Sources, compositions, and health risks of PM$_{2.5}$-bound PAHs at the rural area along with the “Coal to Gas” law

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ABSTRACT

The “Coal to Gas” (CTG) policy in north China markedly altered the characteristics of polycyclic aromatic hydrocarbons (PAHs) in PM$_{2.5}$. Existing researches about CTG impacts on components, sources, and health risks of PM$_{2.5}$-bound PAHs mainly focused on metropolitan area, whereas they were lacking in rural area of north China. Here, we deployed an intensive observation in winter of 2020 at a rural site in the central area of the Beijing–Tianjin–Hebei (BTH) region. A positive matrix factorization (PMF) model and an incremental lifetime cancer risk (ILCR) model were utilized to examine the PAH sources and health risks. Higher daily average PM$_{2.5}$ of 81.5 µg m$^{-3}$ in the sampling period than 75 µg m$^{-3}$ of the National Air Quality Standard Grade II indicated the air pollution in rural area was still serious. The total PAHs increased obviously from diurnal 86.2 ng m$^{-3}$ to nocturnal 151 ng m$^{-3}$ because of the nocturnal high intensity of heating, with the increases of 20.7%, 85.5%, and 76.3% for low, medium, and high molecular weight PAHs, respectively. Vehicular exhaust (VE), coal burning (CB), industrial source (IS), biomass burning (BB), and oil spill and leakages (OSL) were the main PAH contributors, with the average daily contributions of 32.7%, 21.5%, 18.3%, 15.9%, and 11.6%, respectively. Lower CC contribution of 27.6% in winter of 2020 than 27.6% in winter of 2019 indicated the positive role of CTG policy. However, the nocturnal CC fraction increased by 680% compared with the diurnal value, and CC had become the largest contributor in the nighttime. BB contribution was up to 18.3%, evidencing that biomass utility should be managed in term of the biomass burning was prohibited in BTH rural area. Moreover, the nocturnal average BaPeq equivalent concentration exhibited higher levels than those in the daytime. The nocturnal ILCR values of adults and children was 9.35×10$^{-6}$ and 2.66×10$^{-6}$, exceeding the acceptable threshold, suggesting there was a potential carcinogenic risk.

Keywords: Coal to Gas; Rural PAHs; Source apportionment; Health risk assessment
1 INTRODUCTION

Airborne polycyclic aromatic hydrocarbons (PAHs) mainly originated from the incomplete combustion of organic matter are ubiquitous in urban atmospheres, which can be transported over long distances in the gaseous form or bound to particulate (Armstrong et al., 2004; Chao et al., 2019; Zeng et al., 2020). The levels of particle-bound PAHs were highly dependent on fine particles, and more than 80% of these PAHs were related to PM$_{2.5}$ (Li et al., 2020). Source control was an important measure for abatement of crisis from high levels of PM$_{2.5}$ and PAHs (Zhou et al., 2022).

In recent years, China has made remarkable progress in environmental protection along with continuous efforts in air quality improvement (Sun et al., 2022). Since the implementation of “Action Plan on Atmospheric Pollution Prevention and Control (APPC)” in 2013, the PM$_{2.5}$ concentrations have reduced by 30% in 2017 compared with those in 2012 in the Beijing-Tianjin-Hebei (BTH) region and the sources of PM$_{2.5}$ have changed significantly (Cai et al., 2017). At the same time, it was believed that the PAH sources exhibited notable changes as well due to the changes in source types and associated emission intensities (Kong et al., 2018). In addition to natural sources such as volcanic eruptions and earthquakes, PAHs mainly generated through multiple sources of predominantly incomplete combustion and pyrogenic decomposition, such as the production of exhaust during cooking or vehicle use, open burning of biomass, coal combustion, and coke combustion (Chao et al., 2019; Wang et al., 2020a; Sei et al., 2021). Owing to the coal-dominant energy structure, the PAH emissions of China ranked the first in the world and generally showed higher levels in wintertime (Shen et al., 2013). Other than the high emission intensity of combustion sources in the heating season, the atmospheric parameters including oxidants, temperature, and relative humidity were important influence factors (Sun et al., 2022).

