Levels and Sources of PM_{2.5}-associated PAHs during and after the Wheat Harvest in a Central Rural Area of the Beijing-Tianjin-Hebei (BTH) Region

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ABSTRACT

Wheat harvesting and the subsequent straw burning for the planting of maize cause severe PM_{2.5} and polycyclic aromatic hydrocarbon (PAH) pollution. This study collected PM_{2.5} samples from the central area of the Beijing-Tianjin-Hebei (BTH) region on the North China Plain between 18 June and 7 July 2019, during and after the wheat harvest (DWH and AWH, respectively) and analyzed them for 18 PAHs. The average PM_{2.5} concentration DWH, $156 \pm 42.5 \mu\text{g m}^{-3}$, was twice of that AWH ($75.6 \pm 31.9 \mu\text{g m}^{-3}$), which was attributed to fugitive dust generated by the wheat harvesters. However, the opposite trend, AWH > DWH, was observed for the total concentration of the 18 PM_{2.5}-associated PAHs due to the open burning of wheat straw for maize planting. Four PAH sources, namely, biomass burning (BB), coal combustion (CC), vehicle emission (VE), and industry (IN), were identified by positive matrix factorization (PMF), and the elevated contribution from BB AWH demonstrated the effect of open wheat straw burning. CC accounted for the highest proportion DWH, indicating that residential coal combustion for cooking, due to its low economic cost, has remained a common practice despite the implementation of the Coal Removal Campaign in 2013. The 11.6% contribution of BB DWH also confirmed the use of biomass fuel for indoor cooking in rural areas of China. VE was the largest contributor of PAHs during the whole sampling period, reflecting the operation of wheat harvesters and rotary cultivators, but BB was the main source during three peaks in the PAH concentration, which occurred on 22 June, 28 June, and 2 July. Open BB, which also possessed a second source in air masses transported from northeastern China, was responsible for the high levels of benzo[*e*]pyrene (BeP) and 5-ring PAHs. Backward trajectory clustering revealed that the adjacent cities of Shijiazhuang and Baoding were the primary IN source.

Keywords: PM_{2.5}; PAHs; PMF; Backward trajectory clustering; Wheat harvest.

INTRODUCTION

Severe haze pollution characterized by the fine particulate matter had occurred and given rise to some attention of the public in several developing countries with the rapid economic development and urbanization (Wang *et al.*, 2018; Hu *et al.*, 2019; Li *et al.*, 2019a, b, 2020). In the past decade, air pollution had been a hot environmental issue in China and the PM_{2.5}, CO₂, O₃, and VOCs were more concerned (Zong *et al.*, 2016; Maji *et al.*, 2018; Yin *et al.*, 2018; Fu *et al.*, 2020). Polycyclic aromatic hydrocarbons (PAHs) were a class of typical persistent organic pollutants (POPs) derived from incomplete incineration of coal, crop straws, garbage and

the other organic substances (Li *et al.*, 2018; Simayi *et al.*, 2018; Xu *et al.*, 2018; Han *et al.*, 2019; Huang *et al.*, 2019; Tsai *et al.*, 2019; Shibatal *et al.*, 2019; Zhang *et al.*, 2019). Human lung cancer is closely related to inhalation of PAHs and lung cancer has become the fourth leading cause of death in China due to severe air pollution (Chen and Liao, 2006; Zhou *et al.*, 2016). As a class of semi-volatile organic compounds (SVOCs), PAHs can promote the formation of secondary organic aerosol (SOA) in particles (Chen *et al.*, 2018). More than 80% of particle-bound PAHs are associated with PM_{2.5}, and PAH concentrations in particulate matter are highly dependent on these fine particles (Duan *et al.*, 2007). China launched the National Air Pollution Prevention and Control Action Plan (NAPPCAP; 2013–2017), the strictest Action Plan in Chinese history, to tackle the severe and widespread air pollution (Zhai *et al.*, 2019). Its original intention was to markedly improve the air quality by 2017 and reduce the PM_{2.5} up to 25% in major metropolitan areas of China. The Three-year Action Plan to Win the Blue Sky

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Defense War (TYAP) launched in 2018 put forward clean heating in rural areas of North China. PM_{2.5} decreased 30–50% on a national scale due to the implementation of NAPPCAP and TYAP (Zhai *et al.*, 2019).

The Coal Removal Campaign (CRC) has been vigorously launched on a national scale, and the Shift from Coal to Natural Gas (SCNG) or Electric Power (SCTE) has rooted in it. In addition to coal removal measures, traffic restriction, implementation of ultra-low emission in industries, and prohibition of straw burning were all effective measures. In a word, these measures might change the energy consumption structure in Chinese rural region and the emissions from domestic combustion sources such as residential coal and straw for heating and cooking, and open burning of biomass straw for next planting of crops began to become increasing prominent role for air pollution (Li *et al.*, 2018).

Serious atmospheric pollution incidents attributed to biomass burning have been frequently reported for domestic cities in Southeast Asia, India, Russia, and China (Ni *et al.*, 2017; Sun *et al.*, 2017, 2019). Particulate matter (PM) and PAHs from biomass burning, including wildfires, residential wood burning, and deforestation is also of major concern for visibility, climate change and health effects (Koss *et al.*, 2018). China is still a large agricultural country with the highest crop production and agricultural residues regardless of its rapid urbanization and industrialization (Ni *et al.*, 2017; Sun *et al.*, 2019). Open biomass burning (BB) from agricultural residues is an effective, simple and common practice during harvest season to remove crop residues and facilitate the planting of next crops (Ni *et al.*, 2017; Sun *et al.*, 2017; Li *et al.*, 2018). Large amounts of gaseous pollutants and particles emitted from open BB affect local and regional air quality, with severely adverse impact on human health, atmospheric visibility, and radiation balance globally (Ni *et al.*, 2017). Although some regulations are developed by Chinese Ministry of Environmental Protection to limit BB and seek alternatives for animal feed, energy for cooking and heating, and soil amendments, BB is still prevalent regardless of these measures due to high economic cost (Huang *et al.*, 2012). The annual average PM_{2.5} related to Chinese straw burning was identified as 1036 Gg during 1997–2013 based on crop yields and burning counts by satellites (Zhang *et al.*, 2016). The predicted 8% and 26% of anthropogenic PM_{2.5} emissions in China over the year and during harvest season were attributed to the BB (Zhang *et al.*, 2016), and 34% of increased PM_{2.5} derived from BB occurred in the North China Plain (Long *et al.*, 2016). Cheng *et al.* (2014) attributed 37% of PM_{2.5} mass, 70% of organic carbon (OC), and 61% elemental carbon (EC) to the crop burning in southern China.

