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 ± 42.5 µg m$^{-3}$, was twice of that AWH (75.6 ± 31.9 µg 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$_{2.5}$, CO$_2$, O$_3$, 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.
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, air pollution studies are 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 km$^2$. 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.
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[a]pyrene (BbP), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]anthracene (BaA), chrysene (CHR), dibenz[a,h]anthracene (DBA), 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, 278, 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 ($\Sigma_{13}$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 ± 0.202. 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 ± 15% and 95 ± 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-factorizationmod-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:

For $c_i \leq \text{MDL}$, $\text{unc} = \frac{5}{6} \times \text{MDL}$ \hspace{1cm} (1)

For $c_i \geq \text{MDL}$, $\text{unc} = \left(\frac{c_i}{5}\right)^2 + \text{MDL}^2)^{0.5}$ \hspace{1cm} (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 $Q_{\text{robust}}$ 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 (HYSPLIT-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 µg m$^{-3}$ with an average value of 156 ± 42.5 µg m$^{-3}$, while the corresponding values were in the range of 23.4–140 µg m$^{-3}$ with a mean value of 75.6 ± 31.9 µg 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
wheat. The PM$_{2.5}$ concentrations in DWH were much higher than the average value of 65 µg 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 µg m$^{-3}$) (GB3095-2012) in spite of it was twice the 35 µg 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 µg m$^{-3}$, respectively. Also high annual average PM$_{2.5}$ of 201 µg 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 µg m$^{-3}$ for Shijiazhuang in 2016 (Lang et al., 2018), 100.6 µg m$^{-3}$ for Xinxian in 2015 (Feng et al., 2018), and 116 µg m$^{-3}$ for Handan in 2014 (Meng et al., 2016). For AWH, the occurrence of PM$_{2.5}$ peaks (in µg 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 µg g$^{-1}$ with a mean value of 64.8 ± 33.9 µg g$^{-1}$, which were much lower than those of AWH and they were in the range of 82.7–707 µg g$^{-1}$ with a mean of 242 ± 194 µg g$^{-1}$. Also the same trend with PAH contents was found for PAH concentrations. DWH possessed much lower mean value of 8.79 ± 1.74 ng m$^{-3}$ (6.94–10.4) than 14.4 ± 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 µg g$^{-1}$ (mean: 11.5 ± 7.16 µg g$^{-1}$) and 16.4 to 162 µg g$^{-1}$ (mean: 53.6 ± 46.7 µg 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, BkF, 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.](image-url)
Table 1. Mass content of each PAH in PM$_{2.5}$ (µg g$^{-1}$).

| PAHs | DWH | AWH |
|------|-----|-----|
|      | Max | Min | Mean ± SE | Max | Min | Mean ± SE |
| 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 |
| 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 ± SE | Max | Min | Mean ± SE |
| 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 ± 0.061 | 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 µg m$^{-3}$ DWH (18–20 June) and 23.4–140 µg m$^{-3}$ AWH with mean values of 156 µg m$^{-3}$ and 75.6 µg 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 µg g$^{-1}$ and 8.79 µg m$^{-3}$ DWH but 242 ± 194 µg g$^{-1}$ and 14.4 ± 5.16 µg 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
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. 7. Contributions of four sources to each PAH congener.
Fig. 8. Clustering analysis of backward trajectories for DWH, AWH, and whole sampling period.

ACKNOWLEDGEMENTS

This study was supported by the Fundamental Research Funds for the Central Universities (2017MS142), the National Natural Science Foundation of China (21407048), and Prime Minister Fund (DQGG-05-13).

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