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Substantial reductions in ambient PAHs pollution and lives saved as a co-benefit of effective long-term PM_{2.5} pollution controls

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Abstract:

Under great efforts in fighting against serious haze problem of China since 2013, decreasing of air pollutants especially for fine particles ($PM_{2.5}$) has been revealed for several key regions. This study tried to answer whether the reduction of $PM_{2.5}$ -bound polycyclic aromatic hydrocarbons (PAHs) was coincident with $PM_{2.5}$ because of long-term pollution control measures (PCM), and to assess source-oriented health risks associated with inhalation exposure to PAHs. Field measurements were carried out before and after the publishing of local air pollution protection plan for Nanjing, a mega-city in east China. Results indicated that the air quality was substantially improving, with a significant reduction in annual average $PM_{2.5}$ by 34%, and moreover, $PM_{2.5}$ -bound PAHs significantly reduced by 63% ($p<0.001$). The remarkable reduction was mainly attributable to the change of emission sources, compared to the influence of atmospheric circulation patterns, surface meteorological conditions, and atmospheric chemical reaction. Four PAHs sources including coal combustion (CC), petroleum and oil burning (PO), wood burning (WB) and vehicle emission (VE) were identified. On an annual basis, contributions to ambient $PM_{2.5}$ -PAHs from WB, PO, CC and VE sources in the period before the action of control measures were 2.26, 2.20, 1.96 and 5.62 $ng\ m^{-3}$, respectively. They reduced to 1.09, 0.37, 1.31 and 1.77 $ng\ m^{-3}$ for the four source types, with the reduction percentages as 51, 83, 33 and 68%, respectively. The estimated reduction in lifetime lung cancer risk was around 61%. The study that firstly assessed the health effects of PAHs reduction as a co-benefit raised by air PCM sustained for a long period is believed to be applicable and referential for other mega-cities around the world for assessing the benefits of PCM.

Keywords: air pollution control; $PM_{2.5}$ -bound PAHs; source apportionment; exposure risk assessment; source-oriented risk allocation

1. Introduction

China is one of the regions holding the highest atmospheric fine particle ($PM_{2.5}$) concentrations of the world (Donkelaar et al., 2015; Cheng et al., 2016). The Chinese government has been trying to mitigate air pollution for nearly thirty years since the 1980s (Feng and Liao, 2016). In 2012, when the new ambient air quality standard was released, $PM_{2.5}$ pollution has attracted worldwide attention for both scientists and decision makers, especially after the extremely severe and long-lasting haze pollution event occurred in January 2013 (Fu and Chen, 2017; Wang et al., 2017a). In September 2013, the national “Action Plan on Atmospheric Pollution Prevention and Control (APPC)” was promoted, in which the main reduction measures for $PM_{2.5}$ emphasized mainly on coal combustion, industrial manufacturing processes, urban/suburban fugitive dust, cooking activities, vehicle exhaust and fuel quality. It was predicted the implementation of these measures could reduce $PM_{2.5}$ emission by 30% in 2017 relative to 2012 in the Beijing-Tianjin-Hebei region (Cai et al., 2017). It is important and of growing interests to assess the effectiveness of pollution control measures (PCM) on air quality, either for a long-term period (Chen et al., 2016a; Wang et al., 2017a, b), short-term serious air pollution episodes (Xu et al., 2016a; Wang et al., 2017c), or during specific short-term mega-events like APEC (Guo et al., 2016; Wang et al., 2017d). However, to our knowledge, few researchers concerned the role of PCM in potential reductions of toxic chemical components in $PM_{2.5}$, such as heavy metals (Chen et al., 2016b; Li et al., 2016b), black carbon (BC) (Chen et al., 2016c)/elemental carbon (EC) (Wang et al., 2017b) and polycyclic aromatic hydrocarbons (PAHs) (Wang et al., 2011; Xu et al., 2013), which have significant health impacts.

PAHs are a group of organic contaminants formed in nearly all in-complete combustion processes and can be long-range transported in the air (Shrivastava et al., 2017). Carcinogenic and teratogenic PAHs are associated with many adverse health outcomes like increased levels of oxidative stress (Bae et al., 2010), gastroschisis (Lupo et al., 2012), ischaemic heart disease (Burstyn et al., 2005), systemic inflammation (Delfino et al., 2010), adverse health symptoms in survivors of myocardial infarctions (Kraus et al., 2011) and children’s cognitive development (Edwards et al., 2010), obesity (Scinicariello and Buser, 2014) and behavior development (Perera et al., 2012). Since the implementation of APPC from 2013 of China (totally ten types of measures including thirty-five sub-items were published in APPC), sources of $PM_{2.5}$ changed significantly.

For PCM of APPC, coal combustion, industrial processes, cooking activities, biomass burning, and vehicle emissions are in fact the key sources for atmospheric PAHs (Zhang and Tao, 2009). Therefore, it is believed that PAHs sources may exhibit notable changes as well. It is essential to access to what extent the PAHs concentrations and associated health risk that could be reduced when these control measures for PM_{2.5} are implemented at a certain city or region, and it is interesting to clarify whether the decreasing trends of PM_{2.5} and PAHs are same or not. Investigation into the main sources leading to the decreasing of PAHs concentrations and risks and identification roles of influencing factors like meteorological conditions, photochemical reaction and source changes in the variations of PAHs are valuable for the evaluation of PCM. It is also informative for the future researches and policymaking.