Beijing-Tianjin-Hebei (BTH), as a culture and political center in north China, has been experiencing extreme, frequent atmospheric pollution episodes due to rapid urbanization and economic growth. BB is a main contributor of atmospheric particles and PAHs (Zhang *et al.*, 2017; Zhai *et al.*, 2019). BTH has been a most polluted region among five urban agglomerations including BTH, Pearl River Delta, Yangtze River Delta, Fenwei Plain, and Sichuan Basin (Gong and Liao, 2019). BTH in North China Plain is an important winter wheat production base with its harvest season is at

end of June and the subsequent maize rotation during 1–15 July every year. The wheat straw burning for next maize planting is a common practice in BTH and the other regions including three northeastern provinces and Henan (Ni *et al.*, 2017). Li *et al.* (2014) reported that wheat straw burning accounted for over 50% emissions of PM_{2.5}, OC, EC, K, K⁺, and Cl[−] in eastern China.

As one of the most heavily polluted city, Baoding city (located at central areas of BTH) frequently ranked first among the highest polluted cities in China recently. To our knowledge, very few studies focused on atmospheric PM_{2.5} and PM_{2.5}-associated PAHs during and after wheat harvest (DWH and AWH) season for BTH of North China Plain. A systematic PM_{2.5} sampling and analysis works related to wheat harvest season were conducted in a rural area (Wangdu County, the center of Beijing, Shijiazhuang, and Tianjin) to allow a more comprehensive assessment of influence of wheat harvest activities and wheat straw burning on ambient PM_{2.5} and associated PAHs. The main aims of this study were to: 1) analyze the changes of PM_{2.5} and PAHs during DWH and AWH; 2) investigate the air mass sources using backward trajectory clustering analysis; 3) identify the PAH sources using positive matrix factorization (PMF) model and its toxicity analysis.

METHODOLOGY

Sampling Area Description

Fig. 1 showed the location of sampling site in China. As the center of the Beijing-Tianjin-Shijiazhuang triangle in North China Plain, Wangdu County, in Hebei Province, was selected as the sampling site. Wangdu County (115°15'E, 38°72'N) locates near the Baoding city and it is a typically agricultural county in China. It is 200 km from the capital airport, 90 km from the Shijiazhuang airport, 185 km from the Tianjin port and 120 km from the Huanghua port, covering an area of 374 km². The county features a temperature climate with four distinct seasons. The sampling site was on the rooftop of a house in the countryside, the sites were established 10 m above ground to avoid airflow obstacles. Large number of surrounding wheat fields and low bungalow villages with no tall buildings facilitated this sampling campaign. PM_{2.5} samples were consecutive collected using two medium-volume air samplers (TH-150C III; Wuhan Tianhong Ltd., China).

PM_{2.5} Sampling

The daily samples were collected from 18 June to 7 July 2019 using two air samplers at a flow of 100 L min^{−1} and a total of 40 samples were collected. Each sampling lasted for 23 h and conducted from 9:00 a.m. to 8:00 a.m. of the next day. One sampler installed with quarter filter (1 μm pore size and 90 mm diameter; Pall Inc., USA) was used to the analysis of PAHs, OC, EC, and water-soluble ions, and another channel equipped with the Teflon filter (1 μm pore size and 90 mm diameter; Whatman Co., UK) was used to the analysis of inorganic elements. A set of field blank samples were simultaneously gathered by exposing filters in the sampler without airflow in drawing, to evaluate the subsequent analysis bias and precision.

Fig. 1. Sampling site location in North China Plain.

Prior to sampling, quarter filters were heated at 450°C for 4 h and Teflon filters were also heated at 60°C. Teflon filters were stored in a room with a constant 20°C and 50% of relative humidity before weighing (readability: 1 µg, ME-5F; Sartorius). After each sampling, Teflon filters were transported immediately to the laboratory and placed in that room. Net mass was obtained by subtracting pre-weight from post-weight of the Teflon filter weighed by a balance with sensitivity of ± 0.010 mg and used as PM_{2.5} mass during sampling time. The ratio of mass to corrected sampling air volume was used as PM_{2.5} concentration. Meteorological parameters, such as temperature and wind speed, were also recorded at the same time of sample collection.

PAHs Analysis

PAHs in Teflon filters were analyzed using gas chromatography coupled with mass spectrometry (GC/MS; 6890 GC with 5973i MSD; Hewlett-Packard) system. The chromatographic conditions as same as TO-13 method were adopted and showed as follows: 70°C held for 2 min, ramped to 260°C at 10°C min⁻¹ and held for 8 min, then ramped to 300°C at 5°C min⁻¹ and held for 5 min. Helium was used as the carrier gas at a constant flow of 1.0 mL min⁻¹. Detailed analysis procedures of GC-MS could be found in our previous work of Li et al. (2018).

The 18 PAH congeners analyzed in this study included naphthalene (NA), acenaphthylene (ACL), acenaphthene (AC), fluorine (FL), benzo[ghi]perylene (BgP), phenanthrene (PHE), anthracene (AN), fluoranthene (FA), pyrene (PY), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DBA), and

coronene (COR). The 18 PAHs were classified into different homologs based on their ring numbers and they were 2-ring (NA), 3-ring (ACL, AC, FL, PHE, and AN), 4-ring (FA, PY, BaA, and CHR), 5-ring (BbF, BkF, BaP, and BeP), 6-ring (IP, DBA, and BgP), and 7-ring (COR). According their molecular weight, they were also divided to low-molecular-weight (LMW) PAHs (2 and 3 rings), middle-molecular-weight (MMW) PAHs (4 rings), and high-molecular-weight (HMW) PAHs (5, 6, and 7 rings) (Li et al., 2018).