To mitigate still high PM$_{2.5}$ levels in Beijing, China government has enacted a joint regional
control plan covering Beijing, Tianjin, and surrounding 26 cities (“2 + 26” strategy) in 2017 (Chen et al., 2019). The coal-banning plan including “coal to gas” and “coal to electricity” came into being as a part of “2 + 26” strategy, which has largely modified the energy structure in rural areas, hence changed the constituents, sources, and health risks of PAHs (Zhai et al., 2019; Yang et al., 2022). Therefore, it is essential to access to what extent the change of sources and related contributions for PAHs after the implementation of coal banning law in winter of 2017.

Air pollution can seriously damage the ecological environment and human health (Wang et al., 2020a). The dangers of pollution associated with PM$_{2.5}$ can’t be ignored, and approximately 2.9 million deaths worldwide each year were proved to be associated with the exposure to PM$_{2.5}$ (Brauer et al., 2016). Among the heavy metals, black carbon, organic substances and other toxic components contained in fine particles, PAHs have received special attention due to their toxic, mutagenic, and carcinogenic potentials in humans and other organisms (Zeng et al., 2021). Former studies have found that long-term exposure to PAHs through various pathways was connected mainly with cancer, and about 0.91–2.6% of lung cancer cases in China were attributed to the inhalation of PAHs in polluted air (Zhang et al., 2006; Chen et al., 2021). More studies have linked PAHs with the adverse health outcomes such as ischaemic heart disease, obesity, and development in children (Bursyn et al., 2005; Scinicariello and Buser, 2014). Therefore, health risk assessment of environmental pollutant exposure was of great significance to improve human life quality. In addition, knowing the concentration of such pollutants in ambient air was one of the main keys to optimize administrative and management measures (Wang et al., 2020b; Nadali et al., 2021).

Along with the coordinated development strategy, the BTH region has experienced frequent air pollution episodes in recent years due to rapid urbanization and economic development, making it one of the most polluted regions in China (Li et al., 2020; Zeng et al., 2021). Jacobson et al. (2018)
pointed out that the rural and suburban area of underdeveloped small cities should reinforce the comprehensive utilization of coal, natural gas, electricity, and other energy. The situation of comprehensive utility should be in accordance with the social development level. This trend was more obvious in winter due to the heating factor. The impacts of rural pollutant emissions on air quality should be further evaluated accompanied with the changes in energy structure in rural area.

To our knowledge, the former studies mainly focused on the PAH chemistries in urban areas, while few studies were conducted on rural areas, especially for PAH characteristics along with the coal banning plan in rural region (Li et al., 2022; Sun et al., 2022). Therefore, a thoughtful investigation on variations in PAH chemistries at a rural site in Wangdu County within the BTH region was carried out in winter of 2020 covering the daytime and nighttime periods. Wangdu County locates in the central area of the BTH region. It acts as one of the important environmental monitoring sites in China. The main targets of this study included: 1) evaluating the levels of PM$_{2.5}$ and PAHs in winter along with the “clean heating” (CH) policy; 2) identifying the potential sources of PAHs by a positive matrix factorization (PMF) model; and 3) investigating the potential health risk via inhalation exposure to PAHs. As we know, this is the first and maybe the only research to evaluate the PAH chemistries in rural area along with the CH implementation, which has important enlightenment for a rural level improvement of CH measures.

2 METHODOLOGY

2.1 PM$_{2.5}$ Sampling

A rural site (115°15′E, 38°72′N) of the Wangdu County locating in central area of the Beijing-Tianjin-Hebei region was selected as the sampling site (Fig. 1). Wangdu County covers an area of 374 square kilometers, which is a typical agricultural county in China (Li et al., 2020). It is 200 km from the capital airport, 90 km from the Shijiazhuang airport, and 185 km from the Tianjin port,
respectively. The sampling duration was 9 h in the daytime (8:00 a.m. to 5:00 p.m) and 13 h in the
nighttime (6:00 p.m to 7:00 a.m of next day), respectively. A medium-volume sampler (TH–150C
III; Wuhan Tianhong Ltd., China) with a flow rate of 100 L min\(^{-1}\) was used for sample collection.
We collected the PM\(_{2.5}\) samples from January 12 to 31, 2021, and totally 40 samples accompanied
with 8 field blank samples were obtained. More details about collection of PM\(_{2.5}\) sample and blank
samples can be found in Kong et al. (2018).

