

## RESEARCH ARTICLE

10.1002/2015JD023628

## Key Points:

- Level of PM<sub>2.5</sub>-bound PAHs and derivatives was high in heating season in Beijing
- Coal/biomass was the major source of PAHs and derivatives in heating season
- Secondary formation was a main source of PAH derivatives in nonheating season

## Supporting Information:

- Texts S1 and S2, Tables S1–S10, and Figures S1–S9

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## Citation:

Lin, Y., Y. Ma, X. Qiu, R. Li, Y. Fang, J. Wang, Y. Zhu, and D. Hu (2015), Sources, transformation, and health implications of PAHs and their nitrated, hydroxylated, and oxygenated derivatives in PM<sub>2.5</sub> in Beijing, *J. Geophys. Res. Atmos.*, 120, 7219–7228, doi:10.1002/2015JD023628.

Received 4 MAY 2015

Accepted 6 JUL 2015

Accepted article online 7 JUL 2015

Published online 30 JUL 2015

# Sources, transformation, and health implications of PAHs and their nitrated, hydroxylated, and oxygenated derivatives in PM<sub>2.5</sub> in Beijing

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**Abstract** Fine particulate matter (PM<sub>2.5</sub>) is a significant health issue in Chinese megacities. However, little information is available regarding the PM<sub>2.5</sub>-bound toxic organics, especially their sources, atmospheric transformations, and health implications. In this study, we assessed the levels of polycyclic aromatic hydrocarbons (PAHs) and their nitrated, hydroxylated, and oxygenated derivatives (i.e., NPAHs, OHPAHs, and OPAHs, respectively) in PM<sub>2.5</sub> collected in Beijing over a 1 year period. The median concentration of 23 PAHs, 15 NPAHs, 16 OHPAHs, and 7 OPAHs in PM<sub>2.5</sub> was 53.8, 1.14, 1.40, and 3.62 ng m<sup>−3</sup>, respectively. Much higher concentrations and mass percentages for all species were observed in the heating season, indicating a higher toxicity of PM<sub>2.5</sub> during this period of time. Positive matrix factorization was applied to apportion the sources of PAHs and their derivatives. It was found that traffic emissions in the nonheating season, and coal combustion and biomass burning in the heating season, were the major primary sources of PAHs and their derivatives. Secondary formation, however, contributed significantly to the derivatives of PAHs (especially NPAHs and OPAHs) in the nonheating season, suggesting significant impacts of atmospheric transformation on the toxicity of PM<sub>2.5</sub>.

## 1. Introduction

Air pollution due to ambient particulate matter (PM) is a significant public health risk factor, which has caused over 3.2 million premature deaths annually worldwide [Lim *et al.*, 2013]. PM concentration was generally higher in the megacities of China, with daily concentrations of fine particulate matter (PM<sub>2.5</sub>) frequently exceeding 100 μg m<sup>−3</sup> [Cao *et al.*, 2012]. In an earlier study, PM pollution was attributed to be the fourth leading risk factor of human health in China, and responsible for 1.2 million premature deaths in 2010 [Yang *et al.*, 2013].

Many epidemiologic studies have found associations between PM<sub>2.5</sub> exposure and a series of diseases such as lung cancers and cardiovascular diseases [Pope *et al.*, 2011]; however, the biological mechanisms involved are not well understood [Lippmann, 2014; Pope *et al.*, 2011]. In general, the toxicity of PM<sub>2.5</sub> is mainly originated from its chemical components [Bell *et al.*, 2007; O'Donnell *et al.*, 2011], especially those from combustion sources [Janssen *et al.*, 2011; Lin *et al.*, 2011]. In this regard, polycyclic aromatic hydrocarbons (PAHs) could be an important toxic component of PM<sub>2.5</sub>. In addition, derivatives of PAHs, such as nitrated PAHs (NPAHs), oxygenated PAHs (OPAHs), and hydroxylated PAHs (OHPAHs), could be even more toxic than their precursors. For example, the mutagenicity and carcinogenicity of NPAHs could be few orders of magnitude higher than the parent PAHs [Durant *et al.*, 1996; Yang *et al.*, 2010], whereas OPAHs have been suggested as one group of the key species in the formation of reactive oxygen species (ROS) and thus cause oxidative damage in the biological molecules such as DNA and proteins [Chung *et al.*, 2006].

PAHs were emitted in a large amount by various combustion sources and could transport in long distances [Hafner and Hites, 2003; Hafner *et al.*, 2005; Lang *et al.*, 2008; Sun *et al.*, 2006]. As a result, PAHs are found to ubiquitously exist in the environment and hence were extensively studied in the past few decades. Compared with PAHs, limited information on the derivatives of PAHs was available, especially that related to their environmental sources. Although laboratory simulations have shown that NPAHs, OPAHs, and OHPAHs are formed either in combustion processes or via atmospheric transformation of PAHs [Atkinson and Arey, 1994;

R.-J. Huang *et al.*, 2014; Shen *et al.*, 2013a], the relative contribution of those sources to the derivatives in ambient atmosphere is still unclear.

