10^{-4}$) can be considered to be harmful and indicates that respiratory health problems from inhalation should be prioritized (Xia et al., 2010). **Fig. 4** shows the $ILCR_1$ levels of PAHs in the gaseous phase and suspended particles, calculated from Equations 6 and 7. These data show that residents of Nanjing were frequently exposed to gaseous PAHs and $ILCR_1$ levels above or close to the priority level of risk (10^{-4}) in the winter. On several days in the spring and autumn, the levels were close to 10^{-4} , reaching 75% and 95% of the priority level of risk, respectively. Thus, gaseous PAHs reached the levels that are potentially harmful to health in winter in Nanjing City, which suggests that the potential effects on respiratory health should be prioritized.

Fig. 4b shows the $ILCR_1$ values for residents exposed to particle-associated PAHs. The values in spring, summer, autumn, and winter fell within the range of 10^{-7} – 10^{-6} . Two maximum values occurred in autumn ($ILCR_1 = 6.8 \times 10^{-6}$) and winter ($ILCR_1 = 6.7 \times 10^{-6}$) and were significantly lower than the priority level of risk (10^{-4}). Therefore, although significant levels of brown haze occurred in the city and pollution incidents have occurred frequently in autumn and winter in recent

365 years, the $ILCR_1$ values of the particle-associated PAHs were close to acceptable levels and
 366 significantly lower than those of gaseous PAHs. Thus, compared with the PAHs in suspended
 367 particles, those in the gaseous phase posed a more serious health risk to public health.

368 The transport of PAHs from dustfall to vegetable surfaces increases the risk associated with
 369 edible vegetables. An additional lifetime cancer risk of ≥ 1 in 10,000 ($ILCR_2 = 10^{-4}$) for population
 370 groups in Nanjing due to dietary intake of PAHs was calculated using Equation 10:

$$371 \quad ILCR_2 = ED \times EF \times E_D \times SF \times \frac{CF}{BW \times AT} \quad (10),$$

372 where SF is the oral cancer slope factor of benzo(a)pyrene = 7.3 mg/(kg-day), ED is the daily
 373 dietary PAH exposure level (ng/day), ED is the exposure duration (years) for adults ($E_D = 43$), BW
 374 is the body weight (kg) = 57 kg (average body weight of an Asian adult (Walpole et al., 2012)), AT
 375 is the average lifespan of carcinogens = 25,550 days, EF is the exposure frequency = 365 days/year,
 376 and CF is the conversion factor = 10^{-6} mg/ng.

377 The $ILCR_2$ is considered to be a high-priority level of risk. The cumulative probability
 378 distributions of the calculated $ILCR_2$ for population groups in Nanjing were calculated on the basis of
 379 equation 10. The risk values for adults from three vegetables were 6.9×10^{-5} for *S. oleracea*, $1.7 \times$
 380 10^{-5} for *B. pekinensis*, and 6.2×10^{-6} for *B. chinensis*. These values accounted for 69%, 17%, and
 381 6.2%, respectively, of the additional lifetime cancer risk (10^{-4}), which was close to the critical limit
 382 of risk. However, the cumulative $ILCR_2$ for PAH dietary exposure from leafy vegetables has been
 383 reported to be approximately 3.4×10^{-6} (Khillare et al., 2012). In our study, the ingestion of the
 384 studied vegetables appeared to pose a potential risk of cancer. The societal risk can be calculated by
 385 multiplying the $ILCR$ by the current population of Nanjing (8.4 million). We calculated that 51–568
 386 additional cases of cancer are likely related to the lifetime ingestion exposure of the three studied
 387 vegetables. Therefore, consumption of these vegetables should be considered harmful, and limits on

388 their dietary intake should be prioritized.

389 **4. Conclusions**

390 Due to rapid economic development, population growth, and urbanization, various cities in
391 eastern China have frequently experienced haze from approximately October 15 to February 29.
392 Compared with the salts and carbonaceous particulates in the haze, the PAHs might pose a more
393 severe effect on public health. We investigated the seasonal distribution and sources of PAHs in
394 ambient air in Nanjing City, eastern China, during one year to determine the association of PAHs in
395 the gaseous, particulate, and surface-dust phases on haze days and assessed the cancer risks
396 associated with respiratory inhalation and daily diet. In the haze season, the PAHs in the gaseous
397 phase were derived from pyrogenic sources: the primary source was coal combustion, and the
398 secondary source was vehicle exhaust. The ILCR₁ values on haze days were higher than or close to
399 the priority risk level (10^{-4}), and these values should be considered harmful, indicating that potential
400 respiratory health problems from gaseous phase should be prioritized. The PAHs with fewer than
401 four rings in suspended particles were the major components of the Σ_{16} PAHs on haze days
402 (65.2–96.8% in winter). The ILCR₁ values for suspended particles were within acceptable levels
403 (10^{-7} – 10^{-6}). Petroleum hydrocarbons from the oil refining industry carried by suspended particles
404 contributed to the Σ_{16} PAHs. PAHs in suspended particles were transported to vegetables via
405 surface dustfall, thereby increasing the risks associated with vegetables (6.9×10^{-5} for *S. oleracea*,
406 1.7×10^{-5} for *B. pekinensis*, and 6.2×10^{-6} for *B. chinensis*). The dietary intake of these vegetables
407 was close to the critical level of risk (10^{-4}) and should be considered as harmful, indicating that the
408 potential health effects should be prioritized.

409 **Acknowledgments**

410 This work was supported by the National Science Foundation of China (Grant Nos. 41401543,

411 41502170), the National Science Foundation for Postdoctoral Scientists of China (Grant No.
412 2014M561662), the Natural Science Foundation of Jiangsu Province of China (Grant No.
413 BK20140725), the Fundamental Research Funds for the Central Universities (KJQN201518), and
414 the Special Fund for Agro-Scientific Research in the Public Interest, China (201503107).

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525

Figure Legends

Fig. 1. Seasonal variations in PAHs in the gaseous (a) and particulate (b) phases in Nanjing City, eastern China. Spring: March –June; summer: June–August; autumn: September–November; winter: December–February. Haze days usually occur between October 15 and February 29, which spans the entire winter season.

Fig. 2. Principal component analyses of PAHs for four seasons. (a, b) Gaseous PAHs; (c, d) suspended particles.

Fig. 3. Correlation of PAHs among suspended particles, vegetables, and dustfall. The PAH levels in suspended particles were calculated from the average values during the season of vegetation growth (November 15–February 15). The PAH levels in dustfall were calculated from the average values from three samples.

Fig. 4. Incremental lifetime cancer risk (ILCR) values of PAHs in the gaseous (a) and particulate (b) phases. Red dotted line represents the priority level of risk (10^{-4}) considered to be harmful to human health.

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553 **Fig. 3.**

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558 **Fig. 4.**