The m/z values used for identification of PAH congeners were selected as 129, 127 for NA; 153, 152 for ACL; 151, 153 for AC; 165, 167 for FL; 179, 176 for PHE and AN; 101, 203 for FA and PY; 229, 226 for BaA; 226, 229 for CHR; 256, 126 for BbF and BkF; 253, 126 for BaP and BeP; 138, 227 for IP; 139, 279 for DBA; 138, 227 for BgP; and 150, 301 for COR. Correspondingly, the quantitative m/z values were 128, 154, 152, 166, 178, 178, 202, 202, 228, 228, 252, 252, 252, 276, 278, 276, 300 for NA, ACL, AC, FL, PHE, AN, FA, PY, BaA, CHR, BbF, BkF, BaP, BeP, IP, DBA, BgP, and COR, respectively.

Only 13 of 18 PAHs were detectable in this study and they were BgP, IP, DBA, BbF, COR, PHE, FA, BaA, CHR, PY, BaP, BeP, and BkF. So the sum of 13 PAHs (Σ_{13} PAHs) was used to represent the total PAHs.

The entire pre-treatment and analysis procedures were strictly done based on the quality control/quality assurance (QC/QA) programs. The sample blank, sample duplication, matrix-spiked sample, and procedural blank experiments were conducted on schedule every five samples. No target chemicals were found in the solvent or procedural blank experiments.

The method detection limits (MDLs; reported in ng g⁻¹) for the 18 PAHs were in the range of 0.12–1, with a mean

value of 0.230 ± 0.022 . The recovery rates for the 18 PAHs in 54 matrix-added samples ranged from 80% to 121%. The surrogate standards, such as 14-deuterium substituted terphenyl and 4-bromo-2-fluorobiphenyl in 20 samples, had recoveries of $90 \pm 15\%$ and $95 \pm 20\%$, respectively. The relative standard deviation (RSD) values for the four duplicated samples were all less than 10%.

Source Identification by PMF Model

PMF, a multivariate factor analysis tool, has advantages over principal component analysis (PCA) and chemical mass balance (CMB) modeling in the elimination of negative factor loadings and no need of source profiles (Yao *et al.*, 2016; Lang *et al.*, 2018). It can acquire more realistic source information based on the non-negative constraints. PMF version 5.0 was utilized to apportion $PM_{2.5}$ potential source contributions, which are available at the U.S. EPA website (www.epa.gov/air-research/positive-matrix-factorization-model-environmental-data-analyses). The dataset of 18 PAH congeners were used as model inputs, and the abnormal values were excluded to prevent error. Uncertainty was determined by following equations:

$$\text{For } c_i \leq \text{MDL, unc} = 5/6 \times \text{MDL} \quad (1)$$

$$\text{For } c_i \geq \text{MDL, unc} = [(c_i/5)^2 + \text{MDL}^2]^{0.5} \quad (2)$$

The half of MDL was used to represent the values below than MDL. The geometric means of the observed values were used as substitutes for missing values and associated uncertainties were set as four times the geometric mean

(Yao *et al.*, 2016). 20 runs were used for each chemical component. The lowest Q_{robust} value was 2999.30, and the ratio of $Q_{\text{robust}}/Q_{\text{true}}$ was 0.90.

Backward Trajectory Clustering

Backward trajectory cluster analysis is a useful tool to evaluate the origins of air pollutants at the receptor sites (Salvador *et al.*, 2010). Three-dimensional 72 h backward trajectories of air masses arriving at Changzhi were calculated using web version of the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLOT-4) model and a total of 155 (DWH, 40; AWH, 115) trajectories were obtained. These trajectories were classified into four transport paths based on their history and origin using cluster analysis and the homogeneity within clusters was achieved by minimizing the angle distances.

RESULT AND DISCUSSION

Concentrations and Contents of $PM_{2.5}$ and Associated PAHs

Fig. 2 listed the $PM_{2.5}$ concentrations, PAH contents in $PM_{2.5}$, and PAH concentrations for each sampling day and sampling period. The $PM_{2.5}$ concentrations for DWH were ranged from 115 to $200 \mu\text{g m}^{-3}$ with an average value of $156 \pm 42.5 \mu\text{g m}^{-3}$, while the corresponding values were in the range of 23.4– $140 \mu\text{g m}^{-3}$ with a mean value of $75.6 \pm 31.9 \mu\text{g m}^{-3}$. The daily average $PM_{2.5}$ for DWH was twice the corresponding value for AWH indicated the formation of large amounts of fugitive dust due to the stir of dust adsorbed in wheat straw by harvester and transportation of

Fig. 2. $PM_{2.5}$ concentrations, PAH contents, and PAH concentrations for (a) sampling days, and (b) DWH and AWH period.

wheat. The $PM_{2.5}$ concentrations in DWH were much higher than the average value of $65 \mu g m^{-3}$ of cities in northern China implied the adverse effects of harvest activities on $PM_{2.5}$ levels (Ding *et al.*, 2019; Zhai *et al.*, 2019). The AWH possessed the equivalent $PM_{2.5}$ concentration to the Chinese National Ambient Air Quality Standard Grade II ($75 \mu g m^{-3}$) (GB3095-2012) in spite of it was twice the $35 \mu g m^{-3}$ designated by Chinese National Ambient Air Quality Standard Grade I (GB3095-2012), which implied the positive effects of straw burning prohibition in China on $PM_{2.5}$ decrease.