China has the highest emission of PAHs in the world, which was around 106 Gg in 2007 and accounted for nearly 21% of the global emissions [Shen *et al.*, 2013]. Due to the large coal/biomass consumption, emission of PAHs is particularly high in North China [Lin *et al.*, 2015]. In addition to the primary sources, high levels of atmospheric oxidants such as ozone and nitrogen oxides in megacities of the region, such as Beijing and Tianjin, could promote the transformation of PAHs into their derivatives [Lin *et al.*, 2015].

Beijing is the capital of China and has a population of more than 20 million. Due to the high population density and the substantial levels of industrial activities in the neighboring regions, it has become one of the world's most polluted cities in terms of PM<sub>2.5</sub> levels [Parrish and Zhu, 2009]. Particularly, secondary formation in the atmosphere was recently found to be the main cause of the unprecedentedly high levels of PM<sub>2.5</sub> in Beijing [Guo *et al.*, 2014; W. Huang *et al.*, 2014]. In this regard, the possible atmospheric transformation of PAHs into various derivatives could be important in terms of their adverse health effects. However, limited information is available regarding the sources of PAHs derivatives in PM<sub>2.5</sub>. In this study, ambient PM<sub>2.5</sub> samples were collected in Beijing over a 1 year period. A total of 61 PAHs, NPAHs, OHPAHs, and OPAHs were quantified to determine their levels, temporal trend, and sources in the atmosphere. The contributions of primary emissions and secondary formation to PM<sub>2.5</sub>-bound PAH derivatives were quantitatively assessed using positive matrix factorization (PMF). This information is essential for establishing regulatory controls of these pollutants in Beijing.

## 2. Materials and Methods

### 2.1. Sample Collection

Samples were collected at an urban monitoring station (39°59'21"N, 116°18'25"E, ~30 m above the ground) on the campus of Peking University (Beijing, China). Samples of PM<sub>2.5</sub> were collected by a high-volume air sampler at a flow rate of 1.13 m<sup>3</sup> min<sup>-1</sup>, with a ≤2.5 μm inlet (HIVOL-CABLD, ThermoFisher Scientific, Waltham, MA, USA). Samples were collected on quartz fiber filters (20.3 × 25.4 cm<sup>2</sup>, prebaked at 450°C for 4 h; Pall Life Science, Port Washington, NY, USA) for 24 h every sixth day from 3 March 2012 to 1 March 2013. Additional samples were collected on heavily polluted days, mostly in the winter. In total, 66 filter samples were collected. The daily mass concentration of PM<sub>2.5</sub> was determined gravimetrically using a synchronous Teflon filter sampling system.

### 2.2. Sample Preparation and Analysis

For each PM<sub>2.5</sub> sample, about 1/15 of the filter (7.5 × 5.0 cm) was cut into strips, spiked with carbon-13, deuterium-, or halogen-labeled standards as recovery surrogate standards (Tables S1 to S4 in the supporting information), and Soxhlet extracted with 200 mL of hexane/acetone (1:1, vol/vol) for 22 h. The extract was concentrated and divided into two aliquots. The first aliquot was cleaned using silica gel chromatography (0.6 cm ID, 6 cm length, with 0.5 cm anhydrous Na<sub>2</sub>SO<sub>4</sub> on top), and sequentially eluted with 8 mL of hexane and 8 mL of dichloromethane. The analytes were present in the second fraction. After concentration, the eluent was spiked with the internal standards and analyzed for PAHs, NPAHs, and OPAHs using gas chromatography-mass spectrometry (GC-MS, 7890A-5975C; Agilent, Santa Clara, CA, USA). The other aliquot was concentrated under a gentle pure nitrogen flow, spiked with 1 mL of potassium hydroxide solution (0.5 M), and washed 3 times with hexane. Then 300 μL of pentafluorobenzoyl chloride (10% in ethyl acetate; Sigma-Aldrich, St. Louis, MO, USA) was added to the aqueous phase to derivatize the phenolic groups in OHPAHs. After a 10 min reaction at room temperature, the derivatized compounds were extracted for 3 times with hexane. After preconcentration step, <sup>13</sup>C-PCB209 was added as the internal standard for GC-MS analysis. To prevent the photodegradation of PAHs, only red light was used for illumination throughout the sample preparation process. In addition, amber containers, or tubes and vials wrapped with aluminum foil, were used.

PAHs were analyzed by GC-MS with an electron ionization (EI) ion source, whereas NPAHs, OPAHs, and the derivatized OHPAHs were analyzed using an electron-capture-negative ionization (ECNI) ion source. For all the analysis, the injection port of GC was held at 250°C with an injection volume of 1 μL. A 30 m DB-5MS column (250 μm ID, 0.25 μm film thickness; J&W Scientific, Folsom, CA, USA) was used for PAHs analysis,

while a 15 m Rtx-5MS column (250  $\mu\text{m}$  ID, 0.10  $\mu\text{m}$  film thickness; Restek Corp., Bellefonte, PA, USA) was used for the derivatives. The details of the GC oven temperature program and monitored ion couples are provided in the supporting information.

