https://doi.org/10.5194/acp-2020-576
Preprint. Discussion started: 22 June 2020

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Nationwide increase of polycyclic aromatic hydrocarbons in ultrafine particles during winter over China

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are toxic compounds in the atmosphere and have adverse effects on public health, especially through the inhalation of particulate matter (PM). At present, there are limited understandings in size distribution of particulate-bound PAHs and its health risk on a continental scale. In this study, we carried out a one-year PM campaign and simultaneously measured size-segregated PAHs at 12 sites across six regions of China. The annual averages of total 24 PAHs ($\sum_{24}$PAHs) and benzo[a]pyrene (BaP) carcinogenic equivalent concentration (BaP_{eq}) ranged from 7.56 to 205 ng m^{-3} with a mean of 53.5 ng m^{-3} and 0.21 to 22.2 ng m^{-3} with a mean of 5.02 ng m^{-3}, respectively. At all the sites, $\sum_{24}$PAHs and BaP_{eq} were dominated in the ultrafine particles with aerodynamic diameter <1.1 μm, followed by those in the size ranges of 1.1-3.3 μm and >3.3 μm. Compared with the southern China, the northern China witnessed much higher $\sum_{24}$PAHs (87.36 ng m^{-3} vs. 17.56 ng m^{-3}), BaP_{eq} (8.48 ng m^{-3} vs. 1.34 ng m^{-3}) and PAHs inhalation cancer risk (7.4×10^{-4} vs. 1.2×10^{-4}). Nationwide increases in both PAH levels and inhalation cancer risk occurred in winter. The unfavorable meteorological conditions and enhanced emissions of coal combustion and biomass burning together led to severe PAHs pollution and high cancer risk in the atmosphere of the northern China, especially during winter. Our results suggested that the reduction of coal and biofuel consumption in the residential sector could be crucial and effective to lower PAH concentrations and its inhalation cancer risk in China.

Key words: Polycyclic aromatic hydrocarbons; inhalation cancer risk; China; coal combustion; biomass burning

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1. Introduction

Ambient particulate matter (PM) pollution has adverse effects on public health. The global deaths caused by exposure to the PM with aerodynamic diameters less than 2.5 μm ($PM_{2.5}$) kept increasing from 1990 and reached 4.2 million in 2015 (Cohen et al., 2017). In China, $PM_{2.5}$ pollution was ranked the fourth leading factor for mortality (Yang et al., 2013), and caused 1.7 million premature deaths in 2015 (Song et al., 2017). Adverse health impacts of PM are associated with particle size and chemical components (Chung et al., 2015; Dong et al., 2018). Higher risk of cardiovascular disease associated with smaller size-fractioned particulate matter, especially $PM_{1.0}$-bound particulate matter (Yin et al., 2020).

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds composed of two or more benzene rings. Due to the mutagenic, teratogenic, and carcinogenic properties (Kim et al., 2013), PAHs are one of the most toxic components in PM (Xu et al., 2008). Toxic PAHs usually enriches in fine particles, especially the aerodynamic diameters less than 1.0 μm (Wang et al., 2016; Li et al., 2019) and can enter the human respiratory system through inhalation (Yu et al., 2015). Exposure to PAHs likely induces DNA damage and raises the risk of gene mutation (Zhang et al., 2012; Lv et al., 2016) and cardiopulmonary mortality (Kuo et al., 2003; John et al., 2009). Previous studies have demonstrated that inhalation exposure to PAHs can cause high risk of lung cancer (Armstrong et al., 2004; Zhang et al., 2009; Shrivastava et al., 2017).

Atmospheric PAHs are mainly emitted from incomplete combustion of fossil fuels and biomasses (Mastral and Callen, 2000). As typical semi-volatile chemicals, PAHs can transport over long distances (Zelenyuk et al., 2012) and have been detected in the global atmosphere (Brown et al., 2013; Garrido et al., 2014; Hong et al., 2016; Liu et al., 2017a; Hayakawa et al.,

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2018). Emission inventory indicated that developing countries were the major contributors to global PAHs emission (Zhang and Tao, 2009; Shen et al., 2013).

As the largest developing country in the world, China has large amounts of PAHs emission and high cancer risk caused by PAHs exposure. The annual emission of 16 USEPA priority PAHs in China sharply increased from 18 Gg in 1980 to 106 Gg in 2007 (Xu et al., 2006; Shen et al., 2013). China became the largest emitter of PAHs on a global scale, accounting for about 20% of the total emission (Shen et al., 2013). The incremental lifetime lung cancer risk (ILCR) caused by inhalation exposure to PAHs was estimated to be 6.5×10^{-6} in China (Zhang et al., 2009), which was much higher than the acceptable risk level of 1.0×10^{-6} in US (USEPA, 1991). As Hong et al. (2016) estimated, the lifetime excess lung cancer cases caused by exposure to PAHs for China ranged from 27.8-2200 per million people and were higher than other Asia counties.

Moreover, PAHs emission and cancer risk in China have large spatial and seasonal variations. As reported by Tao and coworkers, high emission of PAHs occurred in the North China Plain (Zhang et al., 2007), and the emission in winter was 1.6 times higher than that in summer (Zhang and Tao, 2008). Thus, the lung cancer risk caused by ambient PAH inhalation exposure in the northern China was higher than that in the southern China (Zhang et al. 2009). In addition, through long-range atmospheric transport, PAHs emitted in China could spread to the neighbor countries and regions in Northeast Asia and even reach the western US (Zhang et al., 2011; Inomata et al., 2012).

For more accurate estimation of inhalation exposure to PAHs and its cancer risks in China, it is essential to carry out nationwide campaigns to acquire spatial and seasonal characteristics

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of atmospheric PAHs. The data of PAHs in the ambient air are accumulating in China during the past decades. Among these filed studies, most were conducted in in rapidly developing economic regions, including the North China region (Huang et al., 2006; Liu et al., 2007a; Wang et al., 2011; Lin et al., 2015a; Lin et al., 2015b; Tang et al., 2017; Yu et al., 2018), Yangtze River Delta region (Liu et al., 2001; Zhu et al., 2009; Gu et al., 2010; He et al., 2014) and Pearl River Delta region (Bi et al., 2003; Guo et al., 2003; Li et al., 2006; Tan et al., 2006; Duan et al., 2007; Lang et al., 2007; Yang et al., 2010; Gao et al., 2011, 2012, 2013, 2015; Yu et al., 2016), due to large amounts of combustion emission and high density of population in these regions. These studies provided insight into the fate and health risk of airborne PAHs on a local or regional scale. However, due to the inconsistency in sampling methods, frequency and duration in these local and regional campaigns, it is difficult to draw a national picture of PAHs pollution in the air of China.

There are rare dataset discovering nationwide characteristics of airborne PAHs over China. Liu et al. (2007b) reported PAHs in the air of 37 cities across China using passive polyurethane foam (PUF) disks. Wang et al. (2006) and Liu et al., (2017b) determined $PM_{2.5}$-bound PAHs over 14 and 9 Chinese cities, respectively. PAHs in the total suspended particle (TSP) and gas phase were measured over 11 cities in China (Ma et al., 2018; Ma et al., 2020). Besides these important information of PAHs in the bulk PM, it is vital to determine size distribution of PAHs, since the size of particles is directly linked to their potential for causing health problems. On the national scale, at present, there is only one field study available reporting size-segregated atmospheric PAHs at 10 sites (Shen et al., 2019). Therefore, it is essential to carry out large range campaigns coving multiple types of sites across different regions to investigate the

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distribution and risk of atmospheric PAHs in different size particles over China.