The quartz filters (QFs: 1 µm pore size and 90 mm diameter; Pall Inc., USA) were used in this
sampling process, which were pre-baked in muffle oven at 500°C for more than 4 hours before
sampling. Prior to weighing, the QFs were stabilized for 48 h in a room with the constant
temperature (20°C) and humidity (50%). Each QF was weighed at least three times by an analytical
balance with sensitivity of ± 0.010 mg. After sampling, all the filters were sealed individually using
an aluminum foil and stored at –20°C in a freezer.

2.2 PAH Analysis

For PAHs analysis, a gas chromatography coupled with a mass spectrometer detector (6890
GC/5973i MSD, Hewlett-Packard, USA) was adopted in this study. The pretreatment procedures of
samples included ultrasonic extraction by methylene chloride, concentration by a rotary evaporator,
cleaning and purification by a silica gel column, and re-concentration. According to the EPA
method TO-13A, the chromatographic working conditions were as follows: hold at 70°C for 2
minutes, rise to 260°C at 10°C min⁻¹ for 8 minutes, and then rise to 300°C at 5°C min⁻¹ for 5 minutes. Helium was used as a carrier gas at a constant flow rate of 1.0 mL min⁻¹. More details about analysis and QA/QC procedures can be found in our study as Li et al. (2022).

Totally 18 PAH congeners were analyzed in this study. They were 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), respectively. According to the ring number, 18 PAHs were divided into 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). Furthermore, 2- and 3-ring PAHs were recognized as low-molecular-weight (LMW) congeners, 4-ring PAHs as medium-molecular-weight (MMW) congeners, and 5-, 6-, and 7-ring PAHs as high-molecular-weight (HMW) congeners (Li et al., 2020).

2.3 Source Apportionment by PMF Model

PMF is a multivariate factor analysis tool developed by the U.S. EPA for source apportionment of target pollutants using the least square regression, which broke down response data into major contributing factors and provided profiles for each factor (Liu et al., 2018; Taghvaee et al., 2018; Li et al., 2020).

EPA PMF 5.0 model was used to identify the PAH sources in this application, which was available at the U.S. EPA website (www.epa.gov/air-research/positive-matrix-factorizationmodel-environmental-data-analyses). The algorithm of this statistical model performs factor analysis operations based on the following equation:
\[ X_{ij} = \sum_{k=1}^{P} g_{ik} f_{kj} + e_{ij} \]  

where, \( X_{ij} \) is a data matrix represents the concentration of the \( j \)th specie in the \( i \)th sample; \( P \) is the number of factors; \( g_{ik} \) is the mass concentration contributed by the \( k \)th factor to the \( i \)th sample; \( f_{kj} \) is the total PAH mass concentration of the \( j \)th specie in the \( i \)th sample; and \( e_{ij} \) is the residual matrix that cannot be explained by the model.

To address the optimal non-negative values of source profiles and contributions, the least-squares technique for minimizing the object function \( Q \) was employed in this receptor model:

\[ Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \frac{X_{ij} - \sum_{k=1}^{P} g_{ik} f_{kj} + e_{ij}}{u_{ij}} \]  

where, \( u_{ij} \) is the estimated uncertainty; \( n \) is the number of samples; and \( m \) is the number of species (Taghvaee et al., 2018; Li et al., 2021a).

In the operation, the measured concentrations of the species and associated uncertainties were also used as the model inputs. The uncertainties were estimated by the following equation (Li et al., 2020; Hien et al., 2021):

\[ unc = \frac{5}{6} \times MDL(c_i \leq MDL) \]  
\[ unc = \left[ \left( \frac{c_i}{5} \right)^2 + MDL^2 \right]^{0.5} (c_i \geq MDL) \]

2.4 Health risk assessment of PAHs

BaP equivalent concentration (BaPeq), based on the USEPA developed for cancer risk assessment, can be used to assess the risk of PAHs inhalation effects (Nisbet and LaGoy, 1992). The equivalent concentration was acquired by multiplying the mass concentration of a particular PAH species by the corresponding toxic equivalent factor (TEF) (Xu et al., 2022). As Kong et al. (2018) said, the sum of the BaPeq of each PAH presented the total carcinogenicity of PAHs, which was obtained as below:

\[ BaP_{eq} = \sum_{i=1}^{n} C_i \times TEF_i \]
Where, TEF\textsubscript{i} is the TEF value of the \textit{i}\textsuperscript{th} PAHs, and a total of 17 PAHs were selected referring to Nisbet and LaGoy (1992).