### 2.3. Quality Control

Three field blank samples and seven laboratory blank samples were prepared, and the results are shown in Tables S5–S7 in the supporting information. Because the mean concentrations of naphthalene, biphenyl, dibenzofuran, 1- and 2-nitronaphthalene, 2-nitrobiphenyl, and 1,3-dinitronaphthalene in the blank samples were more than 20% of those in the  $\text{PM}_{2.5}$  samples, they were excluded from further analysis. For the remaining species, their mean concentrations in field and laboratory blank samples were  $1.8 \pm 3.3\%$  and  $1.6 \pm 4.8\%$  of those in the  $\text{PM}_{2.5}$  samples, respectively. The recoveries of 10 surrogate standards were  $82.5 \pm 17.1\%$ , with the statistic of each surrogate standards listed in Tables S5–S7 in the supporting information.

### 2.4. PMF Analysis

Positive matrix factorization (PMF), which is a receptor model developed by *Paatero and Tapper* [1994], has been widely used for the source apportionment of air pollutants [Hu *et al.*, 2010; Lin *et al.*, 2013]. The methodology is described in the supporting information. Source apportionment of the PAHs and their derivatives was performed separately, using the EPA PMF 3.0 version. In the PMF analysis of PAHs ( $\text{PMF}_{20}$ ), 20 PAH species were input to the model to resolve their primary emission sources. Thereafter, 53 species including 20 PAHs, 13 NPAHs, 15 OHPAHs, and 5 OPAHs were input to the model ( $\text{PMF}_{53}$ ) to apportion the source contributions of both primary emissions and secondary formation to the PAH derivatives. Details of the analyses and the quality control procedures applied are provided in the supporting information.

## 3. Results and Discussion

### 3.1. Levels of $\text{PM}_{2.5}$ -Bound PAHs and Their Derivatives

In this study, 23 PAHs, 15 NPAHs, 16 OHPAHs, and 7 OPAHs were quantified, with most species detected in more than 90% of samples. Summaries of all of the species are listed in Tables S5–S7, and the concentration of each species in  $\text{PM}_{2.5}$  samples is shown in Figures S1 and S2 in the supporting information. Briefly, the median concentration was  $53.8 \text{ ng m}^{-3}$  (range, same as below;  $3.54\text{--}904$ ),  $1.14 \text{ ng m}^{-3}$  ( $0.15\text{--}9.27$ ),  $1.40 \text{ ng m}^{-3}$  ( $0.093\text{--}59.9$ ), and  $3.62 \text{ ng m}^{-3}$  ( $0.47\text{--}610$ ) for the sum of PAHs ( $\Sigma_{23}\text{PAHs}$ ), NPAHs ( $\Sigma_{15}\text{NPAHs}$ ), OHPAHs ( $\Sigma_{16}\text{OHPAHs}$ ), and OPAHs ( $\Sigma_7\text{OPAHs}$ ), respectively.

The  $\text{PM}_{2.5}$ -bound concentrations of PAHs, NPAHs, and OPAHs measured in this study were comparable to the reported levels in Beijing in recent years, and other cities in China, such as Xi'an and Nanjing, but were higher than those reported in other cities in the developed countries, such as Atlanta and Madrid (Table 1). To the best of our knowledge,  $\text{PM}_{2.5}$ -bound OHPAHs have only been measured previously in three cities [Bandowe *et al.*, 2014; Barrado *et al.*, 2012; Wang *et al.*, 2007]. The annual average concentration of OHPAHs in Beijing ( $11.1 \text{ ng m}^{-3}$   $\Sigma_{16}\text{OHPAHs}$ ) is the highest among all cities where data are available (i.e., Xi'an:  $3.4 \text{ ng m}^{-3}$ ,  $\Sigma_{10}\text{OHPAHs}$  [Bandowe *et al.*, 2014]; Nanjing:  $0.15 \text{ ng m}^{-3}$ ,  $\Sigma_{10}\text{OHPAHs}$  [Wang *et al.*, 2007]; and Madrid:  $0.015\text{--}0.26 \text{ ng m}^{-3}$ ,  $\Sigma_2\text{OHPAHs}$  [Barrado *et al.*, 2012]). Our measurements suggest that high levels of  $\text{PM}_{2.5}$ -bound PAHs and their derivatives were present in the atmosphere of Beijing.

### 3.2. Temporal Trends of PAHs and Their Derivatives

Clear temporal trends in the concentration of PAHs and their derivatives were observed in this study. As shown in Figure 1, the monthly concentrations of PAHs, NPAHs, OHPAHs, and OPAHs were elevated from November through March, which was exactly coincident with the winter heating period in Beijing. The median concentrations of PAHs, NPAHs, OHPAHs, and OPAHs in the heating season were  $266 \text{ ng m}^{-3}$ ,  $2.15 \text{ ng m}^{-3}$ ,  $18.3 \text{ ng m}^{-3}$ , and  $60.1 \text{ ng m}^{-3}$ , which were 11.0, 3.7, 58.6, and 58.4 times higher than those in the nonheating season (April through October), respectively (Tables S8–S10 in the supporting information). This could be a result of the increased consumption of coal and biomass in the heating season, which are the main fuels used for winter heating in North China [Zhang and Tao, 2008]. In addition, the lower temperature, incoming solar radiation, boundary layer height, and more frequent stable weather conditions in the heating season, could also lead to the accumulation of PAHs and their derivatives in  $\text{PM}_{2.5}$  [Quan *et al.*, 2014].