In this study, we simultaneously collected filter-based size-fractionated PM samples consecutively at 12 sites for one year. We analyzed chemical compositions of PAHs as well as other organic tracers to characterize the spatiotemporal pattern and size distribution of PAHs over China and to explore the possible sources of PAHs on the national scale. This information is helpful to formulate effective policies on controlling PAHs pollution in different regions of China.

2. Materials and Methods

2.1 Field sampling

The PM samples were collected simultaneously at 12 sites in 6 regions of China, including five urban sites, three sub-urban sites and four remote sites (Figure S1 and Table S1 in the supporting information). The Huai River-Qin Mountains Line is the geographical line that divides China into the northern and southern regions. There are central heating systems in urban areas of the northern China, but not so in the southern China. According to their locations, 6 of the 12 sites are situated in the northern China, including Hailun (HL), Tongyu (TYU), Beijing (BJ), Taiyuan (TY), Dunhuang (DH) and Shapotou (SPT). And the remaining 6 sites are located in the southern China, including Hefei (HF), Wuxi (WX), Qianyanzhou (QYZ), Kunming (KM), Xishuangbanna (BN) and Sanya (SY).

Total suspended particles (TSP) were collected using Anderson 9-stage cascade impactors (<0.4, 0.4-0.7, 0.7-1.1, 1.1-2.1, 2.1-3.3, 3.3-4.7, 4.7-5.8, 5.8-9.0, >9.0 μm) at a constant flow of 28.3 L/min. Quartz fiber filters (Whatman, QMA) that were used to collect PM samples were prebaked for 8h at 450 °C. At each site, one set of nine size-fractionated PM samples were

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collected for 48-hr every 2 weeks. A total of 294 sets of field samples were collected from October 2012 to September 2013. Additionally, one set of field blanks were collected at each site in the same way as PM samples for 5 minutes when the sampler was turned off. Detailed information of the field sampling was described elsewhere (Ding et al., 2014).

The data of average temperature (T), relative humidity (RH), the maximum solar radiation (SR) during each sampling episode were available in the China Meteorological Data Service Center (http://data.cma.cn/en). And the boundary layer height (BLH) was calculated using the NOAA's READY Archived Meteorology online calculating program (http://ready.arl.noaa.gov/READYamet.php).

2.2 Chemical analysis

Since not all size-fractionated filters had detectable levels of PAHs, each set of nine filters were combined into three samples with the aerodynamic diameters smaller than 1.1 μm ($PM_{1.1}$), between 1.1 μm and 3.3μm ($PM_{1.1\text{-}3.3}$), and large than 3.3 μm ($PM_{>3.3}$), respectively. Before solvent extraction, isotope-labeled mixture compounds (tetracosane-d_{50}, napthalene-d_8, acenaphthene-d_{10}, phenethrene-d_{10}, chrysene-d_{12}, perylene-d_{12} and levoglucosan-$^{13}C_6$) were spiked into the samples as internal standards. Samples were extracted twice with the mixed solvent of dichloride methane / hexane (1:1, v/v), and then twice with the mixed solvent of dichloride methane / methanol (1:1, v/v). The extracts of each sample were filtered, combined, and finally concentrated to about 1 mL. Then the extracts were divided into two aliquots for silylation and methylation, respectively. Detailed information about the procedures of silylation and methylation can be found elsewhere (Ding et al., 2014; Yu et al., 2016).

The methylated aliquot was analyzed for PAHs and hopanes using a 7890/5975C gas

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chromatography/mass spectrometer detector (GC/MSD) in the selected ion monitoring (SIM) mode with a 60 m HP-5MS capillary column (0.25 mm, 0.25 μm). The GC temperature was initiated at 65 °C, held for 2 min, and then increased to 300 °C at 5 °C min^{-1} and held for 40 min. The silylated aliquot was analyzed for levoglucosan using the same GC/MSD in the scan mode with a 30 m HP-5MS capillary column (0.25 mm, 0.25 μm). The GC temperature was initiated at 65 °C, held for 2 min, and then increased to 290 °C at 5 °C min^{-1} and held for 20 min. The target compounds were identified by authentic standards and quantified using an internal calibration approach. Table S2 lists the 24 target PAHs and their abbreviations.

2.3 Quality control and quality assurance

Field and laboratory blanks were analyzed in the same manner as the PM samples. The target compounds were not detected or negligible in the blanks. The data reported in this study were corrected by corresponding field blanks. To test the recovery of the analytical procedure, we analyzed the NIST urban dust Standard Reference Material (SRM 1649b, n=6) in the same manner as the PM samples. Compared with the certified values for PAHs in SRM 1649b, the recoveries were 81.5±1.9%, 66.6±5.4%, 113.6±4.4%, 76.2±2.5%, 100.4±7.9%, 138.3±3.6%, 109.5±14.2%, 125.8±8.8% and 86.4±10.7% for Pyr, Ret, Chr, BbF, BkF, BeP, Per, IcdP and Pic respectively. The data reported in this study were not recovery corrected. The method detection limits (MDLs) of the target compounds ranged from 0.01 to 0.08 ng m^{-3}.

2.4 Positive matrix factorization (PMF) analysis

A PMF receptor model (USEPA, version PMF 5.0) was employed for source apportionment of PAHs. The model has been widely used to attribute PAH sources (Larsen and Baker, 2003; Belis et al., 2011). In case the observed concentration (*Con*) of a compound was

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below its MDL, half of the MDL was used as the model input data and the uncertainty (*Unc*) was set as 5/6 of the MDL (Polissar et al., 1998). If the *Con* of a compound was higher than its MDL, *Unc* was calculated as $Unc = [(20\% \times Con)^2 + (MDL)^2]^{1/2}$ (Polissar et al., 1998).

2.5 Exposure assessment

Besides BaP, other PAHs like BaA, BbF, DahA and IcdP are also carcinogenic compounds (IARC, 2001). In order to assess the carcinogenicity of bulk PAHs, the BaP carcinogenic equivalent concentration (BaP_{eq}) was calculated by multiplying the concentrations of PAH individuals (PAH_i) with their toxic equivalency factor (TEF_i) as:

$$BaP_{eq} = \sum_{i=1}^{n} PAH_i \times TEF_i \quad (1)$$

In this study, we adopted the TEFs reported by Nisbet and Lagoy (1992) which were 0.001 for Phe, Flu and Pyr, 0.01 for Ant, Chr and BghiP, 0.1 for BaA, BbF, BkF, BeP, and IcdP, and 1.0 for BaP and DahA. Table S3 lists annual averages of PAH individuals and BaP_{eq} at the 12 site.

Incremental lifetime lung cancer risk (ILCR) caused by inhalation exposure to PAHs was estimated as:

$$ILCR = BaP_{eq} \times UR_{BaP} \quad (2)$$

where UR_{BaP} is the unit relative risk of BaP. Based on the epidemiological data from studies in coke-oven workers, the lung cancer risk of BaP inhalation was estimated to be 8.7×10^{-5} per ng m^{-3} (WHO, 2000). Thus, we used a UR_{BaP} value of 8.7×10^{-5} per ng/m^3 in this study.

3. Results and discussion

3.1 General marks

Annual averages of the total 24 PAHs ($\sum_{24}$PAHs) in TSP (sum of three PM size ranges)

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ranged from 7.56 to 205 ng m^{-3} (Figure 1a) among the 12 sampling sites with a mean of 53.5 ng m^{-3}. The highest concentration of $\sum_{24}$PAHs was observed at TY and the lowest level occurred at SY (Figure 1a). Compared with the data in other large scale observations (Table 1), atmospheric concentrations of PAHs measured at the 12 sites in this study were comparable with previously reported values in China in 2013-2014 (Liu et al., 2017b; Shen et al., 2019) and U.S. (Liu et al., 2017a), lower than those measured in China in 2003 and 2008-2009 (Wang et al., 2006; Ma et al., 2018), but higher than those over Great Lakes (Sun et al., 2006), Europe (Jaward et al., 2004), Japan (Hayakawa et al., 2018) and some Asian countries (Hong et al., 2016). Figure 1a also presents the compositions of PAHs. Apparently, 4- and 5-rings PAHs were the majority in $\sum_{24}$PAHs with the mass shares of 36.8±5.6% and 31.4±9.6%, respectively, followed by the PAHs with 3-rings (19.2±9.4%), 6-rings (11.3±3.8%), and 7-rings (1.3±0.6%).

