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Sources and Health Risks of $PM_{2.5}$-bound PAHs in a Small City along with the "Clean Heating" Policy

Zhiyong Li[1,2*], Ziyuan Yue[1], Jixiang Liu[1], Zhen Zhai[1], Jianwei Meng[3,4], Lei Wang[3,4], Jihong Wei[5], Dingyuan Yang[1], Ailian Hu[1], Wenjia Zhu[1], Ning Ding[1], Xiaoxia Lu[1], Chunhao Lin[1]**

[1] Hebei Key Lab of Power Plant Flue Gas Multi-Pollutants Control, Department of Environmental Science and Engineering, North China Electric Power University, Baoding 071003, China
[2] MOE Key Laboratory of Resources and Environmental Systems Optimization, College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China
[3] Hebei Research Center for Geoanalysis, Baoding 071003, China
[4] Hebei Key Laboratory of Mineral Resources and Ecological Environment Monitoring, Baoding 071003, China
[5] Department of Pediatrics, Affiliated Hospital of Hebei University, Baoding 071000, China

ABSTRACT

Levels, composition, and sources of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons (PAHs) vary significantly along with the "Clean Heating" (CH) policy in Beijing-Tianjin-Hebei (BTH) region, whereas the PAH characteristics with CH in small cities still remain unclear. A field observation was conducted in Baoding City, a small city within the BTH region, in winter of 2019 covering both the pre-heating season (PHS) and the heating season (HS). From the PHS to the HS, the mean concentrations for both $PM_{2.5}$ and $\sum_{18}$PAHs increased from 69.1 to 125.0 µg m^{-3} and from 8.09 to 26.2 ng m^{-3} due to the heating activities. The far lower PAHs in this study than those of small cities before CH implementation indicated the CH effectiveness. Higher diagnostic ratios (DRs) of FA/(FA + PY), BaA/(BaA + CHR), and IP/(IP + BgP) in the HS were in agreement with the increased coal/biomass usage. Positive matrix factorization (PMF) demonstrated that biomass/natural-gas burning (BNGB) contributed most to PAHs of 36.9% in the HS, the increased natural gas (NG) usage for heating should be responsible for this contribution due to the policies of biomass-burning prohibition and "Coal to Gas". Coal combustion (CC) shares increased by 152% in the HS despite the "Coal Banning" project. Again, the medium-molecular-weight PAHs (MMW-PAHs) increased most by 400% in the HS, evidencing the increased impacts of fossil-fuel consumptions. As an indicator for carcinogenic risk, BaP increased from 0.937 in the PHS to 1.29 ng m^{-3} in the HS. Furthermore, the incremental lifetime cancer risks (ILCR) and BaP equivalent concentrations (BaPeq) increased in the HS. The mean ILCR values of 1.15×10^{-6} for adults in the HS exceeded the threshold of 1×10^{-6}, while they were lower than 1×10^{-6} for children in both the PHS and the HS, and adults in the PHS due to the CH positive effects.

Keywords: $PM_{2.5}$, PAHs, Source apportionment, Clean heating, Health risk assessment

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*** Corresponding Authors:**
Zhiyong Li
lzy6566@126.com
Lei Wang
wanglei8812@126.com

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1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds consisting of two or more fused aromatic rings, and some of which have carcinogenic and mutagenic effects (Chen *et al.*, 2021; Alvarez-Ospina *et al.*, 2021). Therefore, PAHs were defined as a group I carcinogens by the International Agency for Research on Cancer (Vega *et al.*, 2021; Zhang *et al.*, 2021). PAHs can enter the human body through dietary intake, respiratory inhalation, and dermal contact, and subsequently cause the damage to lung function through direct action on alveolar epithelial

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cells (Zhang *et al.*, 2020a). China was one of countries with the highest $PM_{2.5}$ level in the world (Kong *et al.*, 2018). Over the past few decades, $PM_{2.5}$ has been a key risk driver of the global burden disease, especially in China (Bu *et al.*, 2021). Former studies have highlighted that the toxic components in $PM_{2.5}$ such as heavy metals, black carbon and PAHs can lead to the harmful effects on human health (Zhou *et al.*, 2021). China is the world's largest contributor of PAHs with an average annual emission of 14,000 tons (Zhang *et al.*, 2021). PAHs-derived health risks were more severe in Beijing-Tianjin-Hebei (BTH) region within north China, which was attributed to the winter heating and the regional heavy industries including thermal power generation, iron-steel, and coking (Li *et al.*, 2021; Yang *et al.*, 2022).

The Chinese government's efforts to curb environmental pollution can trace back to the 1980s (Feng and Liao, 2016). However, the air pollution was still serious in northern China, which has caused notable environmental and social problems (Chen *et al.*, 2019; Wu *et al.*, 2021; Yang *et al.*, 2022). To alleviate this crisis, China launched the “Clean Air Action Plan” (CAAC) in September 2013 to markedly reducing $PM_{2.5}$ levels by 25% until 2017 (Kong *et al.*, 2018; Chen *et al.*, 2019). In consequence, the major air pollutants such as $PM_{2.5}$, SO_2 and CO declined significantly from 2013 to 2018 in China by 30%–50% based on the data from Chinese National Environmental Monitoring Center (CNEMC) (Zhai *et al.*, 2019). For example, $PM_{2.5}$ in the heating season of 2018 in Beijing decreased by 40.9% compared with that in 2017 (Pang *et al.*, 2021). However, the still high $PM_{2.5}$, and ever-increasing mass contributions of organic aerosols (OA) (e.g., PAHs) to $PM_{2.5}$ have been the new obstacles in the air quality improvement (Zhai *et al.*, 2019; Zhang *et al.*, 2020b).