Since 2013, the four-year solid efforts to reduce source emissions of air pollutants especially for PM_{2.5} in Nanjing (an industrial city and one of the central megacities located in the Yangtze River Delta (YRD) region) provided a unique opportunity to study the variation in PM_{2.5}-bound PAHs concentrations, as well as the associated risks. A campaign from 2013 to 2016 covered two distinguished periods of March 2013-February 2014 (Period 1) and November 2015-July 2016 (Period 2), that was before and after the AR-APPC (Administrative Rules of Nanjing for further strengthening the APPC) in Nanjing. The AR-APPC was proposed at February 2014 and issued from April 2015. In the APPC of Nanjing published of 2014, six types of control measure were proposed, including optimizing the industrial structure and layout, improving energy structure, strengthening industrial pollution prevention and control, developing green transportation, control fugitive dust, and control pollution from agricultural and human activities (**Table S1**). The initial target of this AR-APPC is to reduce the annual mass concentration of PM_{2.5} in Nanjing by 7%, 13% and 20% in 2015, 2016 and 2017 relative to that in 2013, respectively.

The main objectives of this paper are: (1) to evaluate the reduction of air pollutants and PAHs in Nanjing; (2) to identify the variation in PAHs concentrations, markers, chemical degradation and sources; (3) to interpret the reasons for PAHs variation in view of source emission and meteorological conditions; and (4) to quantify the potential health risk reductions of PAHs and allocated it to various sources. To our knowledge, this is the first and maybe the only research to evaluate the PAHs concentrations of the four years since 2013 in

China. It is helpful to expand the understanding of co-benefits of PCM for PM_{2.5}, which has important enlightenment for regional or city-level assessment of air quality improvement.

2. Method

2.1 Site description and PM_{2.5} sampling

Ambient PM_{2.5} samples were collected on top of a seven-floor building (~20 m above the ground) of Jiangsu Academy of Environmental Sciences. In Period 1, samples were collected during March, June, and September in 2013 and January in 2014, to represent four seasons of spring, summer, autumn and winter. In each season, the sampling lasted for about one week. The sampling flow was ~16.7 L min⁻¹ (Wuhan Tianhong Ltd., China). In Period 2, PM_{2.5} samples were collected on a rooftop of Jiangsu Environmental Monitoring Center (JEC, a six-floor building, about 15 m above the ground) at a flow rate of ~100 L min⁻¹ (TH-150C, Wuhan Tianhong Ltd., China) (Kong et al., 2015a, 2015b) during November of 2015 and January, April and July of 2016. The sampling lasted for about 7-14 days in each season. The two sampling sites are 0.5 km away in the distance, at two close blocks. It is a typical traffic/residential region of urban Nanjing, with residential communities surrounded. There is a steel factory about 15 km to the north of the site and two chemical industry parks about 20 km to the north and northwest. Within the distance from 20 km of the sampling sites, some power plants and industrial plants existed, mostly concentrated in the north, west and south direction. Location of the sampling sites and surrounding major sources are shown in **Figure. 1**.

Each day, the PM_{2.5} sampling lasted for ~24 h (starting from about 08:00) for both the two periods, with quartz fiber filters used. Filters were sealed in aluminum foil bags and weighted by a microbalance (Ohaus Discovery DV214CD) with the balance under controlled environment and stored under -20 °C until laboratory analysis. The detailed treatment method of the filters was listed in Kong et al. (2015a, 2015b).

2.2 Meteorological and air quality data acquisition

The meteorological parameters including ambient temperature (T), relative humidity (RH), wind speed (W_s) and visibility (V_s) were obtained from the Nanjing Meteorological Bureau. The precipitation information was collected from <http://www.wunderground.com/>. The daily averaged mass concentrations of PM_{2.5}, PM₁₀, SO₂, NO₂, CO, and O₃ were collected from the supersite on the rooftop of JEC. The site is the same location for the PM_{2.5} sampling site at Period 2. Organic

carbon (OC) and elemental carbon (EC) were monitored by Sunset Laboratory Semi-Continuous OC/EC Carbon Aerosol Analyzer (Sunset-OCEC, RT-4) in Jiangsu Environmental Center and the corresponding data for sampling periods were provided. For assessing the air quality variation in Nanjing, the daily averaged mass concentrations of PM_{2.5}, PM₁₀, SO₂, NO₂ and CO for nine air quality monitoring sites (the nine sites can be found at <http://106.37.208.233:20035/>) were provided from 1/January/2013 to 30/December/2016. The 8-hours moving average value of O₃ was used for each day.