The incremental lifetime cancer risk (ILCR) was a quantitative assessment of PAHs exposure risk in the environment (Wang et al., 2020b). Inhalation is a crucial way of three main exposure pathways to PAHs in direct ingestion, inhalation and dermal absorption (Shen et al., 2013). The ILCR value was calculated as below:

\[
\text{ILCR} = \text{CSF} \times \frac{\text{CA} \times \text{IR} \times \text{ET} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}}
\]

(6)

where, CA represents BaP equivalent (BaP_{eq}) concentrations (mg m\textsuperscript{-3}). Other parameters can be found in Table S1.

If the ILCR was higher than 1\times10^{-4}, there was likely to be harmful to human beings. If the value was between 1\times10^{-6} and 1\times10^{-4}, there exist potential risk that were comparable to the acceptable levels. The cancer risk can be regarded as negligible when the value was less than 1\times10^{-6} (Wang et al., 2020b).

3 RESULT AND DISCUSSION

3.1 Levels of PM\textsubscript{2.5} and Associated PAHs

The volume concentrations of PM\textsubscript{2.5} and total PAHs were shown in the Fig. 2. There was a positive correlation between the two concentrations, and there were three peaks in the entire observation period, which were January 20–21, 23–24, and 28–29, respectively. The diurnal PM\textsubscript{2.5} concentrations ranged from 23.4 to 331.9 \mu g m\textsuperscript{-3} with a mean value (± standard deviation) of 58.7 ± 54.7 \mu g m\textsuperscript{-3}, while the nocturnal values were in the range of 25.2–385.3 \mu g m\textsuperscript{-3} with a mean value of 97.6 ± 56.0 \mu g m\textsuperscript{-3}. The average nocturnal PM\textsubscript{2.5} concentrations was almost twice the average diurnal value, which was mainly ascribed to the high intensity heating behavior using coal in the nighttime (further discussed in Section 3.2). It was worth noting that PM\textsubscript{2.5} concentration reached
the Chinese National Ambient Air Quality Standard Grade II (75 µg m\(^{-3}\)) (GB3095–2012) at
daytime, while the corresponding values for each night exceeded the concentration limit. The
nocturnal PM\(_{2.5}\) far exceeded 35 µg m\(^{-3}\) designated by Chinese National Ambient Air Quality
Standard Grade I (GB3095–2012) (Li et al., 2020). What’s more, the PM\(_{2.5}\) level in this study was
higher compared to those in the pre-heating period in this site, such as 63.9 ± 46.4 and 69.1 ± 32.3
µg m\(^{-3}\) in the pre-heating in 2017 and 2019 (Zhao et al., 2020; Li et al., 2022). The still higher
PM\(_{2.5}\) in this study than those in previous sampling year evidenced the strong impacts of heating
coal in rural area, which deserved further attention. People’s negative attitude towards natural gas
heating in rural area due to high cost resulted in the increase in coal usage. Therefore,
comprehensive use of clean fuel and advanced furnace in present rural area was highly
recommended (Jacobson et al., 2018; Li et al., 2023).

The ambient PAHs generally existed in the form of vapor phase and particulate phase (Wang et
al., 2011b; Zhang et al., 2013; Alvarez-Ospina et al., 2021). Fig. 3 showed the proportions of PAH
categories with different number of rings using a triangular scale diagram. Former studies indicated
that the LMW-PAHs mainly came from the coal combustion, MMW-PAHs were often related to the
incomplete combustion of fossil fuels at high temperatures, and HMW-PAHs mainly connected with
the internal combustion engine emissions (Feng et al., 2019a; Feng and Cao, 2019b). The LMW-
PAHs held the lowest contents in both the daytime and nighttime, followed by HMW- and MMW-
PAHs. Generally, HMW- and MMW-PAHs were more easily bound to particulate matter than LMW-PAHs. In other words, the LMW-PAHs preferably enriched in the vapor phase, whereas MMW-PAHs always existed in both the vapor and particle phases (Zhang et al., 2013). At the same time, low temperature also affected the distribution of PAHs between vapor and particles, which elevated the HMW-PAHs in particles (Wang et al., 2020b). Moreover, MMW-PAHs increased most by 85.3% in the night compared to that in the daytime, and they were 76.7% and 20.7% for HMW- and LMW-PAHs, respectively. The maximum increase of MMW-PAHs would be attributed to the enhanced coal usage for heating in this study (Feng et al., 2019a). Although LMW-PAHs reacted with other pollutants in the atmosphere to form more toxic PAH derivatives, high concentrations of HMW-PAHs made them more carcinogenic and mutagenic (Zhang et al., 2013).