As a result, the State Council issued the “Three-Year Action Plan for Defending the Blue Sky” (TYAP) on July 3, 2018. In TYAP, measures were mainly taken to reduce pollutant emissions from industries and vehicles, which made the influence of civil combustion sources more predominant (Chen *et al.*, 2019; Zhai *et al.*, 2019; Guo *et al.*, 2020; Li *et al.*, 2020; Yang *et al.*, 2022). Therefore, the “Clean Heating” (CH) project was subsequently promoted to reduce the pollutant emissions in north China in the heating season. CH derived “coal to natural gas” (CTNG) and “coal to electricity” (CTE) were aimed toward eliminating scattered coal, which could alter the PAH levels, composition, and the health risks to a great extent (Kong *et al.*, 2018). For instance, the concentration of PAHs and OPAHs in Urumqi decreased by 74% and 82%, respectively, after the CTNG execution (Ren *et al.*, 2017).

The CTNG penetration-rates varied significantly among different regions in north China along with their degrees of economic and social development (Meng *et al.*, 2020). Jacobson *et al.* (2018) indicated that the comprehensive utilization of coal, natural gas, electricity and other energy in rural and suburban areas of undeveloped small cities was required. To our knowledge, the recent studies were mainly focused on the large cities, while few studies were conducted in small cities (Ren *et al.*, 2017; Yang *et al.*, 2022). Therefore, the systematic evaluation of PAH characteristics along with CH project in small cities was urgently needed (Meng *et al.*, 2020; Yang *et al.*, 2022). Baoding City, one of China's most polluted cities, lies in the central of the BTH region, was chosen for PAH analysis (Li *et al.*, 2020). The main aims of this study were: 1) evaluate the PAH levels with CH policy; 2) access the variations in source contributions between the PHS and the HS; and 3) evaluate the potential health risks of PAHs via inhalation for different groups of people.

2 METHODOLOGY

2.1 Sampling Site Description

Baoding City is situated in the central area of Beijing-Tianjin-Hebei (BTH) region within the North China Plain, which is 146 km south to Beijing, 142 km north to Shijiazhuang, and 180 km east to Tianjin (Fig. 1). The samplers were installed on the roof of a teaching building (38°88′N, 115°51′E) of North China Electric Power University (approximately 20 m above ground), which was surrounded by residential buildings within a 4 km radius and thus identified as a typical residential zone.

2.2 $PM_{2.5}$ Sampling

The sampling procedures were described in detail in Yang *et al.* (2022). Two medium-flow air samplers (TH-150C III, Wuhan Tianhong Ltd., China) was utilized to collect $PM_{2.5}$ with a flow rate

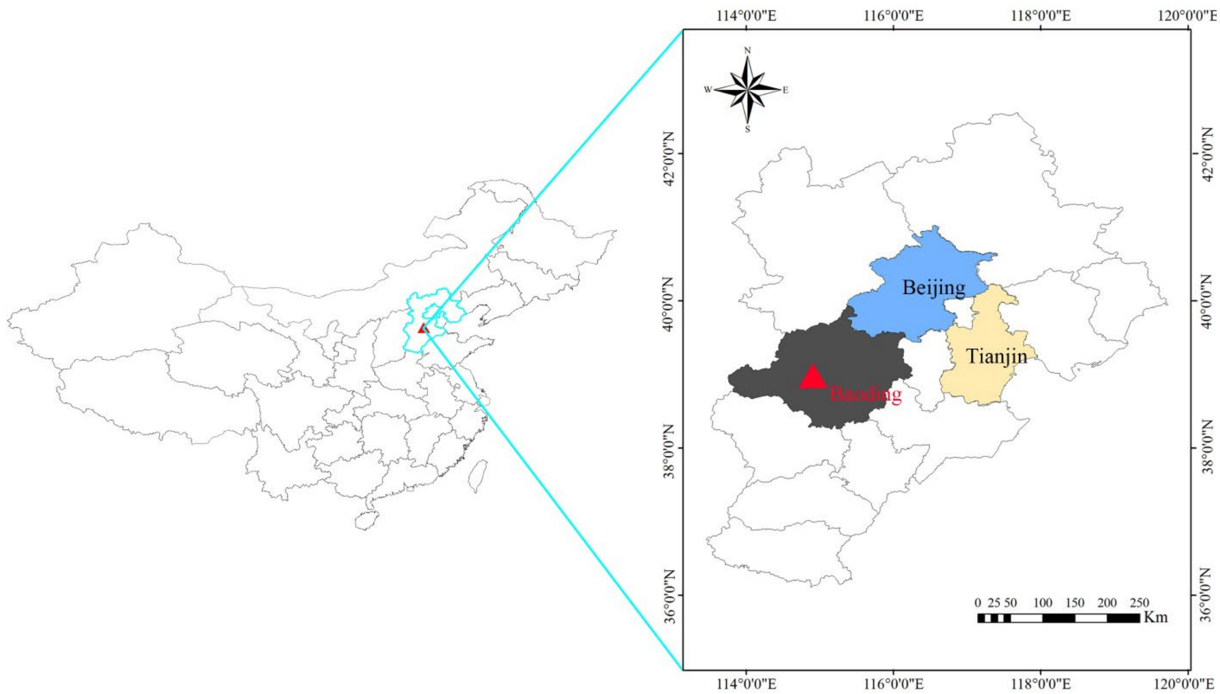

Fig. 1. Location of sampling site in Baoding.

of 100 L min^{-1}. Samples were collected in the winter of 2019–2020 covering the pre-heating season (PHS, 25 October–14 November, 2019) and the heating season (HS, 16 November, 2019–10 January, 2020). Two types of filters (diameter, 90 mm) including the quartz fiber (QF) filters (Pall USA) and Teflon (PTEE) filters were used in this study. Each sampling duration was 23 hours from 8:00 A.M. to the 7:00 A.M. of the next day. A total of 32 samples and 4 field blanks were obtained. QFs and PTEEs were baked and heated at 450°C and 60°C prior to sampling. PTEEs were stabilized for 48 hours at the constant temperature and humidity to obtain the $PM_{2.5}$ mass by subtracting the pre-weight from the post-weight (Yang *et al.*, 2022). Each filter was weighed at least three times by an analytical balance with sensitivity of ± 0.010 mg. Each filter was sealed by aluminum foil and stored at –20°C before analysis.

2.3 Analysis of PAHs

A gas chromatography coupled with mass spectrometry (GC6890/MSD5973i; Hewlett-Packard) system was utilized to analyze eighteen PAH congeners including 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).