**Table 1.** Comparisons of Concentration of PM<sub>2.5</sub>-Bound PAHs, NPAHs, and OPAHs Between Beijing and Other Cities

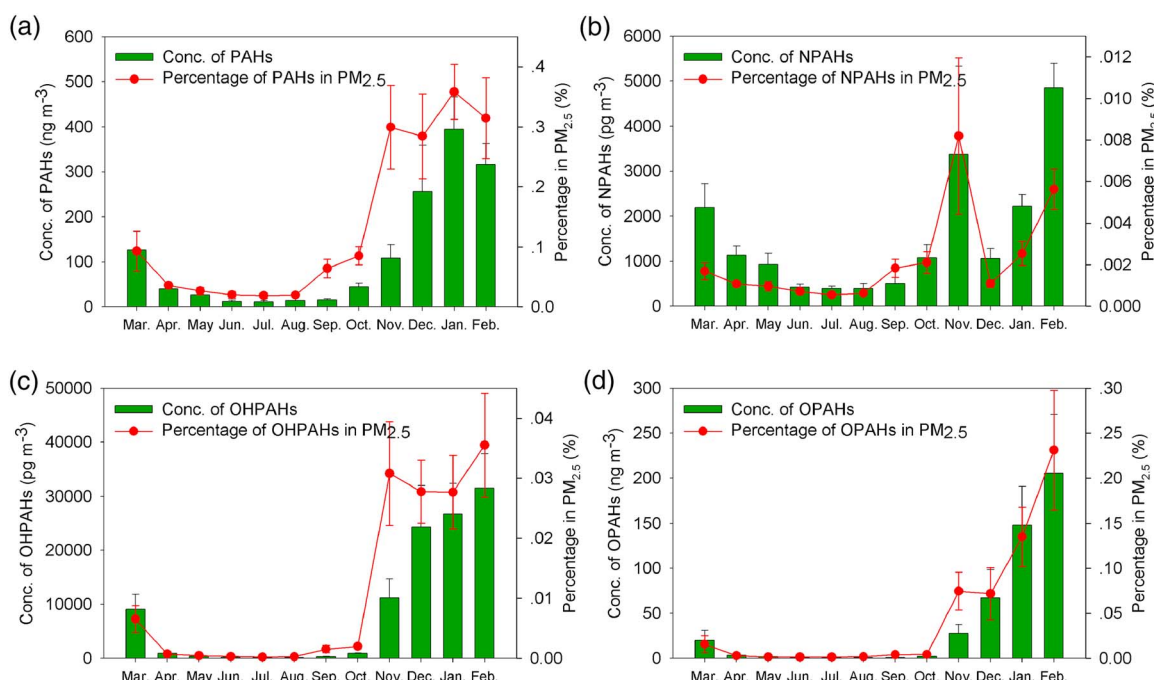
City	Sampling Year	PAHs (ng m <sup>-3</sup> )		NPAHs (pg m <sup>-3</sup> )		OPAHs (ng m <sup>-3</sup> )		Reference
		# of Species	Average	# of Species	Average	# of Species	Average	
China								
Beijing	2012–2013	23	143	15	1730	5	55.9	This study
Beijing	2009–2010	16	107	NA <sup>a</sup>	NA	NA	NA	Liu et al. [2015]
Beijing	2008	28	13.6	11	521	5	0.80	Wang et al. [2011]
Beijing	2004–2005	10	43.7	NA	NA	NA	NA	Jiang et al. [2009]
Beijing	2002–2003	26	78.7	NA	NA	NA	NA	Huang et al. [2006]
Zhengzhou	2011–2012	16	166	NA	NA	NA	NA	Wang et al. [2014]
Nanjing	2004	17	62.5	NA	NA	NA	NA	Wang et al. [2007]
Shanghai	2004–2005	10	10.1	NA	NA	NA	NA	Jiang et al. [2009]
Xi'an	2008–2009	28	87	12	200	15	44	Bandowe et al. [2014]
Other Countries and Regions								
Madrid, Spain	2008	10	0.65	NA	NA	NA	NA	Barrado et al. [2012]
Augsburg, Germany	2007–2008	11	6.17	NA	NA	6	1.94	Pietrogrande et al. [2011]
Umea, Sweden	2009	15	2.5 <sup>b</sup>	NA	NA	12	0.48 <sup>d</sup>	Wingfors et al. [2011]
Athens, Greece	2003–2004	18	15.0	NA	NA	14	5.46	Andreou and Rapsomanikis [2009]
Atlanta, USA	2004	28	1.66	NA	NA	NA	NA	Li et al. [2009]
Los Angeles, USA	2001–2002	15	0.63	NA	NA	NA	NA	Eiguren-Fernandez et al. [2004]
Mexico City, Mexico	2006	19	7.10 <sup>c</sup>	9	122 <sup>c</sup>	NA	NA	Amador-Muñoz et al. [2011]