Fig. S1 shows the mass ratios of 18 PAHS congeners in the total PAH concentrations in both the night and daytime. In addition, Table S2 presented the statistic values for each PAH congener. The percentages of 4-ring PAHs i.e. MMW-PAHs increased from 46.5% in the daytime to 49.1% in the nighttime due to the elevated coal usage. FA was the top congener, followed by PY and BbF in the both periods. PAHs were widely known carcinogenic and mutagenic chemicals (Zhang et al., 2013; Li et al., 2021b; Vega et al., 2021). BaP was widely used as an indicator of the carcinogenic risk of PAHs (Chang et al., 2019). The mean concentrations of BaP during the daytime and night were 7.81 and 10.0 ng m⁻³, respectively, far exceeding the US EPA and Ministry of Environmental Protection of China recommended limit of 1 ng m⁻³, which should be paid more attention (Li et al.,
3.2 Source Apportionment by PMF Model

The source profiles of five PAH sources identified by PMF model in the entire sampling period were given in Fig. S2. Factor 1 was characterized by high loadings of PHE, FA, FL, BbF, and CHR, indicating the emission from biomass burning (BB) (Wang et al., 2020b). CHR was also used to mark the BB emission rather than mark the natural gas combustion (Azimi-Yancheshmeh et al., 2021). Factor 2 was associated with high fractions of ACL and AC and further recognized as the oil spill and leakages (OPL) (Li et al., 2022). Li et al. (2019) indicated the vehicular exhaust (VE) provided high emissions of IP, DBA, BgP and HMW-PAHs (Li et al., 2019). BbF and BkF have been demonstrated as good markers for diesel vehicle emissions (Wang et al., 2013). High concentrations and fractions of aforementioned PAHs in factor 3 proved the vehicle exhaust (VE) emissions. The distinctive markers of coal combustion (CC) such as FA, PY, and BaA prevailed in the 4th factor, thus, factor 4 was recognized as CC emission (Callén et al., 2014; Jamhari et al., 2014). Factor 5 presented high contributions and concentrations of NA, ACL, AC, and FL, hence, it was categorized as the industrial source (IS). FL usually marked the emission from the industrial boiler and thermal power plant. ACL was widely used as an indicator for the cement industry. NA has been reported as the dominant specie in the steel industry. AN was identified as the indicator of the coke oven emission in the coking industry (Aydin, et al., 2014; Cvetković et al., 2015; Dat and Chang, 2017).

Time series of source contributions, and the average contributions in the daytime, night and all day were provided in Fig. 4.
In the daytime, VE, IS, and BB were the top three sources, with the contributions of 35.2%, 30.2%, and 17.7%, respectively. At the same time, the top three were CC (32.8%), VE (31.1%), and BB (14.7%), respectively, in the nighttime. It should be noted that the contributions of CC increased dramatically from 4.2% in the daytime to 32.8% in the nighttime with a growth rate of up to 680%. Consequently, CC has become the biggest contributor in the nighttime. This suggestion agreed with the fact that the rural residents preferred to use coal for heating due to the low cost despite that the strict coal banning law. Based on our field investigation, most rural residents had not heating behavior in the daytime and preferred to use coal as heating fuel in the nighttime. Therefore, some economic subsidy measures should be further implemented to promote the coal banning policy. Attributing to the rapid development of traffic network and increased car ownership in rural areas of north China, VE presented the largest and second largest contributors in the daytime and nighttime. At the same time, biomass was still an important household fuel in north villages. Unlike CC, BB shares decreased from 17.7% in the daytime to 14.7% in the nighttime, agreeing well with the fact the rural residents intended to use biomass for cooking instead of heating.