We consulted TO-13A and carried out the procedures of pre-treatment and analysis in this study. The chromatographic conditions were shown as follows: 70°C held for 2 min, ramped to 260°C at 10°C min^{-1} and held for 8 min, and then elevated to 300°C at 5°C min^{-1} and held for 5 min. More analysis and operation details are consistent with Li *et al.* (2020, 2021). The method detection limits (MDLs) for 18 PAHs varied from 0.010 to 1.10 ng g^{-1} with the mean value as 0.220 ± 0.180 ng g^{-1}. The recoveries for 18 PAHs in 5 matrix-added samples ranged from 75% to 115%. The mean recoveries for two surrogate standards including 14-deuterium substituted terphenyl and 4-bromo-2-fluorobiphenyl in 5 samples were 90 ± 15% and 95 ± 20%, respectively. The relative standard deviation (RSD) values for 6 duplicated samples were all less than 10%.

2.3 Source Apportionment of PAHs

2.3.1 Diagnostic ratios (DRs)

The diagnostic ratios (DRs) have been widely used for source identification and source contribution quantities (Kong *et al.*, 2018). The concentration ratios of AN/(AN + PHE), FA/(FA + PY), BaA/(BaA + CHR), and IP/(IP + BgP) were widely used indicators in previous studies (Suman *et al.*, 2016). In this study, we calculated these four DRs and compared them with typical DRs for emission sources taken from the literatures (Kong *et al.*, 2018).

2.3.2 Positive matrix factorization (PMF) model

PMF is a multivariate factor analysis tool developed by the U.S. EPA to apportion the source contributions for $PM_{2.5}$ and PAHs, which can break down response data into major contributing factors and provide profiles for each factor (Liu *et al.*, 2018; Taghvaee *et al.*, 2018). EPA PMF 5.0 version available at the website of www.epa.gov/air-research/positive-matrix-factorization was used in this study. The measured concentrations of eighteen PAHs were used as the model inputs. The missing values and associated uncertainties were obtained according the documented method in Yao *et al.* (2016) and Yang *et al.* (2022). The uncertainties were estimated by the Eqs. (1) and (2).

$$unc = \frac{5}{6} \times MDL \quad (c_i \le MDL) \tag{1}$$

$$unc = \left[\left(\frac{c_i}{6} \right)^2 + MDL^2 \right]^{0.5} \quad (c_i \ge MDL) \tag{2}$$

A total of 20 runs were used for each PAH. The lowest Q_{robust} value was 3018.8, and the ratio of Q_{robust}/Q_{true} was 0.92. More information about PMF could be available in Yao *et al.* (2016).

2.4 Health Risk Assessment

BaP equivalent concentration (BaPeq) proposed by U.S. EPA for cancer risk assessment was used to assess the risk of PAHs via inhalation (Li *et al.*, 2020). The equivalent concentration is calculated by multiplying the PAH mass concentration by the corresponding toxic equivalent factor (TEF) (Li *et al.*, 2021). The sum of BaP_{eq} of individual PAH can be used to evaluate the total carcinogenicity of PAHs, which is described in Kong *et al.* (2018) and shown as follows:

$$Bap_{eq} = \sum_{i=1}^{n} C_i \times TEF_i \tag{3}$$

The incremental lifetime cancer risk (ILCR) was a quantitative assessment for PAH exposure risks in the environment (Wang *et al.*, 2020) and shown as follows:

$$ILCR = CSF \times \frac{CA \times IR \times ET \times EF \times ED}{BW \times AT} \tag{4}$$

where, CA represents BaP equivalent (BaP_{eq}) concentrations (mg m^{-3}). The meanings and values of the other parameters were listed in Table S1. In this study, a crucial exposure pathway as inhalation was chosen to evaluate the exposure risks for PAHs (Zhang *et al.*, 2009; Shen *et al.*, 2013).

The exposure risks were regarded as dangerous when the ILCR was higher than 1×10^{-4}, as acceptable when the ILCR was between 1×10^{-6} and 1×10^{-4}, and as negligible when the ILCR was less than 1×10^{-6} (Wang *et al.*, 2020).

Exposure to the ambient air pollutants is one of the major reasons, which caused a loss of life expectancy (LLE) (Lelieveld *et al.*, 2020). In this study, LLE was calculated with the following formula (Lelieveld *et al.*, 2020):

$$V_{LL} = 62.16 \times \left(\frac{V_{ILCR}}{10^{-5}} \right) \tag{5}$$

where, V_{LL} is the loss of life expectancy, min; and V_{ILCR} is the lifetime cancer risk.

3 RESULTS AND DISCUSSION

3.1 Levels of PAHs

The volume concentrations of $PM_{2.5}$ and total PAHs, and the mass contents of PAHs in $PM_{2.5}$ were shown in the Fig. 2. The daily average $PM_{2.5}$ concentrations increased from 69.1 ± 32.3 in the PHS to 125 ± 50.7 µg m^{-3} in the HS. The increase of $PM_{2.5}$ by 80.9% in this study was similar to the 79.1% in a rural site in north China due to the elevated coal usage for heating (Zhao *et al.*, 2020). $PM_{2.5}$ in the HS significantly exceeded 75 µg m^{-3} in the Chinese Standard Grade II though the major air pollutants decreased markedly by 30–50% from 2013 to 2018 in China, indicating the urgency to improve air quality in the HS (Zhai *et al.*, 2019; Li *et al.*, 2020).

The variations of PAH mass concentrations and contents were similar to the $PM_{2.5}$ concentrations in the entire sampling period (ESP). Former studies reported the similar variations between PAHs and $PM_{2.5}$ (Chang *et al.*, 2019). The volume concentrations for both PAHs and $PM_{2.5}$ peaked on Oct. 29, Nov. 8, Nov. 22, Dec. 9, and Jan. 3, which was attributed to high emission intensities and unfavorable meteorological conditions such as low temperature, weak wind, and relatively low boundary layer height. The mass contents of total PAHs increased from 168 ± 179 in the PHS to the 234 ± 97.3 µg g^{-1} in the HS, and the mass concentrations of PAHs also enhanced from 8.09 ± 4.30 to 26.2 ± 8.83 ng m^{-3}.