Annual averages of BaP_{eq} in TSP were in the range of 0.21 to 22.2 ng m^{-3} (Figure 1b) with a mean of 5.02 ng m^{-3}. The highest BaP_{eq} occurred in TY and the lowest existed in SY. And 5-rings PAHs contributed most to BaP_{eq} at all sites. In China, the national standard value of annual atmospheric BaP is 1.0 ng m^{-1}. Among the 12 sites, only three sites (QYZ, BN and SY) had the BaP_{eq} levels met the national standard. The BaP_{eq} values at the rest sites exceeded the national standard by factors of 1.5 to 22. ILCR caused by inhalation exposure to PAHs ranged from 1.8×10^{-5} (SY) -1.9×10^{-3} (TY) among the 12 sites in China (Figure S2), which were much higher than the acceptable risk level of 1.0×10^{-6} in US (USEPA, 1991). All these demonstrated that China faced severe PAHs pollution and high health risk (Zhang et al., 2009; Shrivastava et al., 2017).

3.2 Enrichment of PAHs in $PM_{1.1}$

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Figure 2 presents the size distribution of PAHs and BaP_{eq} at the 12 sites in China. Both $\sum_{24}$PAHs and BaP_{eq} were concentrated in $PM_{1.1}$, accounting for 44.6-71.3% and 56.7-79.3% of the total amounts in TSP, respectively. And BaP_{eq} had more enrichment in $PM_{1.1}$ than $\sum_{24}$PAHs. The mass fractions of $\sum_{24}$PAHs and BaP_{eq} in $PM_{1.1\text{-}3.3}$ were 20.6-39.5% and 16.1-38.3%. The coarse particles ($PM_{>3.3}$) had the lowest loadings of $\sum_{24}$PAHs (7.2-23.4%) and BaP_{eq} (3.0-12.9%). Thus, our observations indicated that PAHs in the ultrafine particles ($PM_{1.1}$) contributed most health risk of PAHs in TSP over China. A previous study at three sites in East Asia found that size distribution of PAHs was unimodal and peaked at 0.7-1.1 μm size (Wang et al., 2009). A recent study at 10 sites of China also found that PAHs were concentrated in $PM_{1.1}$ (Shen et al., 2019). Based on the observation at one site in the Fenhe Plain, northern China, Li et al. (2019) pointed out that PAHs in the particles with the aerodynamic diameters <0.95 μm contributed more than 60% to the total cancer risk of PAHs in PM_{10}. All these results demonstrate that high carcinogenicity of PAHs is accompanied with ultrafine particles, probably because small particles are apt to invade the blood vessels and cause DNA damage. Thus, further studies should put more attentions on PAHs pollution in ultrafine particles.

Figure S3 and Figure S4 show seasonal variations in size distribution of $\sum_{24}$PAHs and BaP_{eq}, respectively. $\sum_{24}$PAHs and BaP_{eq} were enriched in $PM_{1.1}$ throughout the year at all sites. The mass fractions of $\sum_{24}$PAHs and BaP_{eq} in $PM_{1.1}$ were the highest during fall to winter (up to 74.6% and 79.7% at the DH site), and the lowest during summer (down to 39.2% and 50.7% at the BN site). Figure S5 presents monthly variations in size distribution of PAHs with different number of rings. The mass shares of 3-rings PAHs in $PM_{1.1}$ (39.2%), $PM_{1.1\text{-}3.3}$ (32.0%) and $PM_{>3.3}$ (28.9%) were comparable. And the highest loading of 3-rings PAHs in $PM_{1.1}$ was observed

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in December 2012. The mass fractions of 4-ring PAHs in $PM_{1.1}$ were the highest in December 2012 (58.4%) and the lowest in July 2013 (39.5%). The higher molecular weight PAHs (5-7 rings PAHs) were enriched in $PM_{1.1}$ throughout the year.

3.3 High levels of atmospheric PAHs in the northern China

Figure 3 shows the differences of atmospheric PAHs between the northern China (HL, TYU, BJ, TY, DH and SPT) and southern China (HF, WX, QYZ, KM, BN and SY). $\sum_{24}$PAHs in the northern China was higher than that in the southern China by a factor of 5.0 (Figure 3a). The concentrations of PAHs with different ring number were all higher in the northern China than those in the southern China, especially for the 4-7 rings PAHs. Moreover, BaP、BaP_{eq} and ILCR in the northern China were 5.8, 5.3 and 5.3 times higher than those in the southern China (Figure 3b). The higher concentrations of PAHs in the air of the northern China than the southern China were also reported in previous field studies (Liu et al., 2017b; Ma et al., 2018; Shen et al., 2019). Based on the emission inventories and model results, previous studies predicted that PAHs concentrations, BaP levels and lung cancer risk of exposure to ambient PAHs in the northern China were all higher than those in the southern China (Xu et al., 2006; Zhang et al., 2007; Zhang and Tao, 2009; Zhu et al., 2015). All these indicated much high PAHs pollution and health risk in the northern China.

The northern-high feature of atmospheric PAHs should be determined by the meteorological conditions and source emissions. As Figure 4 showed, PAHs exhibited strong negative correlations with temperature (T), solar radiation (SR) and the boundary layer height (BHL), especially in the northern China. This indicated that the unfavorable meteorological conditions, such as low levels of temperature, solar radiation and BHL could lead to PAHs

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accumulation in the air (Sofuoglu et al., 2001; Callén et al., 2014; Lin et al., 2015a; Li et al., 2016a). In fact, annual averages of T, SR and BHL in the northern China were all significant lower than those in the southern China ($p<0.05$, Table S4), which could indeed cause the accumulation of PAHs in the air of the northern China. In addition, low temperature in the northern China would promote the condensation of semi-volatile PAHs on particles (Wang et al., 2011; Ma et al., 2020). At the southern sites, the negative correlations between PAHs and meteorological parameters (SR and BHL) were not as strong as those in the northern sites. This implied that the adverse influence of meteorological conditions on PAHs pollution in the southern China might be less significant than that in the northern China.

For PAHs emission, there are apparent differences in sources and strength between the northern and southern regions. For instance, there is a heating season during winter in the northern China, but not so in the southern China. The residential heating during winter in the northern China could consume large amounts of coal and biofuel, and release substantial PAHs into the air (Liu et al., 2008; Xue et al., 2016). Consequently, atmospheric levels of PAHs in the northern China were much higher than those in the southern China. Since central heating systems start heat supply simultaneously within each northern region, atmospheric PAHs should increase synchronously within the northern regions of China. To check the spatial homogeneity of PAHs on a regional scale, we analyzed the correlation of PAHs between paired sites within each region. As Table 2 exhibited, PAHs varied synchronously and correlated well at the paired sites in the northern China ($p<0.001$). And closer distance between sites, stronger correlations were observed. The spatial homogeneity of PAHs observed in the northern regions of China probably resulted from the synchronous variation of PAHs emission in the northern

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China. In the southern China, although the distances between paired sites were closer than those in the northern regions, the correlations between sites within a region was weaker. This indicated that there might be more local emission which sources and strength vary place to place in the southern China.