2.3 Laboratory PAHs analysis and quality controls

Laboratory PAHs analysis was the same as that described in Kong et al. (2015b). Briefly, filters were extracted ultrasonically with dichloromethane, concentrated using a rotary evaporator, and then transferred to a silica gel for cleanup and purification. The elutes were finally concentrated to ~1 mL under a gentle nitrogen stream and then spiked with internal standards prior to instrument analysis. PAHs analyzed by a trace 2000 GC-MS (Thermo Finnigan, USA) operated in selected ion monitoring (SIM) model. Totally 18 PAHs were detected including naphthalene (NaP, 2-ring), acenaphthylene (Acy, 3-ring), acenaphthene (Ace, 3-ring), fluorene (Fl, 3-ring), phenanthrene (Phe, 3-ring), anthracene (Ant, 4-ring), fluoranthene (Flu, 4-ring), pyrene (Pyr, 4-ring), benzo[a]anthracene (BaA, 4-ring), chrysene (Chr, 4-ring), benzo[b]fluoranthene (BbF, 5-ring), benzo[k]fluoranthene (BkF, 5-ring), benzo[a]pyrene (BaP, 5-ring), Benzo(e)pyrene (BeP, 5-ring), dibenz[a,h]anthracene (DBA, 6-ring), indeno[1,2,3-cd]pyrene (InP, 6-ring), benzo[ghi]perylene (BghiP, 6-ring) and coronene (Cor, 7-ring). 2 and 3-ring PAHs are attributed to low molecular weight PAHs (LPAHs). 4-ring PAHs belong to medium molecular weight PAHs (MPAHs) and high molecular weight PAHs (HPAHs) contain 5-, 6- and 7-ring PAHs. Two types of PAHs are also paid attention, named as combustion-derived PAHs (COMPAHs), including Flu, Pyr, Chr, BbF, BkF, BaA, BeP, BaP, InP and BghiP and carcinogenic PAHs (C-PAHs) including Chr, BaA, BbF, BkF, BaP, InP and DBA (Kong et al., 2015b; Wang et al., 2015).

For quality assurance and quality control, field blank and laboratory blank filters were treated following the same procedure in regular samples. Quantification of PAHs was done by the retention times and peak areas of the calibration standards. Internal standard method

was used. Reserve liquid (1000 mg/L) including Perylene-d12, Chrysene-d12, Acenaphthene-d12, Naphthalene-d8 and Phenanthrene-d10 was diluted by n-hexane to 20 mg/L and was stored below 4°C. The recovery test was performed by spiking known amounts of a mixture of PAHs and then the spiked filter was treated the same way as mentioned above. The recoveries of each PAHs were in 81%-93%, and the relative standard deviation was less than 10%. The detection limits for the 18 kinds of PAHs ranged between 3.0-10.0 ng. Results reported were subtracted from blanks, but not corrected by recoveries.

2.4 Back trajectory and mixing layer height calculation

Backward air mass trajectories (72 h) with the starting height of 500 m are calculated using NOAA Air Resource Lab HYSPLIT 4.8 model, driven by the GDAS meteorological dataset (1°×1°) (Wang et al., 2016b; Ye et al., 2017). To achieve the sub-sets of trajectories, the backward trajectories computed every six hour (00:00, 06:00, 12:00 and 18:00) each day were clustered. Clustering process is listed in Hysplit User' s Guide-Version 4. On the NOAA's READY Archived Meteorology online calculating program (<http://ready.arl.noaa.gov/READYamet.php>), the mixing layer height (MLH) was calculated every three hour per day.

2.5 PAHs source apportionment

Positive matrix factorization (PMF) model is adopted to investigate PAHs sources. As a multivariate factor analysis tool, it decomposes a matrix of speciated sample data into factor contribution matrix (G) and factor profile matrix (F), and is expressed as follows:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (1)$$

where x_{ij} is the concentrations of j th PAHs species in the i th sample; g_{ik} is the contribution of the k th source to the i th sample; f_{kj} is the mass fraction of the j th compound from the k th source; e_{ij} is the residual for each sample/species. US Environmental Protection Agency PMF version 5.0 was adopted. Detailed PMF running description was listed in Supplementary file S1 (including Figure S1, Table S2-S4).

2.6 Potential source contribution function and concentration weighted trajectory

Potential source contribution function (PSCF) and concentration weighted trajectory (CWT) were adopted to evaluate the influence of regional PAHs sources and were calculated with the

software Traj-Stat, based on the daily source contributions and backward trajectories. Weighted-PSCF (WPSCF) values were calculated by multiplying PSCF values with a weighting function. A concentration-weighted-trajectory (CWT) model was introduced to add additional information on source contribution levels of different potential regions. WPSCF and weighted CWT (WCWT) were adopted for discussion. The detailed description of PSCF and CWT calculation was listed in **Supplementary file S2**.

2.7 Health risk assessment

Potential health risks of PAHs via inhalational exposure have been widely characterized by calculating incremental lifetime cancer risk (ILCR) as:

$$ILCR = UR_{BaP} \times BaP_{eq} \quad (8)$$

$$BaP_{eq} = \sum_{i=1}^n (C_i \times TEF_i) \quad (9)$$

where UR_{BaP} is the unit cancer risk factor of BaP, as 8.7×10^{-5} per ng m^{-3} (Callén et al., 2014; Chen et al., 2016a; Yu et al., 2016; Pereira et al., 2017); C_i is the concentration of PAHs species (ng m^{-3}); BaP_{eq} is the BaP equivalent concentration (ng m^{-3}), which is calculated by multiplying the C_i with their corresponding toxic equivalent factor (TEF_i). The TEF_i was selected as 0.001 for NaP, Acy, Ace, Fl, Phe, Flu and Pyr, 0.01 for Ant, Chr, BeP and BghiP, 0.1 for BaA, BbF, BkF, and InP, and 1 for BaP and DBA (Khan et al., 2015; Zhu et al., 2015; Chen et al., 2017).