The gradually decreased $PM_{2.5}$ from 18 June to 20 June during DWH period reflected the weakness of the harvest activities. Although enhanced $PM_{2.5}$ levels were found in DWH, they were much lower than those reported values for other Chinese cities before the beginning of NAPPCAP (2013), which implied the effectiveness of $PM_{2.5}$ reduction measures of Chinese governments. He *et al.* (2017) reported the $PM_{2.5}$ concentrations for Taiyuan city in winter of 2009, 2011, 2012, and 2013 were as high as 269, 167, 219, and $181 \mu g m^{-3}$, respectively. Also high annual average $PM_{2.5}$ of $201 \mu g m^{-3}$ in 2011 for Zhengzhou was reported by Wang *et al.* (2014). At the same time, the $PM_{2.5}$ levels in DWH were higher than those corresponding values in some northern Chinese cities after 2013 at the beginning of NAPPCAP. The $PM_{2.5}$ concentrations after 2013 were $91.6 \mu g m^{-3}$ for Shijiazhuang in 2016 (Lang *et al.*, 2018), $100.6 \mu g m^{-3}$ for Xinxiang in 2015 (Feng *et al.*, 2018), and $116 \mu g m^{-3}$ for Handan in 2014 (Meng *et al.*, 2016).

For AWH, the occurrence of $PM_{2.5}$ peaks (in $\mu g m^{-3}$) of 140 for 25 June, 110 for 26 June, 120 for 28 June, and 101 for 6 July reflected the strong influence of wheat straw burning, rotary tillage for maize planting, and low wind speed.

As shown in Fig. 2, the opposite trends for PAH contents in $PM_{2.5}$ and PAH concentrations compared with $PM_{2.5}$ concentrations were found for whole sampling period (WSP). The PAH contents in DWH were ranged from 44.9 to $104 \mu g g^{-1}$ with a mean value of $64.8 \pm 33.9 \mu g g^{-1}$, which were much lower than those of AWH and they were in the range of $82.7\text{--}707 \mu g g^{-1}$ with a mean of $242 \pm 194 \mu g g^{-1}$. Also the same trend with PAH contents was found for PAH concentrations, DWH possessed much lower mean value of $8.79 \pm 1.74 ng m^{-3}$ (6.94–10.4) than $14.4 \pm 5.16 ng m^{-3}$ (7.13–23.9) for AWH. Higher PAH values in AWH reflected the strong impact of wheat straw burning for maize planting. Greater increments for PAH contents than their concentrations were resulted from both higher $PM_{2.5}$ in DWH and higher PAH mass in AWH. Higher PAH contents and concentrations for AWH suggested the impact of wheat straw burning. The increased BB contribution during AWH further validated the wheat straw burning should be responsible for PAH increments (discussed in “Source Apportionment of PAHs by PMF Model”).

Contents and Concentrations of the Individual PAH Congener and Ring Size Distribution

Fig. 3 showed the contents and concentrations for each PAH in each sampling day. Table 1 and Table 2 listed the statistic values of PAH contents and concentrations for each PAH during WSP. The same trends with $\Sigma_{13}PAHs$ were

found for both contents and concentrations of each PAH congener in this study. Each PAH possessed much lower contents and concentrations in DWH compared than those in AWH. The contents peaked at 22 June, 2 July, and 3 July for all the PAH congeners indicated the significant impact of $PM_{2.5}$ concentrations. For PAH concentrations, the vast fluctuations occurred for different PAH congeners although they peaked at 22 June, 28 June, 2 July, and 3 July as well, which indicated the difference of source contributions for these congeners. In regard to mass ratios of PAHs, BeP was the predominant PAH for both DWH and AWH, which was ranged from 6.84 to $19.8 \mu g g^{-1}$ (mean: $11.5 \pm 7.16 \mu g g^{-1}$) and 16.4 to $162 \mu g g^{-1}$ (mean: $53.6 \pm 46.7 \mu g g^{-1}$) for DWH and AWH, respectively. In addition to BeP, mass ratios of four PAHs including BbF, IP, BgP, and COR were dominated in DWH and AWH. Also these five PAHs including BeP, BbF, IP, BgP, and COR were dominated in DWH and AWH based on their concentrations (Table 1). The mean concentrations (in $ng m^{-3}$) for them were 1.52 ± 0.440 , 1.50 ± 0.317 , 1.24 ± 0.269 , 1.09 ± 0.195 , and 0.752 ± 0.194 for DWH, and 3.16 ± 1.35 , 2.50 ± 0.852 , 1.77 ± 0.586 , 1.66 ± 0.706 , and 1.08 ± 0.619 for AWH, respectively (Table 2). Among 13 PAHs, PHE possessed the lowest value for mass ratios and concentrations for both DWH and AWH. High levels of BaP were found for both DWH and AWH, which should be paid more attention due to its toxicity (Li *et al.*, 2018).

Fig. 4 showed the ring size distribution patterns for each sampling day, DWH, and AWH. 5-ring PAHs dominated among all the sampling days, followed by 6-ring PAHs and 4-ring PAHs, and 3-ring PAHs possessed the lowest contributions. The HMW PAHs were the biggest contributors for all sampling days. From DWH to AWH, the contributions of 5-ring PAHs increased from 42.3% to 46.7%, while the 6-ring PAHs decreased from 30.9% to 26.6%, which reflected the differences of source contributions. For the PAH peaks in 22 June and 2 July, 5-ring PAHs possessed the highest contributions and they were 49.2% and 49.3%, respectively.

Source Apportionment of PAHs by PMF Model

Fig. 5 showed four distinct source profiles based on PMF analysis. Factor 1 characterized with high loadings of HMW PAHs including COR and BaP, and low contents of LMW and MMW PAHs such as PHE, FA, and PY, which was identified as coal combustion (CC) based on previous documented data and real cooking fuels used in this region. Coal combustion is more likely to produce PAHs with high ring number like 5-ring and 7-ring PAHs, also the BaP and COR possessed high contents (Kakareka *et al.*, 2005; Zhou *et al.*, 2005; Wang *et al.*, 2020). In general, high loading of 3–5-ring PAHs such as PHE, BbF, BbF, and FA, and low contents of PAHs with ring numbers higher than 5 except for DBA were found for Factor 2, which was designated as industrial emissions (IN) (Yu and Lin, 2005). A certain numbers of factories located at adjacent areas of Wangdu County involve manufacture of machinery, shoes, and plastics further supported this conclusion. In regard to Factor 3, all the PAH congeners had comparable loadings except for COR. Higher contents of PY, CHR and FA, and medium to high loadings of PHE, BaA, and BaP were found

for Factor 3. At the same time, 4- and 5-ring PAHs possessed high proportions in Factor 3 indicated the vehicle exhaust emissions (Zhou *et al.*, 2005). The running of wheat harvesters and rotary cultivators, as well as nearby vehicles in National

Highway 107 further validated it was vehicle emissions (VE). In consideration of Factor 4, the highest loading of BeP and lowest content of DBA were found. Except for the highest contributions of 5-ring PAHs, the PAHs with the other ring

Fig. 3. Time series of the (a) PAH contents and (b) PAH concentrations for each PAH congener during whole sampling period.