We applied diagnostic ratios of PAH isomers to identify major sources of atmospheric PAHs. The ratios of IcdP/(IcdP+BghiP) and Flu/(Flu+Pyr) have been widely used to distinguish possible sources of PAHs (Aceves and Grimalt, 1993; Zhang et al., 2005; Ding et al., 2007; Gao et al., 2012; Lin et al., 2015a; Ma et al., 2018). As summarized by Yunker et al. (2002), the petroleum boundary ratios for IcdP/(IcdP+BghiP) and Flu/(Flu+Pyr) are close to 0.20 and 0.40, respectively; for petroleum combustion, the ratios of IcdP/(IcdP+BghiP) and Flu/(Flu+Pyr) range from 0.20 to 0.50 and 0.40 to 0.50, respectively; and the combustions of grass, wood and coal have the ratios high than 0.50 for both IcdP/(IcdP+BghiP) and Flu/(Flu+Pyr). As Figure 5 showed, the ratios of Flu/(Flu+Pyr) at the 12 sites ranged from 0.49 to 0.76, suggesting that biomass (grass/wood) burning and coal combustion were the major sources. And the ratios of IcdP/(IcdP+BghiP) were in the range of 0.32 to 0.62, indicating that besides biomass and coal combustion, petroleum combustion, especially vehicle exhaust was also an important source of atmospheric PAHs. Thus, as identified by the diagnostic ratios, biomass burning, coal combustion and petroleum combustion were major sources of atmospheric PAHs over China. This is also confirmed by the significant correlations of $\sum_{24}$PAHs with the biomass burning tracer, levoglucosan, the coal combustion tracer, picene, and the vehicle exhaust tracer, hopanes at most sites (Figure 6). As global emission inventories showed, PAHs in the atmosphere were mainly released from the incomplete combustion processes including coal combustion, biomass

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burning and vehicle exhaust (Shen et al., 2013).

To further attribute PAHs sources, we employed the PMF model to quantify source contributions to atmospheric PAHs at the 12 sites in China. Three factors were resolved and the typical factor profiles were presented in Figure S6. The first factor was identified as biomass burning, as it had high loadings of the biomass tracer, levoglucosan and light weight molecular PAHs such as Phe, Ant, Flu and Pyr which are largely emitted from biomass burning (Li et al., 2016b). The second factor was considered to be coal combustion, as it was characterized by high fractions of the coal combustion marker, picene and the high molecular weight PAHs including DahA and BghiP (Oros and Simoneit, 2000). The third factor was regarded as vehicle exhaust, as it was featured by presence of hopanes, which are widely used as the tracers of traffic emission (Cass, 1998; Dai et al., 2015). As Figure S7 showed, there was significant agreement between the predicted and measured PAHs at each site (R^2 in the range of 0.78 to 0.99, $p<0.001$). As the emission inventory of PAHs in China showed, residential/commercial, industrial and transportation were the major sectors of atmospheric PAHs in 2013 (Figure S8, http://inventory.pku.edu.cn). Residential/commercial and industrial sectors mainly consumed coal and biofuel while transportation consumed oil (Shen et al., 2013). Thus, the mainly sources of PAHs in China were coal combustion, biomass burning and petroleum combustion (especially vehicle exhaust).

Figure 7 presents atmospheric PAHs emitted from different sources in China. In the northern China, coal combustion was the predominant source of atmospheric PAHs (73.6 ng m^{-3}, 84.2% of $\sum_{24}$PAHs), followed by biomass burning (11.8 ng m^{-3} and 13.5%) and vehicle exhaust (2.0 ng m^{-3} and 2.3%). In the southern China, coal combustion (9.6 ng m^{-3} and 54.8%)

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and biomass burning (6.8 ng m^{-3} and 39.0%) were the major contributors, followed by vehicle exhaust (1.1 ng m^{-3} and 6.2%). Atmospheric PAHs emitted from the three sources in the northern China were all higher than those in the southern China, especially from coal combustion. Thus, coal combustion was the most important source of atmospheric PAHs in China and caused large increases in PAHs pollution in the northern China. As China statistics yearbook recorded (http://www.stats.gov.cn/english/Statisticaldata/AnnualData/), coal was the dominant fuel in China, accounting for 65.2% (20×10^8 tons of SCE) of total primary energy consumption in 2007, followed by crude oil 17.2% (5.3×10^8 tons of SCE) and biofuel 8.3% (2.5×10^8 tons of SCE). Although the biofuel consumption was lower than crude oil, the poor combustion conditions during residential biofuel burning could led to higher PAHs emissions as compared to petroleum combustion.

We further compared our results with those in the PAHs emission inventory of China (http://inventory.pku.edu.cn) (Figure S9). Our source apportionment results focused on fuel types, while the emission inventory classified the sources into 6 socioeconomic sectors (residential & commercial activities, industry, energy production, agriculture, deforestation & wildfire, and transportation). Since the transportation mainly used liquid petroleum (gasoline and diesel) and the rest sectors mainly consumed solid fuels (coal and biomass), we grouped these sectors into liquid petroleum combustion and solid fuel burning to directly compare with our results. As Figure S9 showed, both our observation and emissions inventory demonstrated that the PAHs contributions from solid fuel burning was higher in the northern China, while the PAHs contributions from liquid petroleum combustion was higher in the southern China.

Here, we concluded that the unfavorable meteorological conditions and intensive emission

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354 especially in coal combustion together led to severe PAHs pollution and high cancer risk in the
355 atmosphere of the northern China.

356 **3.4 Nationwide increase of PAHs pollution and health risk during winter**

357 Figure 8 exhibits monthly variations of BaP_{eq} and ILCR at the 12 sites. BaP_{eq} levels were
358 the highest in winter and the lowest in summer at all sites. As Figure 8 showed, the enhancement
359 of BaP_{eq} from summer to winter ranged from 1.05 (SY) to 32.5 (SPT). And such an
360 enhancement was much more significant at the northern sites than the southern sites. Hence,
361 ILCR was significantly enhanced in winter, especially in the northern China (Figure 8) and was
362 much higher than the acceptable risk level of 1.0×10^{-6} in US (USEPA, 1991). Previous studies
363 in different cities of China also reported such a winter-high trend of atmospheric PAHs (Liu et
364 al., 2017b; Ma et al., 2018; Shen et al., 2019). Thus, there is a nationwide increase of PAHs
365 pollution during winter in China.

366 The winter-high feature of PAHs pollution should result from the impacts of
367 meteorological conditions and source emissions. The winter to summer ratios of PAHs
368 correlated well with that for temperature (Figure S10). And T, SR and BHL were all the lowest
369 during winter and the highest during summer (Table S5-7). Coupled with the negative
370 correlations between PAHs and meteorological factors (Figure 4), the unfavorable
371 meteorological conditions in wintertime did account for the increase in PAHs pollution.

372 Moreover, PAHs emitted from coal combustion and biomass burning apparently elevated
373 during fall-winter (Figure 9). In the northern China, central heating systems in urban areas
374 usually start from November to next March. Meanwhile residential heating in the rural areas of
375 northern China consumes substantial coal and biofuel (Xue et al., 2016). Thus, the energy

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consumption in the residential sector is dramatically enhanced during fall-winter (Xue et al., 2016). In the southern China, although there is no central heating system in urban areas, power plant and industry consume large amounts of coal. And there is also residential coal/biofuel consumption for heating during winter as well as cooking in rural areas (Zhang et al., 2013; Xu et al., 2015). In addition, open burning of agriculture residuals which accounts for a major fraction of the total biomass burning in China will significantly increase during fall-winter harvest seasons in the southern China (Zhang et al., 2013). Our observation and emissions inventory witnessed similar monthly trends that the PAHs from solid fuel combustion (coal and biomass) apparently elevated during fall-winter in the northern and southern China (Figure S11). Previous field studies also found that the contributions of coal combustion and biomass burning to PAHs elevated during fall-winter (Lin et al., 2015a; Yu et al., 2016). Thus, we concluded that the unfavorable meteorological conditions and intensive source emission together led to the increase of PAHs pollution during winter.