3 Results and discussion

3.1 Criteria air pollutants and meteorological conditions before and after the AR-APPC

In **Table 1**, there were no significant differences in average ambient temperature, Ws, RH and MLH between the two periods, while visibility significantly decreased by 34% ($p < 0.001$) in Period 2. The average concentrations of $\text{PM}_{2.5}$, PM_{10} and O_3 for the Period 2 significantly reduced by 34% ($p < 0.001$), 34% ($p < 0.001$) and 18% ($p < 0.05$), respectively, in comparison with those for Period 1 (**Table 2**). There were no significant changes of the other criteria gaseous pollutants like CO, SO_2 , and NO_2 . From the evaluation report on air quality published by Ministry of Environmental Protection of China, reduction of $\text{PM}_{2.5}$ could be clearly found for YRD region from 2013 to 2016 (**Figure S2**). As expected, the average annual mass concentrations of $\text{PM}_{2.5}$, PM_{10} , SO_2 , and NO_2 in Nanjing were all decreasing

gradually from 2013 to 2016, by 38%, 38%, 50% and 20%, respectively (**Figure 2**). It has successfully achieved the goal of 20% reduction for PM_{2.5} proposed in the AR-APPC. The reduction rate of PM_{2.5} for the whole Nanjing was similar with that for the given site and sampling periods of this study. Though the decreasing rate was high to 59% for the PM_{2.5} in the winter season of the two periods, PM_{2.5} concentration in winter was still highest as 72.5±37.7 µg m⁻³ in Period 2. It indicated that the current regulations for winter should be enforced more rigorously, exactly and beneficially.

3.2 Comparison of ambient PAHs before and after the AR-APPC

As shown in **Figure. 3**, the overall averaged PAHs concentrations were significantly reduced by 63% ($p<0.001$) at Period 2, higher than that of 34% for PM_{2.5} mass concentrations. The averaged COMPAHs and C-PAHs exhibited concentration reductions of 55% and 60% ($p<0.001$). Significant reductions were also observed for the averaged concentrations of each PAHs individual, ranging from 45% to 87% ($p<0.01$). To eliminate the influence of meteorological conditions, PAHs mass concentration was normalized by PM_{2.5} concentration (Anastasopoulos et al., 2012; Kong et al., 2015b; Wang et al., 2015) and Ws (Wang et al., 2016a). Ratios of PAHs/PM_{2.5} and PAHs/Ws were statistically lower for Period 2, with the decreasing rates of 82% ($p<0.01$) and 57% ($p<0.001$), respectively. This confirmed the substantial decrease of PAHs for Period 2 and the decreasing rate of PAHs was larger than that of PM_{2.5}. It indicated that the PCM for PM_{2.5} had played a positive role in PAHs reduction. Now the annual averaged PAHs concentrations of Nanjing (4.61±3.29 ng m⁻³) were comparable to the reported levels in Thessaloniki (4.66 ng m⁻³) (Saffari et al., 2013), Hong Kong (4.59 ng m⁻³) (Ma et al., 2016) and Shanghai (6.49 ng m⁻³) (Wang et al., 2016b) and were lower than most of those in other cities as compiled in **Table S5**.

As the most carcinogenic PAHs, the averaged concentrations of BaP decreased by 57% ($P<0.001$) for Period 2 when compared with that of Period 1 (**Table 3**). The ambient BaP in urban Nanjing was continuously decreasing during the last two decades. The averaged BaP in 2001 was 8.05 ng m⁻³ (September, an urban site) (Yang et al., 2005), 4.17 ng m⁻³ in 2001/2002 (five urban sites, whole year) (Wang et al., 2006a), 3.83 ng m⁻³ in 2004 (summer and winter, an urban site) (Wang et al., 2007), 3.73 ng m⁻³ in 2009/2010 (from November 2009 to July 2010, one urban and one suburban site) (He et al., 2014), 0.65 ng m⁻³ in 2013/2014 (this study) and 0.27 ng m⁻³ in

2015/2016 (this study), respectively. The annual averaged guideline value of BaP recommended by the World Health Organization and European Union was 1 ng m^{-3} (Ravindra et al., 2008; Wang et al., 2017d). The annual BaP concentration of Nanjing is now below the guideline value. From 2001/2002 to 2009/2010, the variation of BaP is little, decreased by 10.5%. While from 2009/2010 to 2013/2014, obvious decreasing by 83% was found. We can deduce that the reduction of PAHs may be a longer-term trend in the first decade. While after 2009/2010, the reduction rate accelerated. There should be other forcing favored it, which should be the proposed PCM for air pollutants after 2013. The effective PAHs reduction along with the air pollution control strategies during short-term mega-events was also reported (Wang et al., 2011; Xu et al., 2013; Li et al., 2016c).

From Table 3, clear seasonal variations were observed, with highest PAHs concentrations in winter and lowest concentrations in summer. The winter/summer ratios of PAHs were averaged as 3.3 and 4.7 for Period 1 and Period 2, respectively. PAHs/PM_{2.5} exhibited the similar winter and summer variation. This seasonal variation pattern has been widely reported in former studies (Marchand et al., 2004; Wang et al., 2006b; Akyüz and Çabuk, 2008; Guo et al., 2009; Martellini et al., 2012; Mancilla et al., 2016; Yu et al., 2016). Following reasons could explain the seasonal variations in PAHs in this study: (1) additional emissions in winter from residential heating with coal and wood as fuels in North China (Wang et al., 2006b; Chen et al., 2016a; Lin et al., 2015; Lv et al., 2016), which can transport and affect air quality of Nanjing (detailed discussion in Section 3.4.2 and 3.4.3); (2) reduced atmospheric dispersion due to inversion and lower MLH in winter (as 312 ± 124 and 445 ± 187 m for winter of the two periods, respectively); (3) enhanced partition to particles under lower temperature; (4) less pronounced photochemical degradation processes in winter as low ambient temperature (discussion in Section 3.3.2) (Marchand et al., 2004; Chen et al., 2016a).