The $\sum_{18}$PAHs in the HS was 3 times that in the PHS in Baoding City, which was much lower than 15.2 times in Beijing City in 2015 (Chang *et al.*, 2019), which indicated the effectiveness of CH policy. Meanwhile, the $\sum_{18}$PAHs of 26.2 ng m^{-3} in Baoding City was much lower than 60.4–95.5 ng m^{-3} of $\sum_{8}$PAHs in Beijing City in the HS in 2015, which further evidenced the CH policy on PAHs emission reductions in north China (Chang *et al.*, 2019; Zhai *et al.*, 2019).

3.2 Levels of Individual PAH

A total of fourteen of eighteen PAHs except for AC, ACL, AN, and Fl were detected and the

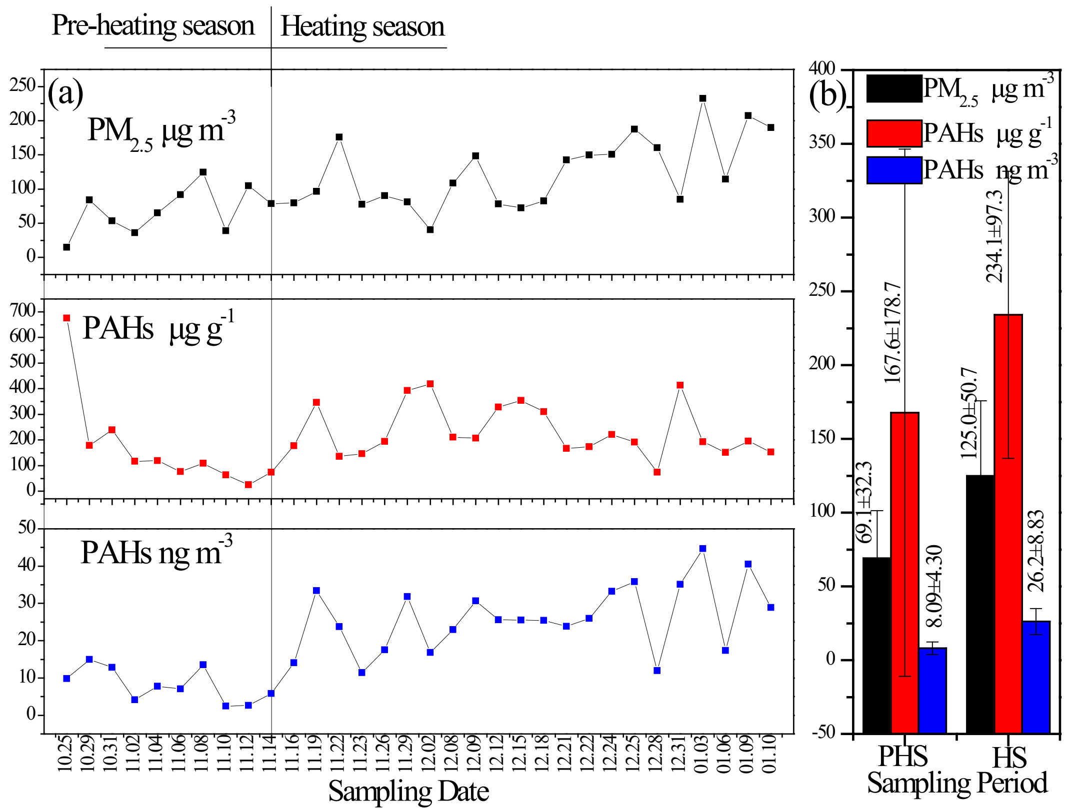

Fig. 2. $PM_{2.5}$ concentrations, PAH contents, and PAH concentrations for (a) each sampling day, and (b) the pre-heating and heating seasons.

concentration statistics were listed in Table S2. BeP was the most abundant PAH, and increased from 2.93 in the PHS to 7.98 ng m^{-3} in the HS, which accounted for 31.2% of the $\sum_{18}$PAHs in the entire sampling period (ESP). BaP was widely used as an indicator of the carcinogenic risks of PAHs (Chang *et al.*, 2019). In this study, BaP was averaged at 0.937 ± 0.090 ng m^{-3} in the PHS, which was slight lower than the recommended threshold of 1 ng m^{-3} by the U.S. EPA (Chang *et al.*, 2019). However, BaP exceeded 1 ng m^{-3} in the ESP (1.04 ng m^{-3}) and in the HS (1.29 ng m^{-3}), which should be ascribed to the heating activities, which should be more concerned. Wang *et al.* (2020) indicated that the main sources of BaP were coal tar, black carbon, and smoke from the combustion processes of coal, petroleum, and biomass, as well as cigarette smoke, vehicle exhaust, and cooking fumes. Therefore, the BaP increase in the HS might be ascribed to the increased coal/biomass consumptions for heating in the surrounding rural areas of Baoding City (Li *et al.*, 2020).

3.3 Composition of PAHs with Different Ring Numbers

PAHs were classified into three groups including low-molecular weight (LMW-PAHs; 2- and 3-ring), medium-molecular weight (MMW-PAHs; 4-ring PAHs), and high-molecular weight PAHs (HMW-PAHs; ring number > 4-ring) (Feng and Cao, 2019; Wang *et al.*, 2021). Fig. 3 showed the composition profiles for aforementioned three PAH groups. Kong *et al.* (2018) suggested that the LMW-PAHs originated mainly from coal combustion, MMW-PAHs from incomplete combustion of