Table 1. Mass content of each PAH in PM_{2.5} (μg g⁻¹).

PAHs	DWH			AWH		
	Max	Min	Mean	Max	Min	Mean
BgP	12.6	5.66	7.99 ± 3.97	86.9	6.91	28.1 ± 23.6
IP	15.1	6.23	9.18 ± 5.07	87.0	8.62	30.0 ± 23.5
DBA	4.87	1.53	2.88 ± 1.76	17.7	1.30	6.43 ± 5.13
BbF	17.7	7.43	11.1 ± 5.77	130	14.2	42.6 ± 35.3
COR	9.70	3.48	5.68 ± 3.49	57.7	0.00	18.5 ± 17.0
PHE	1.57	0.647	1.11 ± 0.461	12.1	1.07	3.46 ± 3.02
FA	4.69	2.59	3.34 ± 1.17	32.6	4.02	11.9 ± 8.90
BaA	3.58	1.40	2.20 ± 1.20	23.7	3.26	9.29 ± 6.67
CHR	4.54	1.94	2.82 ± 1.49	31.4	3.86	10.5 ± 7.67
PY	2.98	1.50	2.05 ± 0.805	22.5	3.09	8.83 ± 5.96
BaP	3.42	2.06	2.65 ± 0.701	29.7	3.42	10.7 ± 7.54
BeP	19.8	6.84	11.5 ± 7.16	162	16.4	53.6 ± 46.7
BkF	3.28	1.37	2.22 ± 0.97	25.7	2.56	7.77 ± 6.89
NA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ACL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
AC	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
AN	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. refers to no detection.

Table 2. Volume concentrations of each PAH congener in air (ng m⁻³).

PAHs	DWH			AWH		
	Max	Min	Mean	Max	Min	Mean
BgP	1.26	0.875	1.09 ± 0.195	3.28	0.810	1.66 ± 0.706
IP	1.50	0.964	1.24 ± 0.269	2.85	1.02	1.77 ± 0.586
DBA	0.486	0.237	0.389 ± 0.133	0.680	0.111	0.370 ± 0.143
BbF	1.77	1.15	1.50 ± 0.317	4.13	1.24	2.50 ± 0.852
COR	0.969	0.595	0.752 ± 0.194	2.44	0.00	1.08 ± 0.619
PHE	0.173	0.123	0.153 ± 0.022	0.335	0.091	0.204 ± 0.079
FA	0.542	0.400	0.470 ± 0.071	1.55	0.34	0.744 ± 0.329
BaA	0.357	0.216	0.298 ± 0.071	0.884	0.276	0.574 ± 0.196
CHR	0.453	0.307	0.382 ± 0.073	1.20	0.329	0.653 ± 0.232
PY	0.297	0.260	0.285 ± 0.021	0.975	0.261	0.557 ± 0.199
BaP	0.487	0.319	0.382 ± 0.091	1.27	0.297	0.665 ± 0.271
BeP	1.97	1.23	1.52 ± 0.440	5.98	1.39	3.16 ± 1.35
BKF	0.402	0.212	0.314 ± 0.961	0.798	0.216	0.451 ± 0.185
NA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ACL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
AC	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
AN	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. refers to no detection.

numbers had the certain contributions, which confirmed the existence of biomass burning (Zheng *et al.*, 2005; Wang *et al.*, 2020).

Fig. 6 showed the contributions of four sources including CC, VE, BB, and IN for each sampling day, DWH, and AWH. The BB possessed the highest contributions for three PAH peaks in 22 June, 28 June, and 2 July, which were 42.8%, 47.5%, and 68.7%, respectively. The high proportions of BB among four sources in three PAH peaks confirmed that BB was the key contributor of PAHs in this period. Also the highest BB contributions for three peaks further explained

the highest proportion of 5-ring PAHs among these three days. High contributions of BB during WSP were the explanation of the highest BeP levels existed among all sampling days.

For WSP, VE was the biggest contributor and accounted for 30.8% of PAH emissions due to the running of harvesters and rotary cultivators, as well as vehicles in adjacent National Highway 107. BB and CC were the second and third highest contributors of PAHs and 27.6% and 27.5% of PAHs were attributed to them.

The BB contributions changed from 11.6% of DWH to 30.5% of AWH suggested the open wheat straw incineration

for maize planting was not completely forbidden in northern rural areas of China. It should be noted that the indoor BB for cooking in DWH confirmed that the BB was still an

important fuel for cooking in rural areas driven by economic interests in spite of the implementation of NAPPCAP. CC possessed the highest contribution of 34.9% in DWH

Fig. 4. PAH ring size distributions for (a) each sampling day, and (b) DWH and AWH periods.

Fig. 5. Source profiles of four PAH sources identified by PMF model for whole sampling period.

Fig. 6. Time series of contributions to PAHs by four sources and source contributions for DWH, AWH, and whole sampling period.

implied the certain lagging in conducting the Coal Removal Campaign. VE elevated from 27.7% of DWH to 31.3% of AWH might be ascribed to the increasing of traffic flow due to Chinese summer vacation.

Fig. 7 showed the contributions of four sources for each PAH congener. VE, BB, and CC were key contributors to PAHs with high concentrations such as BeP, BbF, IP, BgP, and COR.