Fig. 5 showed the mass percentages of 18 PAHs in each PAH source. ACL, FL, AN, and NA
were the top PAHs in emission source of OPL, accounting for 14.0%, 13.4%, 12.5%, and 11.7% of the total PAHs. PHE and PY dominated in BB source, with the contributions of 12.9% and 12.5%, respectively. For the indicator of carcinogenic risk, BaP held high contributions of 8.73% and 7.76% in the CC and VE, which deserved attention. AC was the largest contributor in IS emission, with the fraction of 19.3%.

The recent PAH apportionment results using a PMF model in other Chinese urban/rural areas and in this study were listed in Table 1. The average CC fraction of 21.5% in this study was slightly lower than some urban areas before CH enforcement such as 24.3% and 29.5% of Beijing in 2014–2015 and 2017, 39.6%, 39.6%, and 42.6% of Zhengzhou in 2014, 2015, and 2016, and 26.3% of Anshan in 2014–2015. This comparison indicated the CH policy, especially coal-banning law, played a positive role in rural area (Li et al., 2023). At the same, however, BB fraction in this study outclassed 5.8% and 8.0% of the adjacent Beijing in 2014 and 2017, which indicated more effective implementation of the CH policy in urban area within the Beijing-Tianjin-Hebei (BTH) region (Cheng et al., 2019). Besides, the cities within the BTH region such as Beijing and Tianjin showed the lower BB fractions than those of Zhengzhou in 2014–2016, illustrating the regional difference in the enforcement of CH policy (Zhai et al., 2019). CH policy were reinforced more complete in big cities than small cities and rural area (Li et al., 2023). CC and BB totally contributed 37.4% to the total PAHs in this study exceeded the corresponding 36.0% in Ningbo, 31.8% in Nanjing, 27.6% in Shanghai, and 22.7% in Wuhan, which proved that the coal/biomass prohibition in rural area of north China should be further strengthened. The CC and BB concentrations decreased by 42.4% and 21.8% at this site in winter of 2021 compared those in winter of 2019 (Li et al., 2020), indicating the coal/straw prohibition played an important role. It should be noted that the VE contribution was surprise high up to 32.7% in this study, which was attributed to the decreased contributions of
coal/biomass and the large traffic flow at the nearby National Highway 107. Furthermore, high
contribution of IS was also observed in this study, indicating the emissions from local township
enterprises. Traffic limitation and emission control on industries were needed to further improve the
rural air quality.

3.3 Health risk assessment of PAHs

Fig. 6 shows the daily average BaP equivalent (BaPeq) concentrations and incremental lifetime
cancer risk (ILCR) for adults and children during the entire sampling period. The average BaPeq
concentration in the nighttime exhibited far higher value of 22.0 ng m$^{-3}$ than 10.3 ng m$^{-3}$ in the day
time. The results manifested that the nocturnal average BaPeq concentration was 2.14 times that the
corresponding diurnal value, which might be related to the enhanced PAH emissions from coal
combustion for heating in the nighttime based on the source apportionment result.

For the daily average ILCR values, the adults held 3.5 times that of the children, which were
9.35 $\times 10^{-6}$ and 2.67 $\times 10^{-6}$, respectively. The carcinogenic risks of PAHs posed by inhalation of
PM$_{2.5}$ varied significantly from $2.36 \times 10^{-6}$ to $2.04 \times 10^{-5}$ for adults, which meant the potential carcinogenic risks to adults. The daily ILCR values for adults increased from $6.73 \times 10^{-7}$ in the daytime to $5.83 \times 10^{-6}$ in the nighttime, implying the risks posed by heating behavior using coal. At the same time, however, the corresponding values for children were all lower than the acceptable level in both periods, proving the effectiveness of CH policy. In regard to the daily BaPeq concentrations of the individual PAH congener, BaP held the highest value of 11.7 ng m$^{-3}$, followed by BbF (1.71 ng m$^{-3}$), BaA (1.27 ng m$^{-3}$), DBA (1.14 ng m$^{-3}$), and IP (0.67 ng m$^{-3}$).