The change existed in not only total PAHs mass concentration but also the PAHs composition profile. It can be observed that the overall averaged mass percentage of LPAHs (2 and 3 ring PAHs) decreased from 25% to 14% (decreased by 44%, $p < 0.001$), the overall averaged MPAHs (4 ring PAHs) increased from 22% to 32% (increased by 44%, $p < 0.001$) and the HPAHs (5, 6 and 7 ring PAHs) varied a little bit (from 53% to 54%) (**Figure 3**). Generally, higher LPAHs concentration was related to non-combusted petroleum emission

and HPAHs were mainly from fossil fuel combustions (He et al., 2014). It can be inferred that petroleum emission of PAHs reduced after the AR-APPC.

3.3 Difference in meteorological conditions, atmospheric chemical degradation and sources between the two periods

3.3.1 The role of circulation patterns, surface meteorological parameters and long-range transportation

The circulation patterns can influence the air quality through transport pathways and determine local meteorology (Xu et al., 2016a). The circulation patterns (seasonal mean geopotential height and wind vectors at 10 m above sea level) for four seasons of the two periods were illustrated in **Figure S3**. At first glance, the circulation patterns of the two periods were similar for all the four seasons. In autumn and winter, Nanjing was under control of Siberian high pressure and it was stronger for Period 2 than that of Period 1, which was the typical features of East Asian winter (Kim et al., 2016). The main backward trajectory clusters of the four seasons were also similar for the two periods (**Figure S4**), with north and northwest trajectories dominated in winter and autumn. Thus, the air pollutants at Nanjing were easily affected by the upstream transport at the northwest direction and the impact was more profound in Period 2 at the two seasons. It should be noted that in later autumn and winter period, the North China area exhibits high coal consumptions (**Figure S5**) and high emission densities of many air pollutants from biomass burning (Zhou et al., 2017). Meanwhile, weak negative correlations were found between PAHs and temperature and MLH, especially for higher rings PAHs (**Table S6, Figure S6**). As shown in Figure S6, high rings PAHs also exhibited weak positive correlations (most P values lower than 0.01) with SO₂, NO₂, OC, and EC, that originated mainly from combustion sources (Thornhill et al., 2008; Mancilla et al., 2016). All these can verify the higher PAHs concentrations in winter. Furthermore, above analysis highlighted the importance of coal and biomass burning in north China at cold periods on affecting the PAHs concentrations in Nanjing. For yearly variation, as there were no significant differences in temperature and MLH between the two periods, the role of them in explaining PAHs reduction may be limited.

3.3.2 The role of atmospheric chemical degradation and particle coatings

During the atmospheric transportation, PAHs compounds are exposed to oxidants, such as O₃, OH, NO₂ and nitric acid, which degrade PAHs and thereby change the PAHs compositions and

concentrations (Thornhill et al., 2008; Dvorská et al., 2011; Gao et al., 2011) and the reaction rate is depended on the particle compositions and meteorological factors. BaP/BeP ratio is often used as an indicator of the aging process, as BaP degradation is typically faster than BeP in the air (Ravindra et al., 2008; Pinxteren et al., 2009). In this study, BaP/BeP ratio significantly increased from 0.45 ± 0.15 (Period 1) to 0.70 ± 0.15 (Period 2) ($p<0.001$). This may suggest that PAHs at Period 1 were more aged than those of Period 2, which was consistent with a higher O_3 concentration of Period 1. This may further indicate that the difference in the “initial” ambient PAHs level between the two periods could be even higher than the reduction calculated based on observed concentration now.

In some previous studies, PAHs/EC ratio was suggested to indicate the photochemical degradation of PAHs. Kong et al. (2012) systematically investigated the emission of PAHs and inorganic chemical components in $PM_{2.5}$ of various sources and the PAHs/EC ratios for different sources were shown in **Figure S7**. For all the sources except for gasoline vehicle emission (PAHs/EC ratio as 0.19), the PAHs/EC ratios ranged between 7.2-422 $ng\ \mu g^{-1}$, which were much higher than the ratios of ambient air of this study (3.31 ± 2.34 for Period 1 and 1.20 ± 0.72 for Period 2), further verifying the aging of PAHs. The PAHs/EC ratio is typically low under high O_3 concentrations and high temperature due to stronger photo-degradation of PAHs (**Figure S8**). In this study, although the O_3 concentrations were significantly decreased at Period 2, the PAHs/EC values did not exhibit higher values as expected. Conversely, it was significantly lower than that of Period 1 ($P<0.001$). This appears to say that PAHs from the Period 2 were more aged compared to those in Period 1. One reason is that source profiles were believed to be changed from the Period 1 to Period 2, thus a direct comparison of the overall average PAHs/EC ratios may be inappropriate here to indicate the aging degree between the two studied periods. Decreased emission of PAHs from oil evaporation (which do not contribute to EC) as pollution control at Period 2 can lead to lower PAHs/EC ratio, and increased relatively contributions from vehicle emissions would lower the ratio as well. In fact, even though the sources were not changed or similar, a simple comparison based solely on the PAHs/EC ratio and/or their dependence on ambient O_3 may be biased and associated with high uncertainty, because: (1) O_3 can only partly explain the PAHs losses and the role of OH and other oxidants (like NO_2) in PAHs photolysis can also

dominate the PAHs losses (Marchand et al., 2004); (2) the coating effects of fresh particles with secondary aerosols which can shield PAHs from chemical degradation (Thornhill et al., 2008; Shrivastava et al., 2017). Thornhill et al. (2008) used a criterion of $(\text{PAHs}+10)/\text{BC}>11 \text{ ng } \mu\text{g}^{-1}$ to identify data points representing uncoated particles. In this study, the values of $(\text{PAHs}+10)/\text{EC}$ were 6.16 ± 2.77 and $4.00\pm1.19 \text{ ng } \mu\text{g}^{-1}$ for Period 1 and Period 2, respectively, indicating the particle phase PAHs were both coated by secondary aerosols for the two periods.