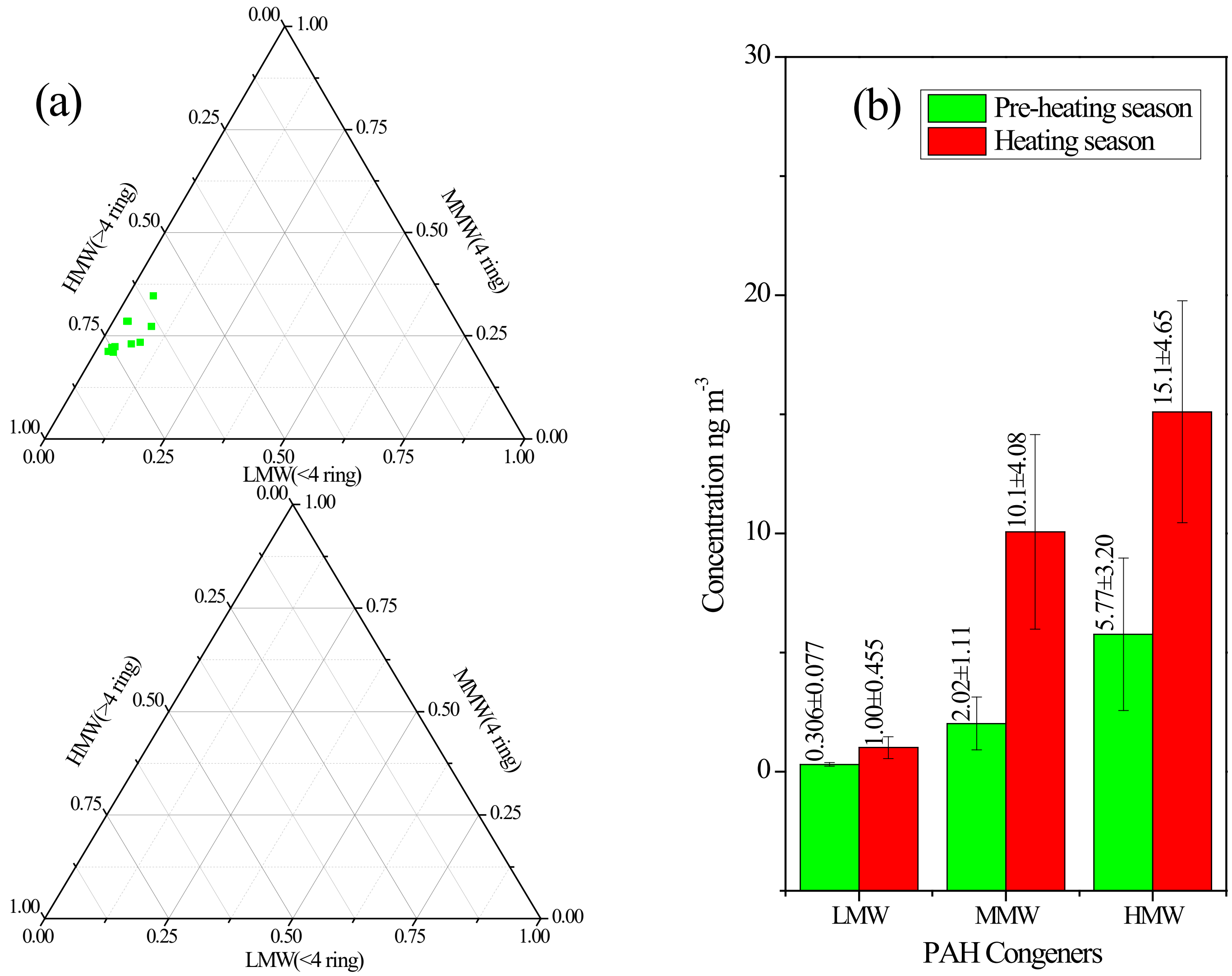

Fig. 3. (a)Triangle diagram of the ratio of PAHs with different ring numbers in $PM_{2.5}$ and (b) average concentrations of three categories of PAHs in the pre-heating and heating seasons.

fossil fuels at high temperatures, and HMW-PAHs from internal combustion engine emissions. Therefore, the difference in the ring distribution of PAHs indicates the impacts of different emission intensities between the PHS and the HS. LMW-PAHs possessed the lowest levels in both the PHS and the HS because they tended to enrich in gas phase, whereas HMW-PAHs hold the highest levels due to their high boiling point (Zhang *et al.*, 2013). The highest increase of MMW-PAHs (from 2.02 in the PHS to 10.1 ng m^{-3} in the HS) by 400% concurred with the enhanced coal/biomass usage for heating in the HS. Accordingly, the mass shares of MMW-PAHs increased from 25.0% in the PHS to 38.5% in the HS. Contrary to MMW-PAHs, HMW-PAH contributions decreased from 71.3% in the PHS to 57.6% in the HS, which might be related to the traffic limitation in the HS (Feng and Gao, 2019; Wang *et al.*, 2020).

3.4 Diagnostic Ratios

Diagnostic ratios (DRs) of PAHs have been widely used as a useful tool to distinguish their sources qualitatively (Kong *et al.*, 2018). In this study, the four mass ratios of FA/(FA + PY), BaA/(BaA + CHR), AN/(AN + PHE) and IP/(IP + BgP) were calculated to qualitatively assess the emission sources of PAHs during the PHS and HS. Fig. 4 showed the four ratios for this study and the related emission sources (Kong *et al.*, 2018). Generally, the values of FA/(FA + PY), BaA/(BaA + CHR) and IP/ (IP + BgP) fell in the range of 0.5–0.6, 0.4–0.5 and 0.5–0.6, reflecting the significant contribution of coal and biomass combustion, vehicle emission, and diesel burning. Meanwhile, higher FA/(FA + PY) and BaA/(BaA + CHR) values were found in the HS, which was in agreement with the increased impacts of coal/biomass combustion in the HS. Furthermore, IP/(IP + BgP) increased much in the HS indicated the PAHs were more affected by coal/biomass burning for heating. However, AN/(AN + PHE) values decreased from 0.168 ± 0.052 in the PHS to 0.068 ± 0.024 in the HS, which highlighted the importance of petroleum in the HS (Kong *et al.*, 2018). Although the AN/(AN + PHE) values yielded the contradictory conclusions with those from the other three kinds of DRs, the enhanced coal and biomass consumptions in the HS should be the explanations for DR variations (Kong *et al.*, 2018).