The source contributions to the ILCR values were apportioned using a PMF model and the analysis results were shown in Fig. 7. The ILCR values for both adults and children increased obviously from $5.62 \times 10^{-6}$ and $1.60 \times 10^{-6}$ in the daytime to $1.20 \times 10^{-5}$ and $2.36 \times 10^{-6}$ in the nighttime. Moreover, adults exhibited higher ILCRs compared to children due to children’s relative low respiratory rate and body weight (Wang et al., 2020b). VE was the largest contributor of ILCRs for both adults and children in the daytime, with the contributions of $1.98 \times 10^{-6}$ and $5.64 \times 10^{-7}$, respectively. CC contributions for adults and children increased from $2.39 \times 10^{-7}$ and $6.81 \times 10^{-8}$ in the daytime to $3.93 \times 10^{-6}$ and $1.12 \times 10^{-6}$. As a result, CC has become the largest ILCR contributor in the nighttime for both adults and children. Attributing to the resurgence of coal combustion for heating due to low cost despite that the coal prohibition law, high CC contributions on ILCRs might be the main reason for nocturnal potential risks.

(Fig. 7)
4 CONCLUSIONS

To examine the “Clean Heating” (CH) policy on PAH constituents, sources, and associated health risks in rural area of north China, we carried out an intensive observation at a rural site in the central area of the Beijing-Tianjin-Hebei (BTH) region covering the daytime and nighttime in the heating period of 2020. Coal combustion contributed to PAHs of 21.5%, lower than some north cities before the CH enforcement, indicated the implementation of coal banning law played a positive role in rural area. However, the average daily PM$_{2.5}$ concentrations in winter of 2020 exceeded those in winter of 2017 and 2019, indicating the coal banning law was passively implemented due to high cost of natural gas. Therefore, a series of measures including the comprehensive utility of clean fuel (clean coal and compressed biomass block), and use of advanced furnace should be promoted (Li et al., 2023). The contributions of biomass burning was still high as 15.9% though this was lower than 27.6% in 2019 at the same site, illustrating the biomass utility should be further managed. What’s more, the nocturnal heating behavior using coal greatly modified the PAH components, levels, and source contributions to the total PAHs and health risks. The medium molecular weight (MMW) PAHs increased most by 85.3% in the nighttime compared to the daytime. Coal combustion (CC) replaced vehicle exhaust (VE) to become the largest contributor to PAHs and incremental lifetime cancer risks in the nighttime, with the contributions of 32.8%, and $3.93 \times 10^{-6}$ and $1.12 \times 10^{-6}$ for adults and children, respectively. CC contributions for adult and children exceeded the recommended threshold of $1.12 \times 10^{-6}$ by the US EPA, which should be more concerned. At the same time, the average BaP equivalent concentration increased from 12.3 ng m$^{-3}$ in the daytime to 22.0 ng m$^{-3}$ in the nighttime. The utility of bulk coal for heating, biomass burning for cooking, and vehicle emissions should be further managed in rural area.
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Table Captions

Table 1
Comparisons of source contributions among different regions in China
Table 1. Comparisons of source contributions among different regions in China (%)

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>BB</th>
<th>CC</th>
<th>VE</th>
<th>OPL</th>
<th>IS</th>
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<td>WD (rural)</td>
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<td>15.9</td>
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BB, CC, VE, OPL and IS represent the biomass burning, coal combustion, vehicular exhaust, oil spill and leakages and industrial source, respectively.

WD, AS, BJ, CFD, NB, NJ, SH, TJ, TP, WH and ZZ represent Wangdu, Anshan, Beijing, Caofeidian, Ningbo, Nanjing, Shanghai, Tianjin, Taipei, Wuhan and Zhengzhou, respectively.
Figure Captions

Fig. 1.
Location of sampling site in the Beijing-Tianjin-Hebei (BTH) region.

Fig. 2.
PM$_{2.5}$ and PAH concentrations for (a) each sampling day, and (b) the daytime, nighttime and all day.

Fig. 3.
(a) Ring distributions of PAHs and (b) average concentrations of three categories of PAHs in the daytime, nighttime and all day.

Fig. 4.
Time series of the contributions of five PAH sources.

Fig. 5.
Mass percentages of individual PAH congener in PM$_{2.5}$ for five emission sources.

Fig. 6.
Time series of BaP equivalent (BaPeq) concentrations and incremental lifetime cancer risks (ILCRs) for adults and children.

Fig. 7.
Source contributions to the incremental lifetime cancer risks (ILCRs).
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