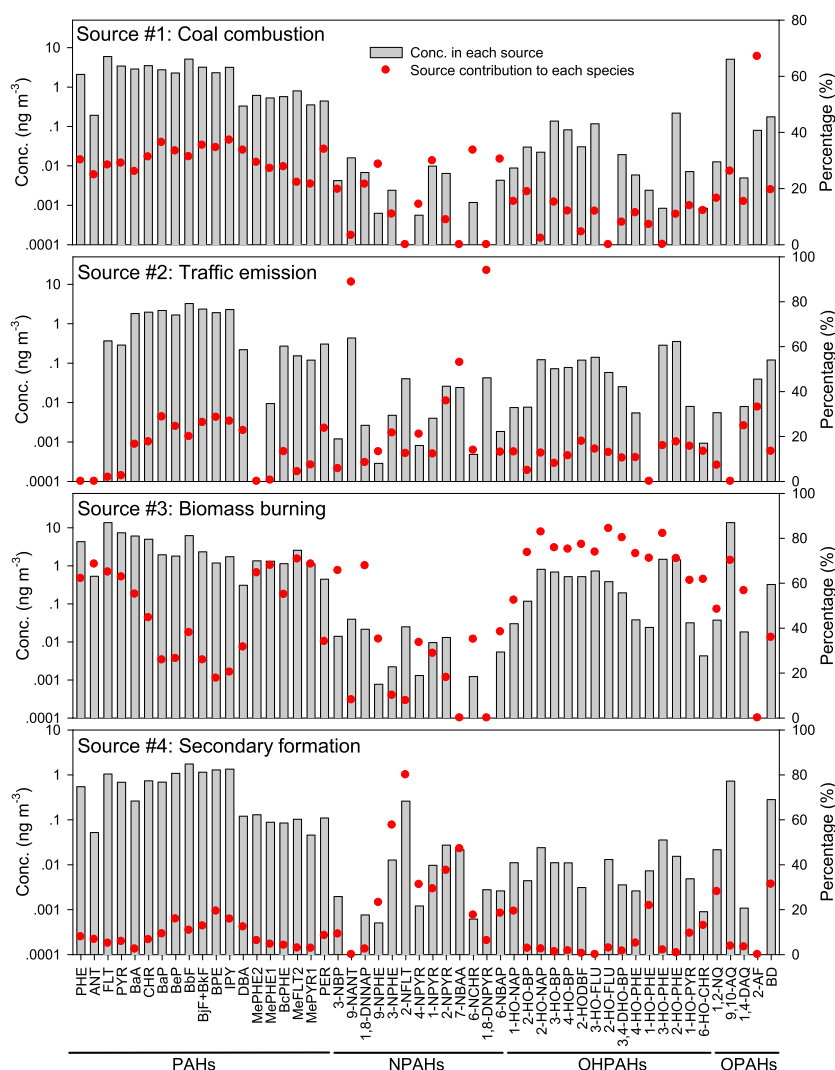
<sup>a</sup>NA, not analyzed.

<sup>b</sup>Geomean.

<sup>c</sup>Median.

Although the mass concentrations of PM<sub>2.5</sub> in Beijing in the heating season (median, 98.2 μg m<sup>-3</sup>) were significantly higher than those in the nonheating season (median, 64.3 μg m<sup>-3</sup>) ( $p < 0.05$ , Mann-Whitney test), the difference in the concentrations of PAHs and their derivatives was even larger. As a result, the mass percentage of PAHs and their derivatives in PM<sub>2.5</sub> was significantly enhanced in the heating season (median, 3.05‰) compared with the nonheating season (median, 0.33‰) ( $p < 0.01$ , Mann-Whitney test). Because PAHs and their derivatives are important toxic components of PM<sub>2.5</sub>, the health implications of exposure to PM<sub>2.5</sub> could vary throughout the year. Based on the toxic equivalency factors (TEFs) of


**Figure 1.** Monthly concentration (mean + standard error) and mass percentage (mean ± standard error) in PM<sub>2.5</sub> of (a) PAHs, (b) NPAHs, (c) OHPAHs, and (d) OPAHs in Beijing.



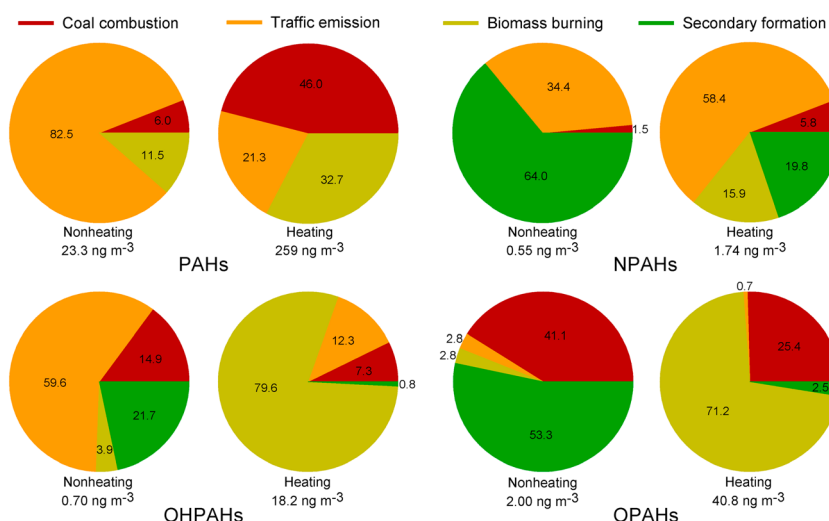
**Figure 2.** Source profiles of PAHs and their derivatives based on the PMF<sub>53</sub> analysis and the relative contribution of each source to the target species.