Backward Trajectory Clustering

Fig. 8 showed the backward trajectories during DWH, AWH, and WSP. All the three periods possessed four wind pathways. For DWH, 25.0% of trajectories were from eastern Bohai Bay, 35.5% from western Quyang County, and 13.3% from northern Mongolia, and 26.1% from southern Shandong Province, Henan Province, Handan city, Xingtai city, and Shijiazhuang city. The BB for cooking in mountain area of Quyang County and dust from northern desert area of Mongolia might also be the PM_{2.5} and PAH sources in DWH.

In regard to AWH, 41.7% of trajectories were from Tianjin and Cangzhou, 28.6% from southern Shijiazhuang and Dingzhou, 13.1% from northern Zhangjiakou, and 16.7% from northeastern Liaoning, Tangshan, and Baoding. The northeastern Liaoning Province might be another BB source in addition to the local BB. Ni *et al.* (2017) reported the northeastern China was the severest BB area. Industrial emissions from Shijiazhuang and Baoding would be the important PAH source.

CONCLUSIONS

PM_{2.5} and PAHs were emitted during and after the wheat harvest (DWH and AWH, respectively) in the Beijing-Tianjin-Hebei (BTH) region on the North China Plain, a major national production base for winter wheat that is characterized as the most polluted area among five domestic urban agglomerations. In this study, PM_{2.5} samples collected for both DWH and AWH (28 June–7 July 2019) were analyzed for 18 PAHs in order to determine: 1) the PM_{2.5} and PAH concentrations both DWH and AWH following the implementation of the National Air Pollution Prevention and Control Action Plan; 2) the PAH sources and their respective contributions DWH and AWH; and 3) the daily intake (DI) via dermal adsorption (DERM), ingestion (ING), and inhalation (INH).

The daily PM_{2.5} averages fell in the range of 115–200 $\mu\text{g m}^{-3}$ DWH (18–20 June) and 23.4–140 $\mu\text{g m}^{-3}$ AWH with mean values of 156 $\mu\text{g m}^{-3}$ and 75.6 $\mu\text{g m}^{-3}$, respectively. The higher concentration DWH (twice of that AWH) was attributable to the large amounts of fugitive dust generated by wheat harvesters, demonstrating that these machines can be a significant source of PM_{2.5} for local and remote areas.

The reverse trend was found for the PAH levels: The average PAH mass and volume concentrations were 64.8 $\mu\text{g g}^{-1}$ and 8.79 $\mu\text{g m}^{-3}$ DWH but $242 \pm 194 \mu\text{g g}^{-1}$ and $14.4 \pm 5.16 \mu\text{g m}^{-3}$ AWH. The notable change in the PAH mass concentration was caused by high PM_{2.5} concentrations and low PAH levels AWH, the former factor being potentially related to

Fig. 7. Contributions of four sources to each PAH congener.

the increased frequency of wheat straw burning for maize planting.

Due to the operation of wheat harvesters and rotary cultivators, PMF identified VE as the largest PAH contributor during the whole sampling period (WSP), followed by BB (27.6%) and CC (27.5%).

The increased contribution from BB to the PAHs AWH (from 11.6% DWH to 30.5% afterward) indicated that open wheat straw burning for maize planting was not completely prohibited in northern rural areas. Additionally, the 11.6% contribution from BB DWH confirmed the importance of biomass as a cooking fuel in rural areas. CC's contribution

peaked at 34.9% DWH, suggesting the continued frequent use of CC for residential cooking in spite of the Chinese Coal Removal Campaign. VE also rose from 27.7% DWH to 31.3% AWH, which could be ascribed to the increased traffic flow during summer vacation.

The maximum contributions from BB, which occurred on 22 June (42.8%), 27 June (47.5%), and 2 July (68.7%), accounted for three peaks in the PAH concentration on 22 June, 28 June, and 2 July, during which the highest BeP and 5-ring PAH levels were also measured. The substantial contributions from BB throughout WSP resulted in elevated BeP levels both DWH and AWH.

Fig. 8. Clustering analysis of backward trajectories for DWH, AWH, and whole sampling period.

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REFERENCES

- Chen, C.L., Li, L.J., Tang, P. and Cocker III, D.R. (2018). SOA formation from photooxidation of naphthalene and methylnaphthalenes with m-xylene and surrogate mixtures. *Atmos. Environ.* 180: 256–264.
- Chen, S.C. and Liao, C.M. (2006). Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. *Sci. Total Environ.* 366: 112–123.
- Cheng, Z., Wang, S.X., Fu, X., Watson, J.G., Jiang, J.K., Fu, Q.Y., Chen, C.H., Xu, B.Y., Yu, J.S., Chow, J.C. and Hao, J.M. (2014). Impact of biomass burning on haze pollution in the Yangtze River Delta, China: A case study of summer in 2011. *Atmos. Chem. Phys.* 14: 4573–4585.
- Ding, A.J., Huang, X., Nie, W., Chi, X.G., Xu, Z., Zheng, L.F., Xu, Z.N., Xie, Y.N., Qi, X.M., Shen, Y.C., Sun, P., Wang, J.P., Wang, L., Sun, J.N., Yang, X.Q., Qin, W., Zhang, X.Z., Cheng, W., Liu, W.J., Pan, L.B. and Fu, C.B. (2019). Significant reduction of PM_{2.5} in eastern China due to regional-scale emission control: Evidence from SORPES in 2011–2018. *Atmos. Chem. Phys.* 19: 11791–11801.
- Duan, J., Bi, X., Tan, J., Sheng, G. and Fu, J. (2007). Seasonal variation on size distribution and concentration of PAHs in Guangzhou city, China. *Chemosphere* 67: 614–622.
- Feng, J.L., Yu, H., Mi, K., Su, X.F., Li, Y., Li, Q.L. and Sun, J.H. (2018). One year study of PM_{2.5} in Xinxiang city, North China: Seasonal characteristics, climate impact and source. *Ecotoxicol. Environ. Saf.* 154: 75–83.
- Fu, K., Zhang, P., Wang, L.M., Huang, X.Y. and Fu, D. (2020). Viscosity of 2-ethylhexan-1-amine (EHA)-tetraglyme non-aqueous solutions and its effect on initial absorptive rate. *J. Mol. Liq.* 302: 112518–112527.
- Gong, C. and Liao, H. (2019). A typical weather pattern for ozone pollution events in North China. *Atmos. Chem. Phys.* 19: 13725–13740.
- Han, S.H., Lee, J.Y., Heo, J.B. and Kim, Y.P. (2019).