Therefore, it is believed that the measured PAHs for both the two periods were aged. However, it is difficult to quantitatively evaluate and compare the degree of photochemical aging in the present study. Considering the comparable O_3 and NO_2 concentrations and similar meteorological conditions of the two periods, it is believed the photochemical degradation played a limited role in explaining the significant reduction of averaged mass concentrations of PAHs from Period 1 to Period 2 in this study.

3.3.3 The role of pollution control measures

In China, the PCM is initially to reduce the regular air pollutants of CO , SO_2 , NO_x , $\text{PM}_{2.5}$, PM_{10} , and VOCs. The higher reduction rate of $\text{PM}_{2.5}$ associated PAHs than $\text{PM}_{2.5}$ itself observed in this study indicated that effective controls could have a positive influence on ambient PAHs pollution. According to the report of Nanjing Environmental Protection Bureau, the main sources of $\text{PM}_{2.5}$ in Nanjing were coal combustion (27.4%), industrial production (19.0%), vehicle emission (24.6%), fugitive dust (14.1%) and other sources (14.9%) in 2014 (<http://jsnews2.jschina.com.cn/system/2015/04/30/024548067.shtml>). A series of emission sources have been controlled or improved after 2015 (Table S7). The total coal consumption was controlled to below 30 million tons. The gasoline, gasoline oil and solvent oil consumption amount decreased by 15.6%, 8.6% and 54.1% in 2015 when compared with those in 2013. The use of clean energy like coal gas and natural gas increased by 24.3% and 7.4%, respectively. Meanwhile, many improving measures were adopted for coal and oil burning, industrial processes and domestic activities, etc. These all lead to the reduction of $\text{PM}_{2.5}$ and also associated PAHs. Sources of $\text{PM}_{2.5}$ could be more complex than those of PAHs. The significant weak positive correlations between high ring PAHs (4-7 rings) and SO_2 , NO_2 , OC and EC (Figure S6) indicating that there may exist similar sources of PAHs with the precursors and key components of $\text{PM}_{2.5}$. However, their sources were not the same. No significant correlations were found for 2 and 3 ring

PAHs with SO₂, NO₂, OC, and EC, suggesting different sources or formation pathways. Therefore, the control measures of PM_{2.5} and its precursors may not play the same role for PAHs reduction of different rings, which can explain the difference in reduction rate of PM_{2.5} (34%) and PAHs (63%) in this study.

PAHs markers are powerful to identify and attribute emission sources (Mancilla et al., 2016). Typical PAH markers were Chr, BkF, Flu, Pyr, BaA and BaP for coal burning (Bourotte et al., 2005; Ravindra et al., 2008; Teixeira et al., 2015); Acy, Ant, Phe, Flu, Pyr, Chr, BbF and BkF for wood burning (Marchand et al., 2004; Bourotte et al., 2005; Teixeira et al., 2015); BghiP, Cor and InP for gasoline emission (Pinxteren et al., 2009; He et al., 2014; Shen et al., 2014; Pereira et al., 2017); Flu, Pyr, Chr, BbF, BkF and BeP for diesel emission (Marchand et al., 2004; Bourotte et al., 2005; He et al., 2014; Mancilla et al., 2016); Pyr, BaP and BaA for natural gas combustion (Bourotte et al., 2005) and Pyr, Flu and Phe for incineration (Ravindra et al., 2008). We summed the concentrations of these markers and adjusted to PM_{2.5} mass concentration for each source type of the two periods. The calculated ratios were significantly reduced for sources including wood burning (Acy, Ant, Phe, Flu, Pyr, Chr, BbF and BkF) ($p < 0.05$), gasoline vehicle emission (BghiP, Cor and InP) ($p < 0.01$) and diesel vehicle emission (Flu, Pyr, Chr, BbF, BkF and BeP) ($p < 0.05$). This indicated that the PCM played an effective role in reducing the contributions of wood burning and vehicle emission to PAHs in Nanjing. The open biomass burning was strictly monitored and forbidden in recent years. For coal combustion, many efforts have been made mainly for industrial activities in China, while the pollutants control from domestic coal burning was still limited, which can contribute 10.7% of PAHs emission of China (Zhang and Tao, 2009). For vehicle emission, the improved fuel quality (lower sulfur and aromatic content) (Ravindra et al., 2008), the adoption of catalytic converters (Ravindra et al., 2008), the adoption of clean energy vehicles, eliminating the vehicles which cannot meet the higher emission standards and so on all make fundamental contributions to the PAHs reduction. In short, along with the economic and social development, though more energies are consumed, the PAHs concentrations can be effectively reduced with comprehensive pollution control measures for PM_{2.5}.

To sum up, as the similarity in the circulation patterns and surface meteorological parameters for the two sampling periods, the observed significant reduction in ambient PAHs levels of Nanjing was mainly associated with the source change raised by strict and effective PCM.