Data availability

The data are given in the Supplement.

Author contributions

Qingqing Yu analyzed the data, wrote the paper and performed data interpretation. Quanfu He and Ruqin Shen analyzed the samples. Weiqiang Yang ran the PMF model and helped with the interpretation. Ming Zhu, Sheng Li and Runqi Zhang provided the meteorological data and prepared the related interpretation. Yanli Zhang and Xinhui Bi gave many suggestions about the results and discussion. Yuesi Wang helped the field observation and performed data interpretation. Xiang Ding, Ping'an Peng and Xinming Wang performed data interpretation,

https://doi.org/10.5194/acp-2020-576
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reviewed and edited this paper.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgement

This study was funded by the National Key Research and Development Program (2016YFC0202204), National Natural Science Foundation of China (4191101024/41722305/41907196), the Chinese Academy of Sciences (XDA05100104/QYZDJ-SSW-DQC032), and Guangdong Foundation for Science and Technology Research (2019B121205006/2017BT01Z134/2017B030314057).

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683 Table 1 PAHs concentration measured in this study and comparison with those of other large scale
684 observations.

Site/type	Sampling period	Sample type	# of sites	# of species	PAHs (ng/m^3)	Reference
China[a]	Oct, 2012-Sep, 2013	$PM_{1.1}$	12	24	3.4-126.2	This study
China[a]	Oct, 2012-Sep, 2013	$PM_{1.1-3.3}$	12	24	2.4-55.7	This study
China[a]	Oct, 2012-Sep, 2013	$PM_{>3.3}$	12	24	1.8-22.7	This study
China/Urban	2003	$PM_{2.5}$	14	18	1.7-701	Wang et al., 2006
China[b]	2005	PUF	40	20	374.5[e]	Liu et al., 2007
China/Urban	2013-2014	$PM_{2.5}$	9	16	14-210	Liu et al., 2017b
China/Urban	Aug, 2008-July, 2009	$PM_{2.5}$	11	16	75.4-478	Ma et al., 2018
China[c]	Jan, 2013-Dec, 2014	$PM_{9.0}$[e]	10	12	17.3-244.3	Shen et al., 2019
Great Lakes	1996-2003	PUF	7	16	0.59-70	Sun et al., 2006
Asian countries[d]	Sep, 2012-Aug, 2013	PUF	176	47	6.29-688	Hong et al., 2016
U.S.	1990-2014	PUF	169	15	52.6	Liu et al., 2017a
Japan	1997-2014	TSP	5	9	0.21-3.73	Hayakawa et al., 2018
Europe	2002	PUF	22	12	0.5-61.2	Jaward et al., 2004

685 a: including 5 urban sites, 3 sub-urban sites and 4 remote sites in China
686 b: including 37 cities and 3 rural locations in China
687 c: including 5 urban sites, 1 sub-urban site, 1 farmland site and 3 background sites in China
688 d: including 82 urban sites, 83 rural sites and 11 background sites in China, Japan, South Korea,
689 Vietnam, and India
690 e: the unit was ng/day
691

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692 Table 2 Correlation coefficient (r), significance (p) of PAHs between paired sites in each region.

	Northern China			Southern China	
regions	north	northeast	northwest	east	southwest
paired sites	BJ-TY	HL-TYU	DH-SPT	WX-HF	KM-BN
distance between sites	400 km	450 km	940 km	280 km	380 km
r	0.97	0.80	0.63	0.77	-
p	<0.001	<0.001	0.001	<0.001	0.09

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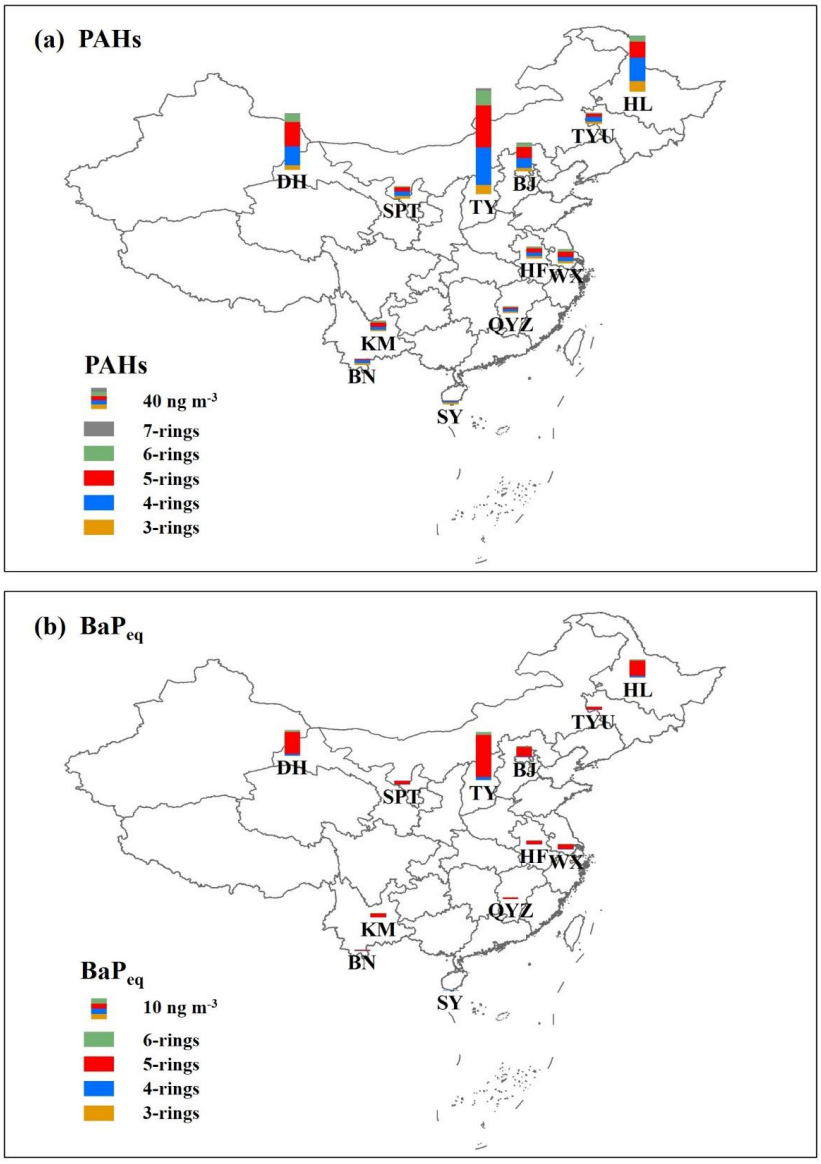

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697 Figure 1 Annual averages of PAHs (a) and BaP_{eq} (b) at 12 sites in China.