benzo(a)pyrene (BaP) [Wei *et al.*, 2015; Bandowe *et al.*, 2014], it was estimated that the toxicity from PAHs in PM<sub>2.5</sub> in the heating season (median, 0.38 ng BaP<sub>eq</sub>/μg PM<sub>2.5</sub>) was 6.9 times higher than in the nonheating season (median, 0.055 ng BaP<sub>eq</sub>/μg PM<sub>2.5</sub>). The toxicity from NPAHs in PM<sub>2.5</sub> in the heating season (median, 0.84 pg BaP<sub>eq</sub>/μg PM<sub>2.5</sub>) was 4.4 times higher than in the nonheating season (median, 0.19 pg BaP<sub>eq</sub>/μg PM<sub>2.5</sub>). It was not possible to estimate the toxicity for OHPAHs and OPAHs due to the lack of corresponding TEFs, but we could speculate a similar trend as that for PAHs.

As discussed above, the temporal trend of PAHs and their derivatives indicated a significant impact of winter heating activities on the ambient abundance of these pollutants. Therefore, a quantified attribution of PAHs and their derivatives to various sources in different time periods is essential for formulating effective pollution control policy. To achieve this objective, a PMF-based source apportionment was performed to quantitatively investigate the sources of those pollutants.

### 3.3. Source Apportionment of PAHs and Their Derivatives

Previous studies have shown that PAHs in the atmosphere are mainly released from the incomplete combustion processes including biomass burning, coal combustion, and vehicle emissions [Shen *et al.*, 2013; Zhang and Tao, 2008, 2009]. From the PMF<sub>20</sub> analysis, we apportioned the contributions of these



**Figure 3.** Source contributions (%) for PAHs, NPAHs, OHPAHs, and OPAHs in the heating (November–March) and nonheating seasons (April–October).

three combustion sources of  $\text{PM}_{2.5}$ -bound PAHs in Beijing, and the results are shown in Figures S3 and S4 in the supporting information.

The profile of  $\text{PMF}_{20}$ -source#1 was similar to that of industrial coal combustion in power plants and heating stations in Beijing [Zhang *et al.*, 2008a]. This is a significant source of almost all PAH species. The profile of  $\text{PMF}_{20}$ -source#2 indicated high loadings of PAHs with more than four rings and was similar to that of vehicle emissions measured in a tunnel study in China [He *et al.*, 2008]. The profile of  $\text{PMF}_{20}$ -source#3 was similar to that of residential straw burning in Beijing [Zhang *et al.*, 2008b] and was the dominant source of three- and four-ring PAHs. Although the profiles of  $\text{PMF}_{20}$ -source#1 and #2 had similarities,  $\text{PMF}_{20}$ -source#2 was found to display less seasonal variation than  $\text{PMF}_{20}$ -source#1. In addition, as we discuss later,  $\text{PMF}_{20}$ -source#1 was the predominant contributor of PAHs in the heating season, whereas  $\text{PMF}_{20}$ -source#2 was dominant in the nonheating season. This suggests that coal combustion in the heating season and traffic emissions in the nonheating season are the main sources of PAHs in Beijing, which is consistent with previous investigations in Beijing [Huang *et al.*, 2006; Wang *et al.*, 2011]. All these evidences have allowed us to better distinguish  $\text{PMF}_{20}$ -source#1 (coal combustion) and  $\text{PMF}_{20}$ -source#2 (traffic emissions) in Beijing.

In addition to the primary combustion sources, the derivatives of PAHs may originate from atmospheric secondary formation [Atkinson and Arey, 1994]. Therefore, a further PMF analysis with 53 species ( $\text{PMF}_{53}$ ) was performed to identify the sources of PAH derivatives in Beijing, and the results are shown in Figure 2 and Figure S5 in the supporting information. As expected, PAHs were mainly resolved in sources#1 to #3 in the  $\text{PMF}_{53}$  analysis, matching the results of  $\text{PMF}_{20}$  analysis. In contrast,  $\text{PMF}_{53}$ -source#4 was the major source of 3-nitrophenanthrene (3-NPHE), 2-nitrofluoranthene (2-NFLT), and 2-nitropyrene (2-NPYR). All of these nitrated species have a secondary formation source in the atmosphere of North China, as shown in our previous study [Lin *et al.*, 2015]. Therefore,  $\text{PMF}_{53}$ -source#4 was allocated as secondary formation in the atmosphere.

### 3.4. Sources and Health Implications in the Heating and Nonheating Seasons

As discussed above, heating activities could be the main reason for the elevated level of PAHs and their derivatives in Beijing. The relative contributions of the four sources in both heating and nonheating seasons were compared. The source apportionment of PAHs was based on the  $\text{PMF}_{20}$  analysis, whereas that of their derivatives was based on the  $\text{PMF}_{53}$  analysis.