- Temporal trend of the major contributors for the particulate polycyclic aromatic hydrocarbons (PAHs) in Seoul. *Aerosol Air Qual. Res.* 19: 318–330.
- He, Q.S., Yan, Y.L., Guo, L.L., Zhang, Y.L., Zhang, G.X. and Wang, X.M. (2017). Characterization and source analysis of water-soluble inorganic ionic species in PM_{2.5} in Taiyuan city, China. *Atmos. Res.* 184: 48–55.
- Hu, Y., Li, Z.Y., Wang, Y.T., Wang, L., Zhu, H.T., Chen, L., Guo, X.B., An, C.X., Jiang, Y.J. and Liu, A.Q. (2019). Emission factors of NO_x, SO₂, PM and VOCs in pharmaceuticals, brick and food industries in Shanxi, China. *Aerosol Air Qual. Res.* 19: 1785–1797.
- Huang, K.L., Liao, Y.H. and Chen, S.J. (2019). Effects of operating parameters on gas-phase PAH emissions from a direct methanol fuel cell. *Aerosol Air Qual. Res.* 19: 2196–2204.
- Huang, X., Song, Y., Li, M., Li, J. and Zhu, T. (2012). Harvest season, high polluted season in East China. *Environ. Res. Lett.* 7: 044033.
- Kakareka, S.V., Kukharchyk, T.I. and Khomich, V.S. (2005). Study of PAH emission from the solid fuels combustion in residential furnaces. *Environ. Pollut.* 133: 383–387.
- Koss, A.R., Sekimoto, K., Gilman, J.B., Selimovie, V., Coggon, M.M., Zarzana, K.J., Yuan, B., Lerner, B.M., Brown, S.S., Jimenez, J.L., Krechmer, J., Roberts, J.M., Warneke, C., Yokelson, R.J. and Gouw, J.D. (2018). Non-methane organic gas emissions from biomass burning: Identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment. *Atmos. Chem. Phys.* 18: 3299–3319.
- Lang, J.L., Li, S.Y., Cheng, S.Y., Zhou, Y., Chen, D.S., Zhang, Y.Y., Zhang, H.Y. and Wang, H.Y. (2018). Chemical characteristics and sources of submicron particles in a city with heavy pollution in China. *Atmosphere* 9: 388–407.
- Li, J.F., Song, Y., Mao, Y., Mao, Z.C., Wu, Y.S., Li, M.M., Huang, X., He, Q.C. and Hu, M. (2014). Chemical characteristics and source apportionment of PM_{2.5} during the harvest season in eastern China's agricultural regions. *Atmos. Environ.* 92: 442–448.
- Li, Z.Y., Fan, L., Wang, L., Ma, H.Q., Hu, Y., Jiang, Y.J., An, C.X., Liu, A.Q., Han, J.B. and Jin, H. (2018). PAH profiles of emitted ashes from indoor biomass burning across the Beijing-Tianjin-Hebei region and implications on source identification. *Aerosol Air Qual. Res.* 18: 749–761.
- Li, Z.Y., Wang, Y.T., Guo, S.T., Li, Z.X., Xing, Y.R., Liu, G.Q., Fang, R., Hu, Y., Zhu, H.T. and Yan, Y.L. (2019a). PM_{2.5} associated PAHs and inorganic elements from combustion of biomass, cable wrapping, domestic waste, and garbage for power generation. *Aerosol Air Qual. Res.* 19: 2502–2517.
- Li, Z.Y., Wang, Y.T., Hu, Y., Chen, L. and Zhu, H.T. (2019b). Emission of NO_x, PM, SO₂, and VOCs from coal-fired boilers related to coal washing, iron-steel production, and lime and gypsum making in Shanxi, China. *Aerosol Air Qual. Res.* 19: 2056–2069.
- Li, Z.Y., Guo, S.T., Li, Z.X., Wang, Y.T., Hu, Y., Xing, Y.R., Liu, G.Q., Fang, R. and Zhu, H.T. (2020). PM_{2.5} associated phenols, phthalates, and water soluble ions from five stationary combustion sources. *Aerosol Air Qual. Res.* 20: 61–71.
- Long, X., Tie, X.X., Cao, J.J., Huang, R.J., Feng, T., Li, N., Zhao, S.Y., Tian, J., Li, G.H. and Zhang, Q. (2016). Impact of crop field burning and mountains on heavy haze in the North China Plain: A case study. *Atmos. Chem. Phys.* 16: 9675–9691.
- Maji, K.J., Dikshit, A.K., Arora, M. and Deshpande, A. (2018). Estimating premature mortality attributable to PM_{2.5} exposure and benefit of air pollution control policies in China for 2020. *Sci. Total Environ.* 612: 683–693.
- Meng, C.C., Wang, L.T., Zhang, F.F., Wei, Z., Ma, S.M., Ma, X. and Yang, J. (2016). Characteristics of concentrations and water-soluble inorganic ions in PM_{2.5} in Handan City, Hebei province, China. *Atmos. Res.* 171: 133–146.
- Ni, H.Y., Tian, J., Wang, X.L., Wang, Q.Y., Han, Y.M., Cao, J.J., Long, X., Chen, L.W.A., Chow, J.C., Watson, J.G., Huang, R.J. and Dusek, U. (2017). PM_{2.5} emissions and source profiles from open burning of cropresidues. *Atmos. Environ.* 169: 229–237.
- Shibata, K., Enya, L., Ishikawa, N. and Sakamoto, K. (2019). EC/OC and PAHs emissions from a modern diesel engine with DPF regeneration fueled by 10% RME biodiesel. *Aerosol Air Qual. Res.* 19: 1765–1774.
- Simayi, M., Yahefu, P. and Han, M.X. (2018). Spatiotemporal variation, source analysis, and health risk assessment of particle-bound PAHs in Urumqi, China. *Aerosol Air Qual. Res.* 18: 2728–2740.
- Sun, J., Shen, Z.X., Cao, J.J., Zhang, L.M., Wu, T.T., Zhang, Q., Yin, X.L., Lei, Y.L., Huang, Y., Huang, R.J., Liu, S.X., Han, Y.M., Xu, H.M., Zheng, C.L. and Liu, P.P. (2017). Particulate matters emitted from maize straw burning for winter heating in rural areas in Guanzhong Plain, China: Current emission and future reduction. *Atmos. Res.* 184: 66–76.
- Sun, J., Shen, Z.X., Zhang, L.M., Zhang, Y., Zhang, T., Lei, Y.L., Niu, X.Y., Zhang, Q., Dang, W., Han, W.P., Cao, J.J., Xu, H.M., Liu, P.P. and Li, X.X. (2019). Volatile organic compounds emissions from traditional and clean domestic heating appliances in Guanzhong Plain, China: Emission factors, source profiles, and effects on regional air quality. *Environ. Int.* 133: 105252–105263.
- Tsai, J.H., Chen, S.J., Lin, S.L., Huang, K.L., Hsueh, C.K., Lin, C.C. and Li, P.M. (2019). Emissions of PM_{2.5}-bound polycyclic aromatic hydrocarbons and metals from a diesel generator fueled with biodiesel converted from used cooking oil. *Aerosol Air Qual. Res.* 19: 1555–1565.
- Wang, J., Geng, N.B., Xu, Y.F., Zhang, W.D., Tang, X.Y. and Zhang, R.Q. (2014). PAHs in PM_{2.5} in Zhengzhou: concentration, carcinogenic risk analysis, and source apportionment. *Environ. Monit. Assess.* 186: 7461–7473.
- Wang, S.B., Ji, Y.Q., Zhao, J.B., Lin, Y. and Lin, Z. (2020). Source apportionment and toxicity assessment of PM_{2.5}-bound PAHs in a typical iron-steel industry city in northeast China by PMF-ILCR. *Sci. Total Environ.* 713: 136428–136439.