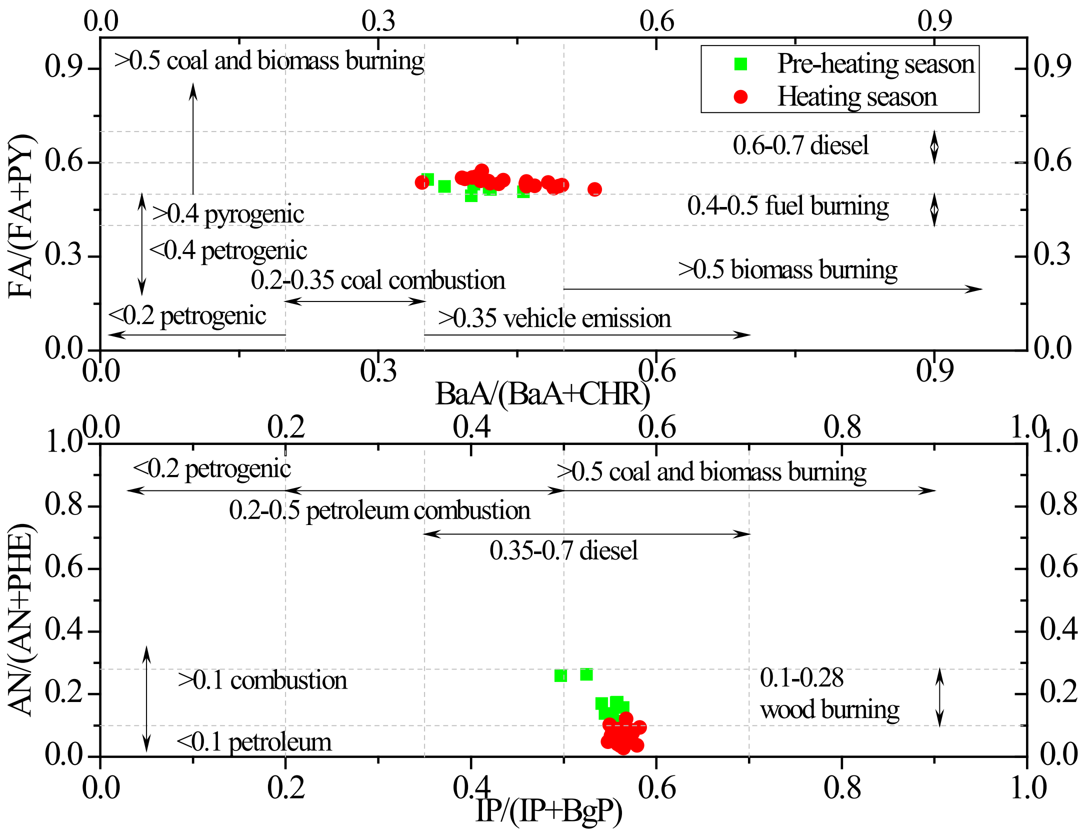

Fig. 4. Graphic illustration of the diagnostic ratios for the identification of PAHs sources.

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3.5 Source Apportionment by PMF Model

In the entire sampling period (ESP), totally five PAH sources were recognized by PMF model and their profiles were shown in Fig. S1. Factor 1 was characterized by high loadings of CHR, PHE, FA, FL, and BbF, which could be attributed to biomass/natural-gas burning (BNGB) (Wang *et al.*, 2020; Azimi *et al.*, 2021). PHE, FA, FL, and BbF were widely used as the indicators for biomass burning (BB) (Wang *et al.*, 2020). CHR often marked the PAH emissions from natural gas burning though CHR also was released from agricultural incineration of charcoal (Azimi *et al.*, 2021). Factor 2 possessed high levels of IP, DBA, BgP, BkF, and HMW-PAHs, which might be related to the vehicular exhaust (VE) (Li *et al.*, 2019). BkF has been demonstrated as good markers of diesel-vehicle emissions (Wang *et al.*, 2013). At the same time, high loadings of HMW-PAHs was associated with VE (Zhou *et al.*, 2005; Kong *et al.*, 2018). High laodings of FA, PY, and BaA were found in Factor 3, suggesting the emissions from coal combustion (Callénet *al.*, 2014; Jamhari *et al.*, 2014). Factor 4 was associated with high ACL and AC and identified as the oil spill and leakages (OPL) (Liu *et al.*, 2018). Factor 5 was featured by the high loadings of NA, ACL, AC, and FL, which was identified as the industrial sources (IS). FL was the marker for industrial boilers and thermal power plants, ACL was for the cement industry, NA was the dominant species in the steel industry, and AN was for the coking industry (Dat and Chang, 2017).

Fig. 5 listed the source contributions in each sampling day, the pre-heating season (PHS), the heating season (HS), and the entire sampling period (ESP). The source contributions varied significantly between the PHS and the HS. Vehicle exhaust (VE) was the biggest contributor and accounted for 29.4% of the total PAHs in the PHS, whereas the corresponding source and contribution were biomass/natural-gas burning (BNGB) and 36.9%. BNGB shares increased by 221% from the PHS to the HS, which should be associated with the increased usage in natural gas (NG) and biomass, especially for NG, when the biomass-burning prohibition and "Coal to NG" were taken into accounted (Chen *et al.*, 2019; Li *et al.*, 2021). Coal combustion (CC) contributions increased markedly from 9.89% in the PHS to the 24.9% in the HS despite the implementation of "coal-banning" policy, which was in accordance with the significant increase of MMW-PAHs in the