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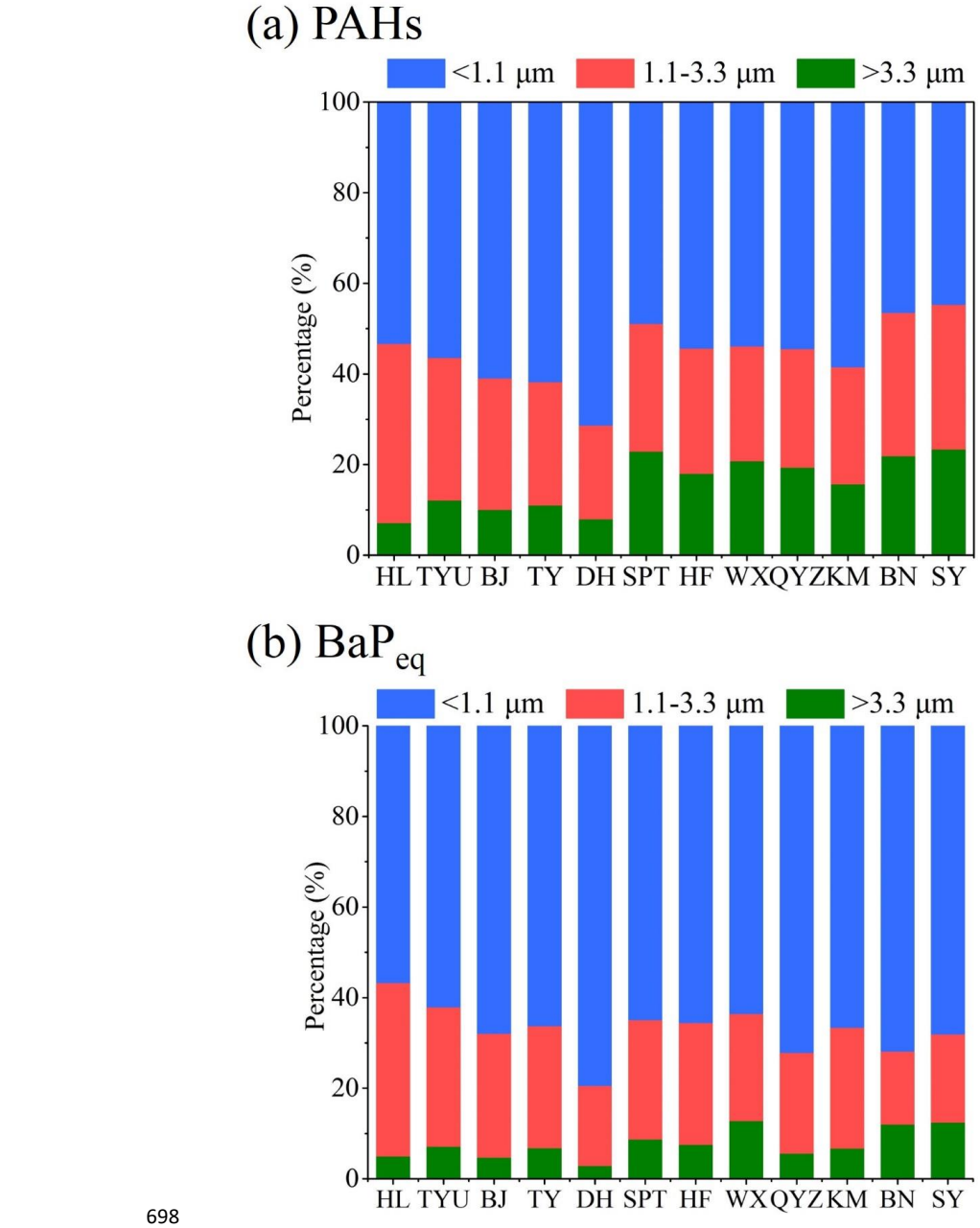

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699 Figure 2 Size distribution of total measured PAHs (a) and BaP_{eq} (b) at 12 sites over China.

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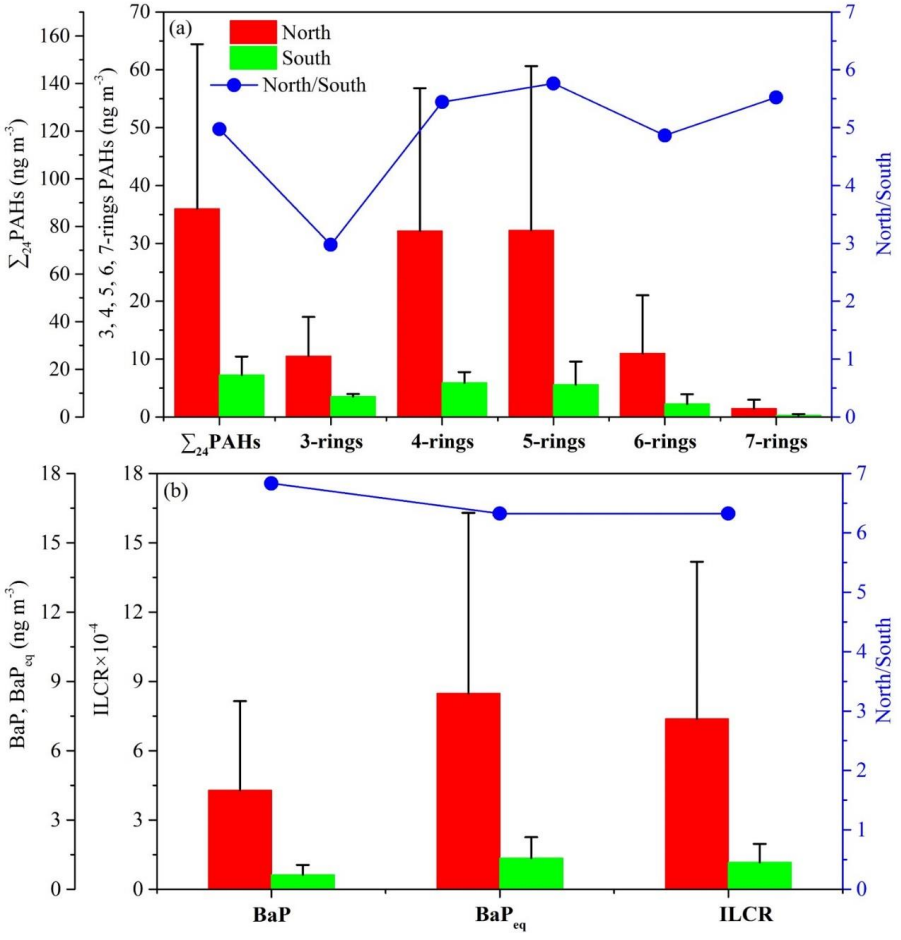

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702 Figure 3 Comparison between the northern and the southern China in $\sum_{24}$PAHs, 3-7 rings PAHs

703 (a) and BaP, BaP$_{eq}$ and ILCR (b).