As shown in Figure 3, the three primary sources significantly contributed to the PAHs in  $\text{PM}_{2.5}$  collected in Beijing, but the relative percentage was different in the heating and nonheating seasons. In the



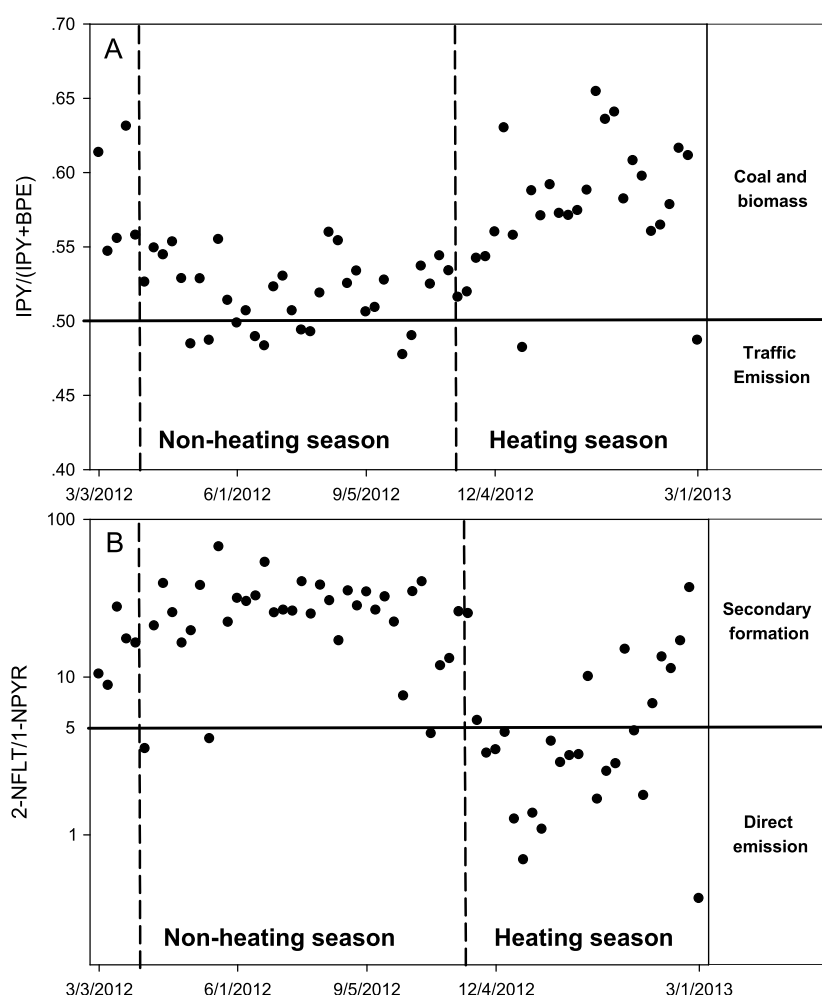
nonheating season, the major source of PAHs was traffic emissions, whereas in the heating season, coal combustion was the major source, followed by biomass burning. When BaP<sub>eq</sub> was used as an indicator of PM<sub>2.5</sub> toxicity due to the presence of PAHs, coal combustion was identified as the major cause for increased PM<sub>2.5</sub> toxicity in the heating season, because it contributed 51.6% of the total PAHs toxicity in this period. Biomass burning only contributed 15.7% of the total PAHs toxicity in the heating season, because it mainly generated PAHs with a relatively lower toxicity. In the nonheating season, traffic emissions were the dominant source of BaP<sub>eq</sub> and thus contributed 91.2% of the total PAH toxicity.

Secondary formation and traffic emissions were the two main sources of NPAHs in both heating and nonheating seasons. In the nonheating season, NPAHs were mainly generated via secondary formation and then through vehicle emissions. This was consistent with the results of a previous study carried out in the nonheating season of 2008 in Beijing [Wang *et al.*, 2011]. In the heating season, although the levels of NPAHs from secondary formation were similar, their relative abundance decreased because of an increased contribution from traffic emissions, biomass burning, and coal combustion. Biomass burning and coal combustion were not considered to be the major sources of NPAHs in previous studies [World Health Organization, 2003]; however, in this study, we found that they were significant contributors to PM<sub>2.5</sub>-bound NPAHs in the heating season, probably due to the intensive biomass burning and coal combustion activities in Beijing and the surrounding region during the heating season. The different source distributions in the heating and nonheating seasons could also alter the profile of NPAHs. For example, the combined concentration of 3-NPHE, 2-NFLT, and 2-NPYR, which are secondarily formed in the atmosphere [Lin *et al.*, 2015], was 0.44 ng m<sup>-3</sup> (60.2% of the total) in the nonheating season. Although the total concentration of these three NPAHs increased slightly to 0.64 ng m<sup>-3</sup>, it comprised only 22.4% of total NPAHs (2.83 ng m<sup>-3</sup>) in the heating season. In comparison, the combined concentration of the primary NPAHs (i.e., 9-NANT, 1-NPYR, and 7-NBaA) [R.-J. Huang *et al.*, 2014; Zhu *et al.*, 2003] was 0.23 ng m<sup>-3</sup> (31.8% of the total) in the nonheating season, but it increased to 1.77 ng m<sup>-3</sup> (62.4% of the total) in the heating season.