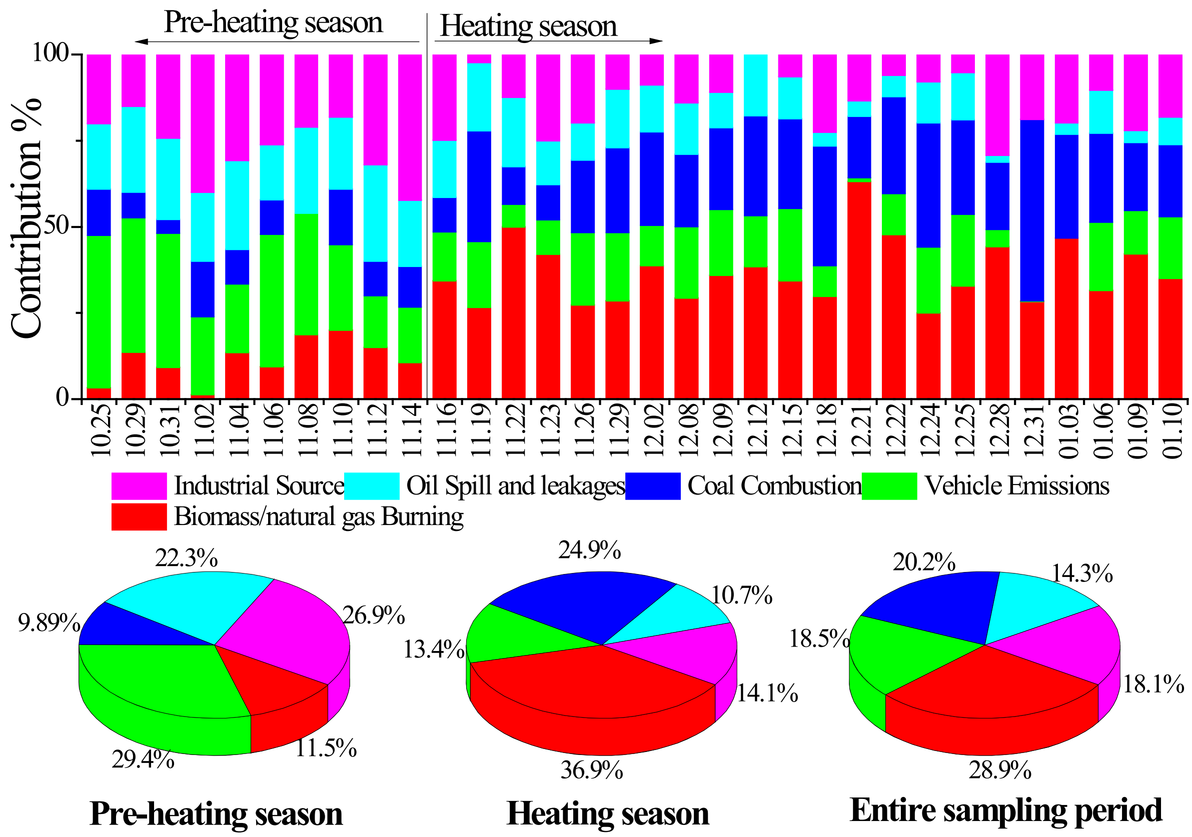

Fig. 5. Time series of the contributions of five PAH sources.

HS (Feng and Gao, 2019). The coal utilization for heating should be further managed (Zhai *et al.*, 2019). As the biggest contributor in the PHS, VE declined most by 54.4% due to the traffic limitation in the HS, which concurred with the decrease of mass shares of HMW-PAHs in the HS (Wang *et al.*, 2020). Fig. S2 listed the source contributions for each PAH congener. For the most concerned BaP, the main contributors included CC, VE, and BNGB. The variations of their contributions resulted in the increase of BaP in the HS.

3.6 Health Risk Assessment of PAHs

Fig. 6 showed the BaP equivalent (BaP_{eq}) concentrations and the incremental lifetime cancer risk (ILCR) for adults and children on a daily basis throughout the entire sampling period (ESP). The BaP_{eq} concentrations in the ESP varied from 0.193 to 3.24 ng m^{-3} with mean value of 1.69 ng m^{-3}. The mean value of 1.69 ng m^{-3} was far lower than Anshan in 2018 (13.8 ng m^{-3}) (Wang *et al.*, 2020), Tianjin in 2010 (9.46 ng m^{-3}) (Han *et al.*, 2014), and Beijing from 2003 to 2006 (43.7 ng m^{-3}) (Wang *et al.*, 2014). BaP_{eq} values have decreased significantly compared with those in other Chinese cities in the pre-implementation period of "Clean Heating" project, indicating that relevant governance has achieved certain results. However, they were still higher than Kuala Lumpur (0.334 ng m^{-3}), Petaling Jaya (0.640 ng m^{-3}) and Bangi (0.389 ng m^{-3}) in 2010–2011, which meant that the management of $PM_{2.5}$ and related PAHs in China should be strengthened (Zhai *et al.*, 2019). Meanwhile, BaP_{eq} values increased much from 0.748 ng m^{-3} in the PHS to the 2.16 ng m^{-3} in the HS due to the elevated contributions of coal combustion and biomass/natural-gas burning to the total PAHs.

The incremental lifetime cancer risk (ILCR) values for both adults and children in the PHS were lower than the recommended threshold value of 1×10^{-6} by the U.S. EPA, while there were up to 14 of 22 days in the HS with the ILCR values higher than 1×10^{-6} for adults. At the same time, the mean ILCR values for adults increased from 3.28×10^{-7} in the PHS to the 1.15×10^{-6} in the HS. The mean ILCR values for children and adults in the HS were much lower than the corresponding 5.99×10^{-6} and 8.36×10^{-6} in winter of 2014–2015 in Anshan City (Wang *et al.*, 2020), which might be attributed to the effects of "Clean Heating". The contributions of sources to the mean ILCR values in the PHS, the HS, and the ESP were shown in Fig. 7 based on their source profiles and mass contributions to the total PAHs. In consequence, the values of loss of life expectancy (LLE) increased from 0.72 and 2.03 mins for children and adults in the PHS to 2.53 and 7.15 mins in the HS.