3.4 PAHs source apportionment and variations between two periods

3.4.1 Diagnostic ratios

Diagnostic PAHs ratios are a useful tool to distinguish their sources qualitatively (Guillon et al., 2013). Four widely used ratios including Flu/(Flu+Pyr), BaA/(BaA+Chr), Ant/(Ant+Phe) and InP/(InP+BghiP) (Ravindra et al., 2008; Wang et al., 2011; Lin et al., 2015; Li et al., 2016a; Mancilla et al., 2016; Yu et al., 2016) were adopted in **Figure 4**, with the indicative sources for different values summarized. The values of Flu/(Flu+Pyr) and InP/(InP+BghiP) distributed mainly within 0.5-0.6 and 0.4-0.6, reflecting the marked contributions of coal and biomass burning and petroleum combustion. For BaA/(BaA+Chr), the values ranged between 0.11-0.5, covering the sources of petrogenic, coal combustion, vehicle emission, and biomass burning. The values of Ant/(Ant+Phe) (varying in 0.06-0.34) highlighted the importance of wood burning and petroleum. Significant differences were only found for Ant/(Ant+Phe) ratios, decreasing from Period 1 (0.20 ± 0.07) to Period 2 (0.14 ± 0.05) ($P < 0.001$). However, the ratios of the two periods still indicated the similar sources. It also proposed the cautions that atmospheric reactivity can modify the atmospheric PAHs levels and thus the ratios between PAHs (Ravindra et al., 2008; Mancilla et al., 2016).

3.4.2 Source apportionment using PMF

To better explain the variation in PAHs sources of the two periods, the PMF modeling was performed with the source profiles and contributions shown in **Figure 5**. Oil combustion was associated with the high concentration of the more volatile PAHs such as Fl, Flu, and Pyr, along with moderate levels of the higher molecular weight PAHs, i.e. BbF and InP (Ravindra et al., 2008). Acy, Ace, Fl, Phe, and Ant were typical markers for volatilization of crude oil and petroleum products (Wang et al., 2016b). Therefore, a mixed source of petroleum and oil burning source (PO) was confirmed in this study. PO was also resolved by Chen et al. (2016c), with high loadings on Flu, Pyr and moderate loadings on Pyr, Chr, BeP, BaP, and BghiP. According to the markers listed in section 3.3.3 and the resolved source profiles, totally four sources were identified as coal combustion (CC), PO, wood burning (WB) and vehicle emission (VE), accounting for

18.7%, 26.1%, 15.3% and 39.8% of total PAHs at Period 1, respectively (**Figure 5a**). The corresponding contributions were 24.2%, 15.7%, 24.4% and 35.7%, respectively at Period 2 (**Figure 5b**).

Overall, the PAHs concentrations contributed from the four types of sources all reduced in Period 2, by 83%, 68%, 51% and 33% for PO, VE, WB, and CC, respectively (**Figure 5c**). The decreased absolute contributions of them reflected the PCM was effective in reducing PAHs from the sources. Though great efforts have been done by the local government for controlling coal and wood/biomass burning in Nanjing, the long-range transport of the two types of sources from North China partly offset these efforts. It can explain the fewer reduction rates of WB and CC when compared with those for PO and VE. From **Table S8**, it can be found that in the cities of North China, the contributions of CC were always at a high level, for example, as 38-40% in Zhengzhou (Wang et al., 2015; Wang et al., 2017b) and 52.1% in Taiyuan (Li et al., 2016a). The contributions of wood/biomass burning at northern Chinese cities ranged in 12% (Zhengzhou) (Wang et al., 2015)-37.1% (Xi'an) (Wang et al., 2016b). The contributions of PO as 27% and 41% (for marine vessels) were reported for coastal sites in Taiwan (Chen et al., 2016a) and Hong Kong (Ma et al., 2016), respectively. The VE contribution to PAHs in this study was similar to that in Shanghai (43%) (Liu et al., 2017). Though the PAHs sources differed in various studies, varying with space and time, the PAHs sources in Nanjing exhibited mixture properties, characterized by contributions from local/regional, inland/coastal and southern/northern of China.

Clearly, seasonal variation of the four types of source contributions is illustrated in **Figure 6**. The contributions from WB (5.57 ± 3.21 and 1.86 ± 0.91 ng m⁻³ for Period 1 and Period 2) and CC (3.26 ± 1.49 and 2.81 ± 1.86 ng m⁻³ for Period 1 and Period 2) both exhibited highest values in winter, which could be related to the additional fuels combustion for heating purpose. The vehicle emission also contributed most in winter (9.74 ± 5.36 and 3.04 ± 1.61 ng m⁻³ for Period 1 and Period 2), implying the enhanced emission at cold start mode. The extreme higher contribution of VE at Spring of Period 1 may be related to the lowest temperature at that period as 8.8 ± 3.0 °C. For PO emission, it held slightly higher contributions in summer owing to more evaporation under the higher ambient temperature.

The seasonal variation in source contributions all favored well to the seasonal variation of PAHs concentrations as discussed above.

3.4.3 Source region analysis

As the results of WPSCF in **Figure 7**, the source regions with high probabilities of WB were mainly located at the west, northwest and north side of Nanjing and the regions extending to a larger area at Period 2. For CC, the source regions at Period 1 located mainly at the southwest-northeast directions, while they changed to the north and northwest directions at Period 2. The variation in source regions for WB and CC highlighted the importance of the domestic coal and wood burning for heating. For VE, the main source regions were on the southeast side, surrounding Nanjing at Period 1 and then changed to the northwest, north and northeastern of China in Period 2. For PO, the source regions at Period 1 were mainly concentrated in the lower reaches of the Yangtze River and the offshore sea area; while in Period 2, the main source regions moved to the middle reaches of the Yangtze River, the coastal area of PRD and near offshore areas. These regions all hold intensive emissions from both ocean (Fan et al., 2016) and inland vessels/ships (Song, 2015). The geographic origins of the four sources were consistent for weighted concentration weighted trajectory (WCWT) analysis (**Figure 8**). Higher contributions of WB and CC were found at Period 2 from north China. Lower level contributions of PO and VE at Period 2 were also verified, owing to the shrinkage of the regions with higher WCWT values.