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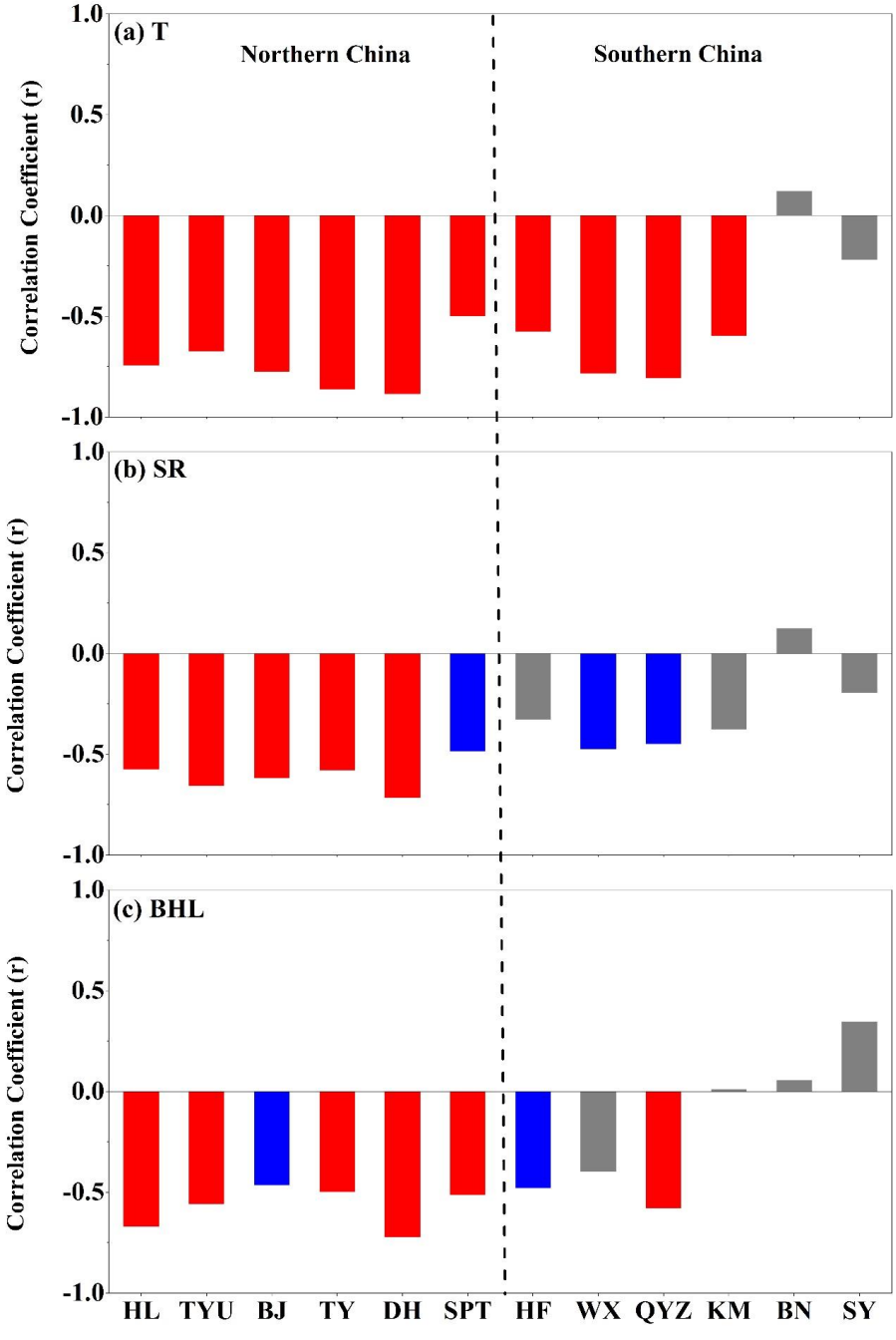

Figure 4 Correlation coefficient (r) of PAHs with T (a), SR (b) and BHL (c) at 12 sites. The red, blue and gray bars indicate $p<0.01$, $p<0.05$ and $p>0.05$, respectively.

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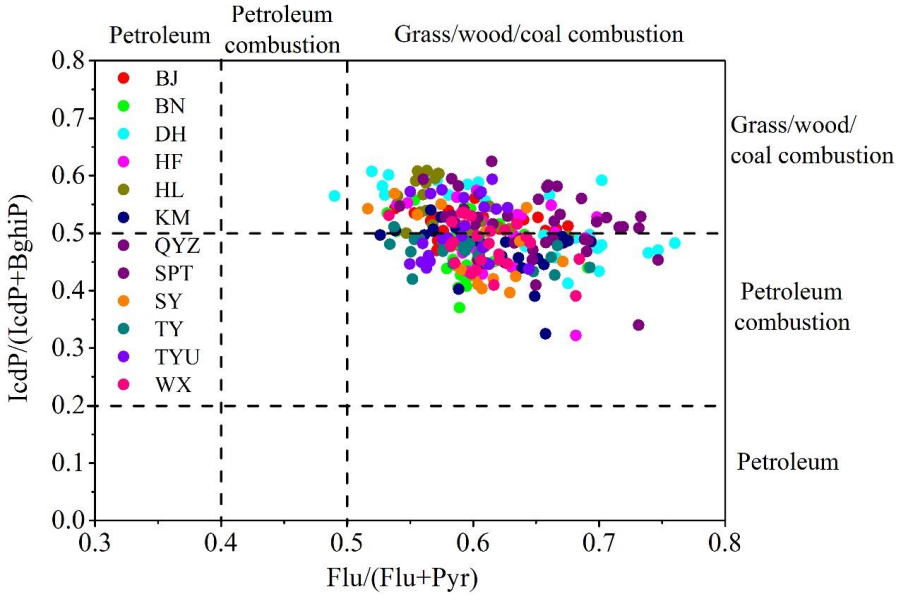

709

710 Figure 5 Diagnostic ratios of IcdP/(IcdP +BgiP) versus Flu/(Flu+Pyr) at 12 sites in China.

711 Ranges of ratios for sources are adopted from Yunker et al. (2002).

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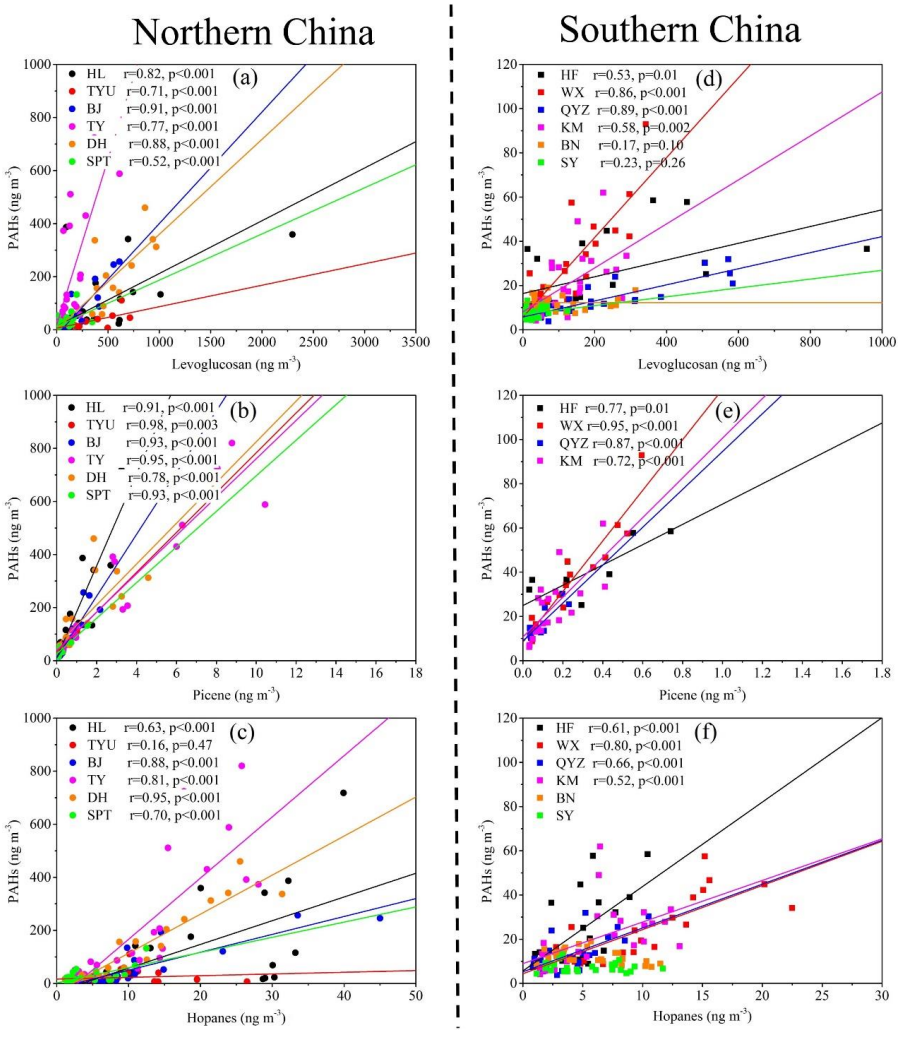

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714 Figure 6 The correlation between PAHs and levoglucosan, picene and hopanes at sites in the

715 northern China (a-c) and the southern China (d-f).