- Wang, X., Wei, W., Cheng, S., Li, J., Zhang, H. and Lv, Z. (2018). Characteristics and classification of PM_{2.5} pollution episodes in Beijing from 2013 to 2015. *Sci. Total Environ.* 612: 170–179.
- Xu, S.X., Chen, T., Li, X.D., Yan, J.H. and Cen, K.F. (2018). Behavior of PCDD/Fs, PCBs, CBzs and PAHs during thermal treatment of various fly ash from steel industry. *Aerosol Air Qual. Res.* 18: 1008–1018.
- Yao, L., Yang, L.X., Yuan, Q., Yan, C., Dong, C., Meng, C.P., Sui, X., Yang, F., Lu, Y.L. and Wang, W.X. (2016). Sources apportionment of PM_{2.5} in a background site in the North China Plain. *Sci. Total Environ.* 541: 590–598.
- Yin, H., Pizzol, M., Jacobsen, J.B. and Xu, L.Y. (2018). Contingent valuation of health and mood impacts of PM_{2.5} in Beijing, China. *Sci. Total Environ.* 630: 1269–1282.
- Yu, F. and Lin, Y.S. (2005). PAHs pollution characteristics in soils of typical industrial production areas and nearby residential areas in cities. *Ecol. Environ.* 14: 6–9 (in Chinese)
- Zhai, S.X., Jacob, D.J., Wang, X., Shen, L., Li, K., Zhang, Y.Z., Gui, K., Zhao, T.L. and Liao, H. (2019). Fine particulate matter (PM_{2.5}) trends in China, 2013–2018: contributions from meteorology. *Atmos. Chem. Phys.* 19: 11031–11041.
- Zhang, L.B., Liu, Y.Q. and Hao, L. (2016). Contributions of open crop straw burning emissions to PM_{2.5} concentrations in China. *Environ. Res. Lett.* 11: 014014.
- Zhang, Y., Yang, L.X., Gao, Y., Chen, J.M., Li, Y.Y., Jiang, P., Zhang, J.M., Yu, H. and Wang, W.X. (2019). Comparative study of PAHs in PM₁ and PM_{2.5} at a background site in the north China plain. *Aerosol Air Qual. Res.* 19: 2281–2293.
- Zhang, Z.Z., Wang, W.X., Cheng, M.M., Liu, S.J., Xu, J., He, Y.J. and Meng, F. (2017). The contribution of residential coal combustion to PM_{2.5} pollution over China's Beijing-Tianjin-Hebei region. *Atmos. Environ.* 159: 147–161.
- Zheng, X.Y., Liu, X.D., Zhao, F.H., Duan, F.K. Yu, T. and Cachier, H. (2005). The seasonal characteristics of biomass burning emissions contribute for atmospheric particulate matter in Beijing. *Sci. China Ser. B* 35: 346–352. (in Chinese)
- Zhou, J.B., Wang, T.G., Huang, Y.B., Mao, T. and Zhong, N.N. (2005). Seasonal variation and spatial distribution of polycyclic aromatic hydrocarbons in atmospheric PM₁₀ of Beijing, People's Republic of China. *Environ. Contam. Toxicol.* 74: 660–666.
- Zong, Z., Wang, X.P., Tian, C.G., Chen, Y.J., Qu, L., Ji, L., Zhi, G.R., Li, J. and Zhang, G. (2016). Source apportionment of PM_{2.5} at a regional background site in North China using PMF linked with radiocarbon analysis: Insight into the contribution of biomass burning. *Atmos. Chem. Phys.* 16: 11249–11265.
- Zou, J., An, J., Wang, H., Shao, P., Duan, Q., Xue, G. and Pang, B. (2014). Distribution characteristics of pollution gases and water soluble ion in aerosol during the Asian Youth Games of Nanjing, China. *Environ. Sci.* 35: 4044–4051. (in Chinese)

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