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Ambient $PM_{2.5}$-bound polycyclic aromatic hydrocarbons (PAHs) in rural Beijing: Unabated with enhanced temporary emission control during the 2014 APEC summit and largely aggravated after the start of wintertime heating☆

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ABSTRACT

For human health benefits it is crucial to see if carcinogenic air pollutants like polycyclic aromatic hydrocarbons (PAHs) are reduced accordingly along with the control of the criteria pollutants including fine particles ($PM_{2.5}$). A number of studies documented that enhanced temporary emission control during the 2014 Asia-Pacific Economic Cooperation summit (APEC) in Beijing resulted in substantial drops of observed ambient $PM_{2.5}$, as well as PAHs, in urban areas of Beijing, yet it is not clear whether $PM_{2.5}$-bound PAHs in the rural areas were also lowered during the APEC. Here filter-based $PM_{2.5}$ samples were collected at a rural site in northeast of Beijing, and analyzed for 25 PAHs before (Oct. 27-Nov. 2, 2014), during (Nov. 3–12, 2014) and after (Nov. 13, 2014–Jan. 14, 2015) the APEC. Observed concentrations of $PM_{2.5}$, OC and EC during the APEC dropped by about 30%, however, average $PM_{2.5}$-bound PAHs and their incremental lifetime cancer risk (ILCR), 25.65 ng/m^3 and 3.2×10^{-4}, remained almost unchanged when compared to that of 25.48 ng/m^3 and 3.5×10^{-4}, respectively, before the APEC. After the APEC with the start of wintertime central heating in urban Beijing on Nov. 15, 2014, average total concentration of PAHs and their ILCR highly elevated and reached 118.25 ng/m^3 and 1.5×10^{-3}, respectively. Source apportioning by positive matrix factorization (PMF) revealed that coal combustion was the largest source that contributed 63.2% (16.1 ng/m^3), 78.5% (20.1 ng/m^3) and 56.1% (66.3 ng/m^3) to the total PAHs before, during and after the APEC, respectively. Uncontrolled residential coal use during the APEC was found to be the reason for unabated levels of PAHs, and the largely aggravated PAHs after the APEC was resulted from increased coal consumption for wintertime residential heating. Our results suggested reducing emission from residential coal combustion is crucial to mitigate carcinogenic PAHs in ambient air, especially in rural areas.

1. Introduction

Air pollution is a significant source of health burden on the global scale (Lelieveld et al., 2015; Brauer et al., 2016). Exposure to outdoor air pollution, particularly by fine particulate ($PM_{2.5}$), is estimated to cause 3.3 million premature deaths per year worldwide, predominantly in Asia (Lelieveld et al., 2015). $PM_{2.5}$ pollution ranked the fourth in leading factor for mortality in China in 2010

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(Yang et al., 2013). Polycyclic aromatic hydrocarbons (PAHs) are among the most toxic components in $PM_{2.5}$. Human exposure to PAHs has been proved to have high cancer risk (Armstrong et al., 2004; Xu et al., 2008; Shrivastava et al., 2017) with global incremental lifetime cancer risks (ILCR) by ambient PAH exposure as high as 3.1×10^{-5} (Shen et al., 2014). In China, the world's largest emitter of PAHs with 21.0% (106 Gg/a) burden of the global emissions in 2007 (Shen et al., 2013), inhalation exposure to PAHs was estimated to have an ILCR of 6.5×10^{-6} (Zhang et al., 2009), much higher than the acceptable risk level of 1.0×10^{-6} (USEPA, 1991). PAHs are ubiquitous in the atmosphere and emitted from various sources such as vehicle emission, coal and biomass combustion (Shen et al., 2013), shipping emission (Pongpiachan et al., 2015) and other anthropogenic sources (Pongpiachan et al., 2017a, 2018, 2017b). Therefore, it is a long-lasting challenge to reduce PAH emissions for health benefits, particularly in China.