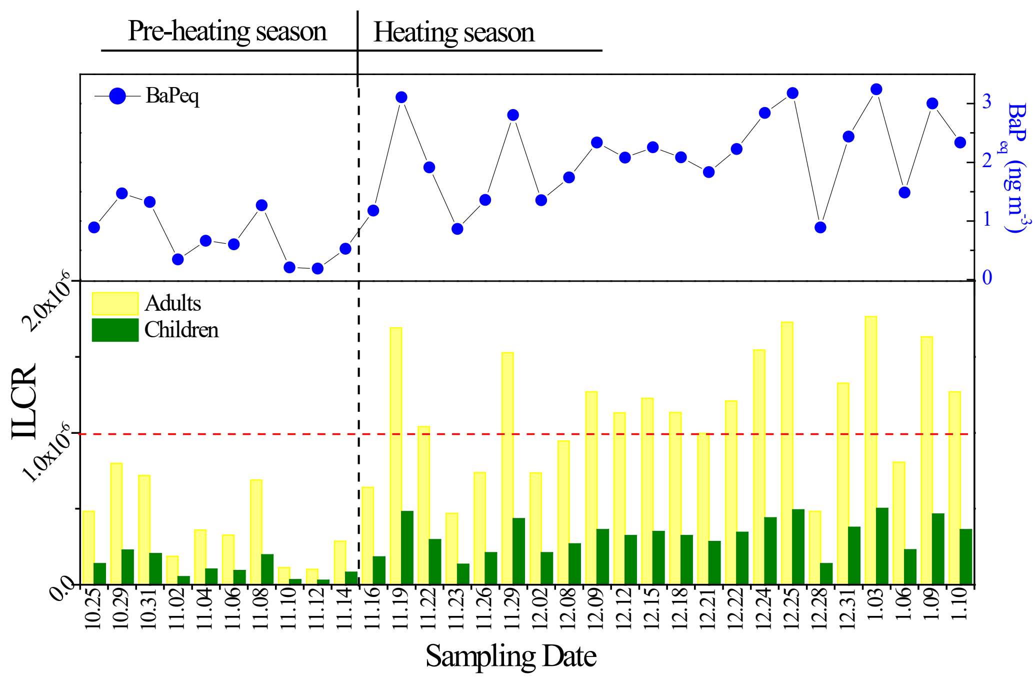

Fig. 6. Time series of BaP equivalent (BaPeq) concentrations and incremental lifetime cancer risks (ILCRs) for adults and children.

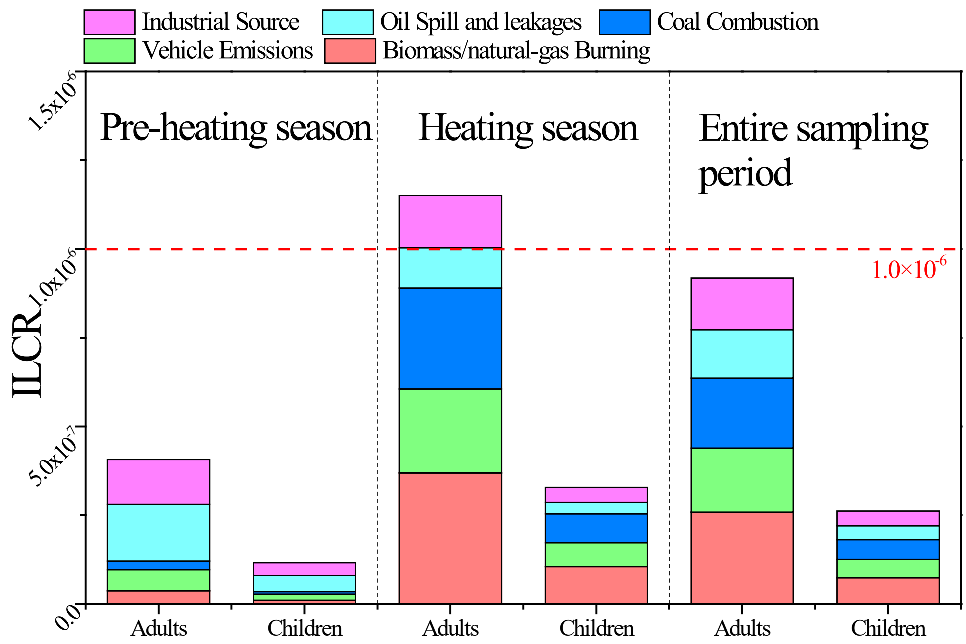

Fig. 7. Source contributions to the incremental lifetime cancer risks (ILCRs).

4 CONCLUSIONS

We systematically evaluate the "Clean Heating" policy impacts on variations of source contributions, levels, health risks of $PM_{2.5}$-bound PAHs between the pre-heating season (PHS) and the heating season (HS) in a small city (Baoding City) in winter of 2019–2020.

1) $\sum_{18}$PAHs increased by 224% in the HS compared with that in the HS. As an indicator of carcinogenic risks posed by PAHs, BaP increased from 0.937 to 1.29 ng m^{-3}. Furthermore, the mean value of total 18 PAHs of 26.2 ± 8.83 ng m^{-3} in the HS was far lower than that of other cities before CH implementation, indicating the positive effects of CH.
2) Comparing with those in the PHS, the mass concentrations of MMW-PAHs increased most by 400% in the HS and followed by LMW-PAHs with the increase rate of 227%, which might be associated with the increased consumptions of fossil fuels for heating. However, the mass shares of HMW-PAHs decreased from 71.3% in the PHS to 57.6% though MMW-PAHs concentrations increased in the HS due to the traffic limitation. Higher values of FA/(FA + PY), BaA/(BaA + CHR), and IP/(IP + BgP) were found in the HS due to the increased usage of coal and biomass for heating.
3) Positive matrix factorization (PMF) model analysis indicated that biomass/natural-gas burning (BNGB) contributed most to the total PAHs of 36.9% due to the "Coal to Gas" policy. Coal combustion (CC) shares increased from 9.89% in the PHS to 24.9% in the HS despite the implementation of "Coal-Banning". Instead, the shares of vehicle exhaust (VE) and industrial sources (IS) decreased much due to the traffic limitation and the implementation of ultra-low emission measures in industries.
4) Attributing to the CH effects, the incremental lifetime cancer risk (ILCR) values for adults and children in the PHS and children in the HS were lower than the accepted threshold value of 1×10^{-6}. However, the ILCR values for adults in 14 of 22 sampling days in the HS exceeded 1×10^{-6}. PMF showed that the BNGB and CC contributed higher to the total ILCRs in the HS than PHS.

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SUPPLEMENTARY MATERIAL

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