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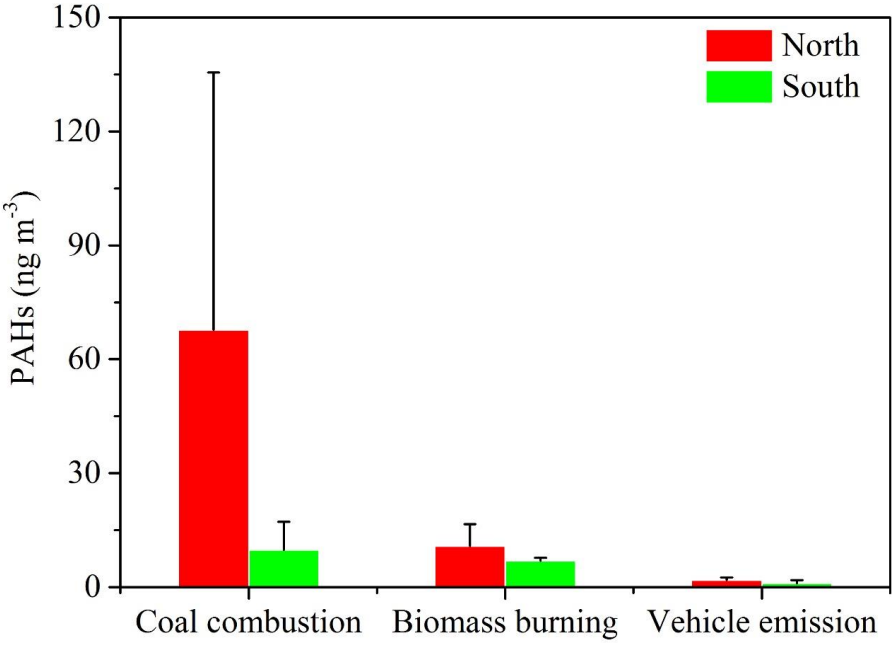

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717 Figure 7 Source apportionment of atmospheric PAHs in the northern and the southern China.

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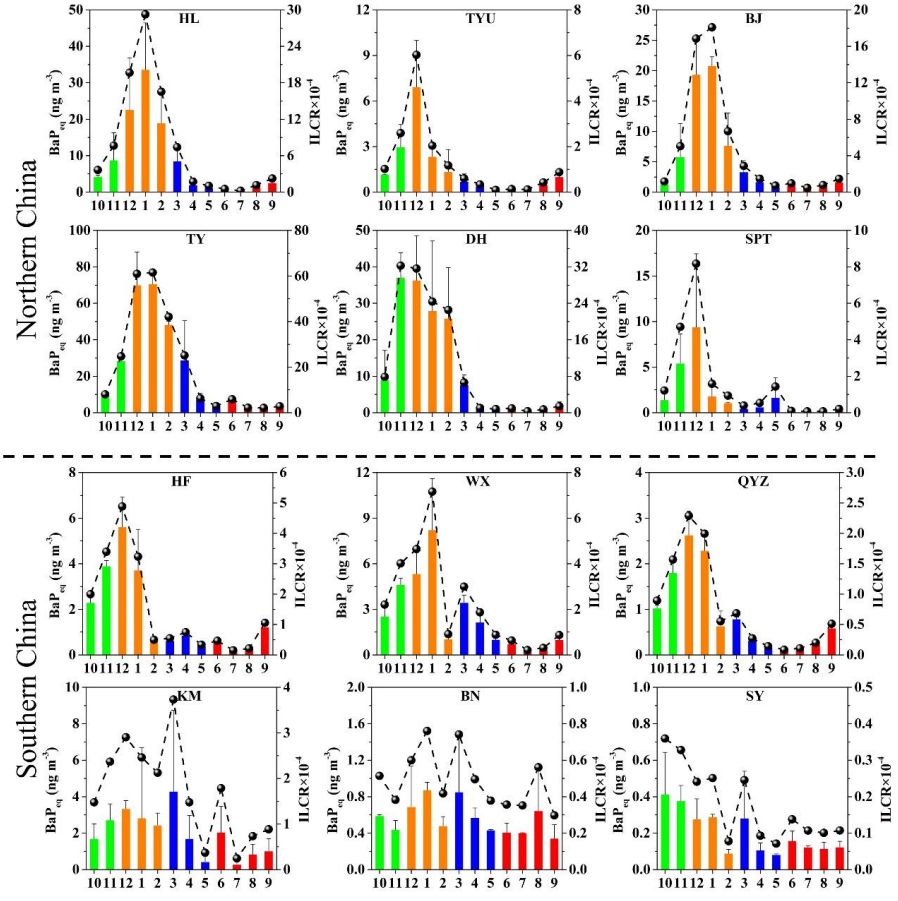

Figure 8 Monthly variations of BaP_{eq} and ILCR at sites in the northern China and the southern China. The green, yellow, blue and red bars represent BaP_{eq} in fall (October − November, 2012), winter (December 2012 – February 2013), spring (March – May, 2013), and summer (June − September, 2013), respectively.

https://doi.org/10.5194/acp-2020-576
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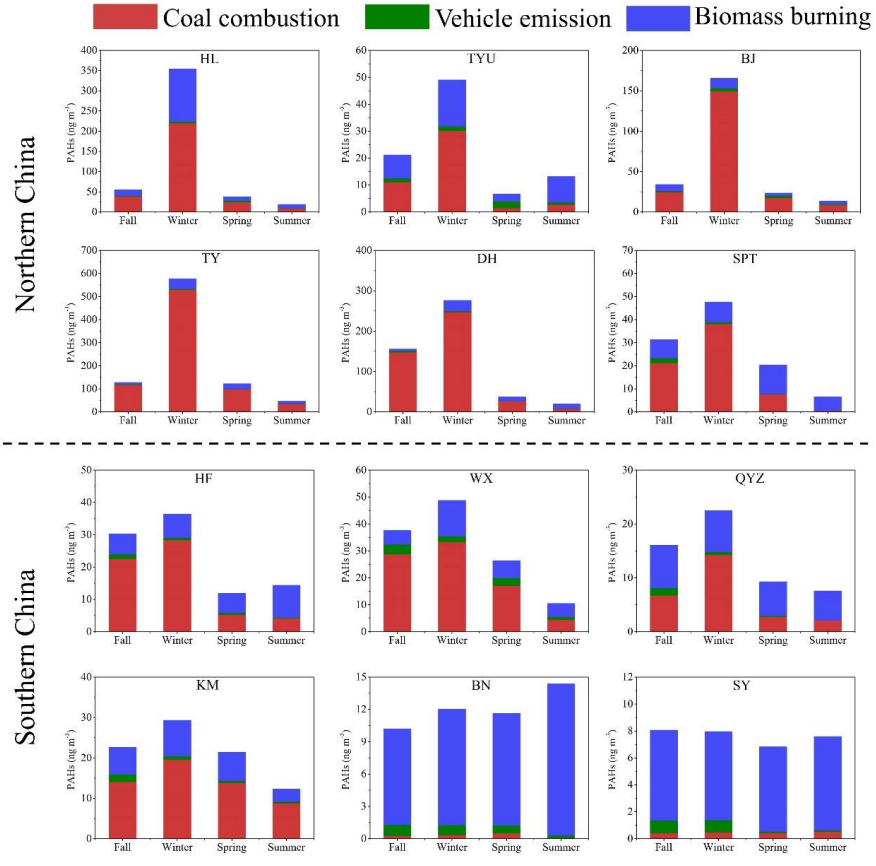

Figure 9 Seasonal variations of PAHs source contributions in China.