To conclude, after the effective control of air pollutants, the sources of PAHs at Nanjing at Period 2 were mainly influenced by the regional transport of CC and WB from North China especially for domestic use, local+regional transports of ocean and inland vessels/ships and local+regional transports of vehicle emission from North China. It indicated the control of WB, CC and VE should be more strictly in North China. To obtain the local/regional contributions of various sources, a quantitative research is needed based on an accurate emission inventory in the future.

3.5 Reduced health risks of PAHs and source allocation

Through the effective source control, the PAHs obviously reduced from Period 1 to Period 2 in Nanjing. It suggested that the human health risks also decreased. By adopting the simple point-estimate approach (Wang et al., 2011), the estimated ILCR for Period 1 and Period 2 were 4.13×10^{-4} and 1.07×10^{-5} , respectively (**Figure 9**). Thus, the overall cancer risks due to inhalation

exposure to PAHs reduced significantly by 61% for Period 2 ($p<0.001$). However, it still exceeded the acceptance limit of cancer risk (10^{-6}) (Chen et al., 2016a; Lv et al., 2016). Reduced cancer risks were also found for the periods with mega-events, such as the APEC meeting (Xie et al., 2017). It should be noted that uncertainties are inherent in cancer risk assessment, as a lack of knowledge about the factors affecting exposure or toxicity assessment (Hong et al., 2016).

To interpret the risk reduction, contributions of the four types of sources were calculated by PMF model as listed in **Figure 10**. CC dominated the contributions to ILCR, similar for the two periods, as about 52%. The contributions to ILCR of PO obviously reduced from 23.5% to 4.5% from Period 1 to Period 2; while the contributions of WB and VE increased from 1.75% to 13.7% and from 22.3% to 29.9%. Though still, the dominant sources were coal combustion and vehicle emission, their relative contribution varied in mass concentration and incremental cancer risks. Source pollution controls should not only focus on mass pollution level, but also those having larger toxic and contributing significantly to the health impacts.

Health risks associated with exposure to other pollutants like CO, SO₂, NO_x, O₃, PM_{2.5} and associated toxic components (heavy metals, BC, etc.) are interesting and hot topics. The present study only evaluated risks associated with PM_{2.5}-bound PAHs exposure. When taking other pollutants into account, health benefits received from the effective PCMs could be more significant. This is worthy to be investigated in the future, with big datasets (including air pollutants, personal exposure monitoring data, human disease and meteorological parameters) collected and dose-equivalence relationships for different chemicals with health effects clarified.

4 Conclusion

As a non-routine monitored pollutants, PAHs were focused in a four-year study in Nanjing to answer whether the air pollution control measures (PCM) can substantially affect the PAHs concentrations, in view of that PAHs can also be impacted by meteorological parameters and atmospheric chemical reaction. Two sampling campaigns in March 2013-January 2014 (Period 1) and November 2015-July 2016 (Period 2) just before and after the local air pollution plan published in April 2014 were completed.

In Period 2, the average concentrations of $PM_{2.5}$ significantly reduced by 34% of that for Period 1. The total PAHs concentrations exhibited a significantly higher reduction rate as 63% than $PM_{2.5}$, indicating the PCM for $PM_{2.5}$ have played a positive role in PAHs reduction unexpectedly. The nonlinear reduction of $PM_{2.5}$ and associated PAHs was related to their different sources and the different effects of PCM played on $PM_{2.5}$ and its precursors as well as the different ring of PAHs. The similarity in atmospheric circulation patterns and no obvious differences in meteorological parameters indicated that the main reason for controlling PAHs reduction was the source variation.

Diagnostic ratios and PMF modeling identified four sources, as coal combustion (CC), petroleum and oil burning (PO), wood burning (WB) and vehicle emission (VE). Contributions from all these four source types to ambient PAHs had substantially decreased, from 33% to 83%. The reduction percentages were more notable for VE and PO, compared to the reduction percentages in CC and WB. A co-benefit of cancer risk reduction by 61% was obtained. The cancer risk was still higher than 10^{-6} , with CC dominated the contributions as about 52%. In Nanjing, as the dominated contributions of coal burning and vehicle emission to atmospheric PAHs, effective emission mitigation strategies of PAHs should be developed from both local and regional views. Meanwhile, the obvious seasonal variation in PAHs concentrations and source contributions and potential source regions highlighted the importance of further efforts on the reduction of coal and wood burning in North China at a heating period.

This study provides useful data and new insights for assessing the effects of air pollution control measures, from the view of human health, not only just from the reductions of routine air pollutants. The outcomes could be important to regional air quality management and decision makers. The analysis and main findings here are also applicable and helpful for other areas around the world.

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Appendix

Materials associated with this manuscript is provided in the supporting file available free of charge
via the internet.

Data are available on request to Shaofei Kong (kongshaofei@cug.edu.cn).

Competing interests

The authors declare that there is no conflict of interest.

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