Beijing, as the capital city of China, has suffered from serious $PM_{2.5}$ pollution in recent years (Zheng et al., 2015), and inhalation exposure to PAHs in Beijing had an ILCR of 13.5×10^{-6}, over 2 times of the average in China (Zhang et al., 2009). To combat severe air pollution particularly by fine particles, many long-term and short-term measures have been implemented in Beijing, and control measures were much more stringent during some important international events, such as the 2014 Asia-Pacific Economic Cooperation summit (referred to as "APEC" hereafter), which was held during November 3–12, 2014 in Beijing. This practice of short-term enhanced emission control in Beijing and its adjacent regions has been proved to be very successful in improving air quality and visibility (Li et al., 2015; Liu et al., 2016b). During the APEC, for example, observed mass concentrations of $PM_{2.5}$ and $PM_{1.0}$ decreased by over 50% (Tang et al., 2015; Xu et al., 2015), and trace gases, including SO_2, NO_2, CO and VOCs, also decreased by 4–33% (Li et al., 2015; Sheng et al., 2015) as observed in urban Beijing. This kind of the short-term enhanced emission control during some big events in Beijing, on the other hand, offered very good rehearsal opportunities to study how and in what extent various control measures would take effect in reducing air pollutants and improving atmospheric visibility. Many works have been done on how the control measures impacted the haze-related aerosol optical properties (Tao et al., 2016) and the compositions and sources of submicron aerosols ($PM_{1.0}$) (Chen et al., 2015; Xu et al., 2015). The precious studies, however, were focused on the air pollution reduction in the urban areas; and it is very important to see how these temporary measures would influence air quality in rural areas and in a regional scale. Moreover, for human health benefits, it is also of great importance to make sure if hazardous air pollutants, such as $PM_{2.5}$-bound PAHs, are reduced accordingly along with the criteria pollutants including $PM_{2.5}$, O_3, SO_2, NO_2 and CO. With the enhanced emission control during the 2014 APEC, a recent study by Xie et al. (2017) revealed that the total PAH concentrations monitored at an urban site decreased from 70.28 ng/m^3 in the normal period to 52.70 ng/m^3 in the control period. As biomass burning and domestic coal burning are among important sources of PAHs (Xu et al., 2006; Zhang and Tao, 2009), and solid fuels including biomass in the form of wood, dung and crop residues, as well as coal briquette, are widely used for cooking and heating with relatively lower combustion efficiency in rural areas, it is crucial to check if the control measures would also induce the reduction of PAHs in the rural areas. While the organic carbon (OC) concentrations monitored at a site inside the Yanqi Lake Campus of the University of Chinese Academy of Sciences (UCAS) in rural Beijing decreased by 53.8% during the APEC (Liu et al., 2016b) and VOCs observed at this site were also decreased by about 50% during the APEC (Yang et al., 2018), it is not clear whether and to what extent the emission control measures during the APEC have reduced the levels and health risks of toxic components of OC, such as PAHs, in the rural areas of Beijing.

In this study, we collected filter-based $PM_{2.5}$ samples consecutively at a rural site inside the campus of UCAS to the northeast of urban Beijing before, during and after the 2014 APEC, and analyzed chemical compositions of PAHs and other organic components. The purposes of this study are (1) to check if the enhanced control measures during the APEC were also effective in lowering risks of PAHs in ambient air; (2) to track the changes of source contributions to PAHs before, during and after the APEC for implicative policy suggestion in future control of PAHs in ambient air; (3) to study the influence of wintertime heating on levels, compositions and risks of PAHs in ambient air as wintertime heating started immediately after the APEC in Beijing and lasted until March in the next year.

2. Experimental

2.1. Sample collection

The sampling site (40.4°N, 116.7°E; Fig. 1) is on the rooftop of a four-story teaching building (about 16 m above the ground) inside the Yanqi Lake Campus of the UCAS in the Huairou District of Beijing. It is a rural site about 60 km away from the urban center in the northeast of Beijing, and just about 1 km from the main venue of the APEC summit. There are several villages in the neighborhood and no obvious industrial emission sources in the surrounding. A high volume sampler (Tisch Environmental, Inc., USA) was used to collect 24-hr $PM_{2.5}$ samples onto 8 inch × 11 inch quartz fiber filters (Whatman, Mainstone, UK) at a rate of 1.1 $m^3\ min^{-1}$ from 27 October 2014 to 14 January 2015, covering three periods, i.e. before (27/10/2014-2/11/2014), during (3/11/2014-12/11/2014) and after the APEC (13/11/2014-14/1/2015). Hereafter the periods before, during and after are referred to as T1, T2 and T3, respectively. The sample on December 16, 2014 was not collected due to unexpected power failure.

Daily average temperature (T), relative humidity (RH), wind speed (WS), the maximum solar radiation (SR) and atmospheric pressure (P) during the whole campaign were provided from the China Meteorological Data Sharing Service System (http://cdc.nmic.cn/home.do), and boundary layer height (BLH) was calculated using NOAA's READY Archived Meteorology online calculating program (http://ready.arl.noaa.gov/READYamet.php). These meteorological parameters are summarized in Table 1.

2.2. Chemical analysis

A punch (1.5 × 1.0 cm) of each filter was taken to measure OC and element carbon (EC) using the thermo-optical transmittance (TOT) method (NIOSH, 1999) by an OC/EC analyzer (Sunset Laboratory Inc., USA).

A quarter of each filter sample was cut for the analysis of organic compounds in the $PM_{2.5}$. Before ultrasonic solvent extraction, isotope-labeled mixture compounds (tetracosane-d_{50}, napthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12} and levoglucosan-$^{13}C_6$) were spiked into samples as internal standards. Samples were extracted twice with the mixed solvent of dichloride methane (DCM)/hexane (1:1, v/v), and then twice with the mixed solvent DCM/methanol (1:1, v/v). Each extraction time is 10 min, and the total extraction time is 40 min. The extracts of each sample were combined, filtered and concentrated to ~1 mL. Then