The source apportionment of PAHs and NPAHs could be further confirmed by the classic diagnostic ratios of these compounds including IPY/(IPY + BPE) (IPY indicates indeno(1,2,3-cd)pyrene, while BPE indicates benzo(g,h,i)perylene) and 2-NFLT/1-NPYR (Figure 4). For IPY/(IPY + BPE), a value greater than 0.5 was linked with coal combustion and biomass burning, while a value smaller than 0.5 was linked with traffic emission [Lin *et al.*, 2015]. As shown in Figures 4a, IPY/(IPY + BPE) were significantly higher in the heating season ( $p < 0.05$ , Mann-Whitney test), indicating elevated contributions of coal combustion and biomass burning in this time period. For 2-NFLT/1-NPYR, a value greater than 5 was linked with secondary formation, while a value less than 5 was linked with direct emissions [Lin *et al.*, 2015]. As shown in Figure 4b, the 2-NFLT/1-NPYR ratio revealed secondary formation was the major contributor to NPAHs in the nonheating season, while direct emissions became the predominant source in the heating season. This finding was also consistent with what we obtained from the PMF analysis (Figure 3).

The oxygenated products of PAHs were all quinones, and 9,10-anthraquinone was found to be the most abundant in this study. Although several previous studies have identified their emissions from coal combustion and biomass burning, a quantitative assessment of their sources in the atmosphere is not available [R.-J. Huang *et al.*, 2014; Shen *et al.*, 2013a, 2013b]. In this study, we found coal combustion to be an important source of OPAHs throughout the year, and biomass burning was the major source in the heating season. Secondary formation of OPAHs predominated in the nonheating season. Because OPAHs are considered to be the key species in the generation of harmful ROS [Chung *et al.*, 2006], our findings highlighted a significant health impact from their secondary formation in the atmosphere, particularly in the nonheating season when NPAHs were also mainly secondarily formed.

Information on the sources of OHPAH in the atmosphere is not well known, and we initially assumed that they produced from the reaction of PAHs with hydroxyl radical (or other oxidants) in the atmosphere. However, it turned out that OHPAHs are mainly emitted from primary sources. In the nonheating season, traffic emission was the major source of OHPAHs, followed by secondary formation. In the heating season, although a similar concentration of OHPAHs was apportioned to secondary formation, it accounted for a much smaller proportion of the total OHPAHs due to the higher emissions from primary sources, particularly biomass burning. This was probably because (i) biomass burned with a lower efficiency in residential stoves, which favored the generation of PAHs derivatives [Shen *et al.*, 2012], and (ii) most



**Figure 4.** Temporal trends of (a)  $IPY/(IPY + BPE)$  and (b)  $2-NFLT/1-NPYR$ .

OHPAHs species measured in this study had less than four phenyl rings, which were mainly emitted by biomass burning, as discussed above. In addition, coal combustion and traffic emissions were also important sources of OHPAHs in the heating season.

The atmospheric transformation of PAHs was an important source of all three groups of PAHs derivatives in the nonheating season. Higher ratios of 2-NFLT/FLT and 2-NPYR/PYR were observed in this time period (Figure S6 in the supporting information), which indicates higher transformation rates of parent PAHs in nonheating season than those in the heating season. This may be due to the higher temperature and stronger solar radiation during the nonheating season [Reisen and Arey, 2005]. However, it was noteworthy that the absolute contribution from secondary formation did not decrease much in the heating season (Figure S5 in the supporting information). This could be partly explained by the higher levels of parent PAHs emitted from coal combustion and biomass burning in the heating season. This suggests that winter heating activities could have a significant health impact not only through the direct emission of toxic pollutants into the atmosphere but also by producing more precursors to form more oxygenated and toxic compounds, e.g., NPAHs and OPAHs, via atmospheric secondary formation. This in turn could further increase the toxicity of  $PM_{2.5}$  in Beijing.

In summary, a significant increase in the level of  $PM_{2.5}$ -bound PAHs and their derivatives has been found in the heating season in Beijing. This tendency was attributed to the increased emissions of these pollutants from various primary sources in the heating season, especially coal combustion and biomass burning. In addition, secondary formation was an important source of PM toxicity from the PAHs derivatives in the



nonheating season. Further studies are required to investigate the secondary formation processes as well as the corresponding alternation of toxicity due to these pollutants in the atmosphere, especially in the nonheating season. Effective emission mitigation methods of PAHs should be developed, especially in the heating season. This will help to formulate a better regulation and control strategy of air pollution in Beijing.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (21322705, 41121004, 21477102, and 21190051), the Ministry of Science and Technology of China (973 program, 2015CB553401), the Collaborative Innovation Center for Regional Environmental Quality, and the Chinese Scholarship Council. All the data necessary to reproduce the experiments are available from the authors upon request (xhqu@pku.edu.cn).

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