Submicron aerosols during the Beijing Asia–Pacific Economic Cooperation conference in 2014

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HIGHLIGHTS
- Submicron aerosols decreased by 63% during the APEC period.
- The contributions of nitrate to PM$_1$ and light extinction decreased substantially.
- The concentration of PAHs decreased from 29 to 21 ng m$^{-3}$.
- Vehicles and industry are important PM$_1$ pollution sources in Beijing.

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Abstract
Approximately 30%–40% of industrial practices and 50% of vehicles in operation were limited in Beijing and its surroundings regions during the Beijing Asia–Pacific Economic Cooperation (APEC) conference in 2014. Compared with values obtained prior to the APEC conference, the atmospheric concentration of submicron aerosol particles (PM$_1$) decreased from 101 to 36.9 ng m$^{-3}$, or 63%. Of all the inorganic species and black carbon present, the concentrations of nitrate to the total concentration of PM$_1$ decreased the most in terms of both mass concentration, from 25.5 to 7.1 mg m$^{-3}$, and relative contribution, from 21% to 14%. In addition, both sulfate and ammonium decreased substantially by 9.5 and 8.5 mg m$^{-3}$, respectively. Accordingly, the relative contributions of ammonium nitrate and ammonium sulfate to light extinction decreased by 10% and 5%, respectively, as a result of the pollution control measures implemented during that period. In addition, polycyclic aromatic hydrocarbons in vehicle emissions were reduced significantly.

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1. Introduction

Fine particulate matter, also known as aerosol particles, affects human health, air quality and visibility, and the Earth’s climate (Huang et al., 2008; IPCC, 2013; Minguillón et al., 2015; Parworth et al., 2015). The Intergovernmental Panel on Climate Change (2013) noted that despite the extensive research that has been performed in recent decades, substantial uncertainty in the knowledge of the climatic effects of aerosols remains.

In recent years, the frequency of substantial fine particulate matter pollution events has increased in Beijing, China. The city has a residential population of 21.1 million; in 2013, the total amount of motor vehicles in operation exceeded 5.4 million, and energy consumption was equivalent to 73.5 million tons of standard coal (Beijing Statistical Yearbook, 2014). Many studies have determined that vehicle and industrial pollution, such as that from power plants, steel mills, cement mills, and the petrochemical industry, are two of the most important sources of fine particulate matter in Beijing (Guo et al., 2014; Lang et al., 2012; Mijling et al., 2009; Song et al., 2008; Sun et al., 2006; Zhao et al., 2013).

Strict controls of air pollutant emissions were enacted to ensure good air quality for the 2014 Asia–Pacific Economic Cooperation (APEC) conference; these include a series of emission control measures (APEC–ECMs) that were enforced in Beijing and its surrounding municipalities and provinces, including Tianjin, Hebei, Inner Mongolia, Shanxi, and Shandong. Consequently, more than 460 businesses in Beijing known to have high emissions were required to stop or limit production during 3–12 November, 2014. Moreover, the number of private vehicles in
operation during the same period was reduced by 50% through an odd/even number plate rule. Further, 9298 enterprises were suspended, 3900 enterprises were ordered to limit production, and more than 40,000 construction sites were shut down in all six municipalities and provinces. In addition, various outdoor burning practices, such as that for straw, garbage, and tree leaves, were forbidden in these areas. As a result, the air quality during all days of the APEC period was classified as “excellent” with an air quality index (API) of 0–50 (Huang et al., 2014); the API on the anomalous day, 101–200, was classified as “light pollution”. Beijing residents refer to the days during the APEC conference as “APEC blue” days in reference to the good visibility and blue sky observed during that period.

In the present study, the characteristics of submicron aerosol particles (PM$_1$), their variations, and their effects on light extinction during the APEC conference in Beijing are evaluated. In addition, the variations and sources of polycyclic aromatic hydrocarbons (PAHs) are examined.

2. Experimental methods

Submicron aerosols were measured in situ from 17 October to 12 November, 2014, at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences. The measurement period covered two sub-periods, in the first there were no APEC–ECMs in place (17 October to 2 November; before APEC) and, during the second sub-period, the APEC–ECMs were being enforced (3 November to 12 November; during APEC).

2.1. Study site

The observation site is located in the region north of third Ring Road and north of fourth Ring Road in Beijing (39°58′28″N, 116°22′16″E; Fig. S1); This area is approximately 1 km from third Ring Road, 200 m west of Badaling Highway, which runs north–south, and 50 m south of Beitucheng West Road, which runs east–west. Sampling was conducted on the roof of a two-story building ~10 m high.

2.2. Instrumentation and methods

The size-resolved composition of non-refractory PM$_1$ was measured by using a high-resolution time-of-flight aerosol mass spectrometer (HR–ToF–AMS; Aerodyne Research Inc., Billerica, MA, USA; DeCarlo et al., 2006). A multi-angle absorption photometer (MAAP; model 5012, Thermo Electron Corporation) was used to measure the black carbon (BC) component of PM$_1$. The MAAP (Petzold and Schauer, 2004) was operated at an incident light wavelength of 670 nm on the principle of light attenuation due to absorption by aerosols deposited on a quartz–fiber filter. The visibility was measured by using a visibility sensor (Belfort 6000, USA), which consisted of a transmitter, receiver and controller, and had a range of 10 m–50 km (BelfortLi et al., 2013). Meteorological data were also obtained from an automatic meteorological observation instrument (Milos520, Vaisala, Finland).

The details of HR–ToF–AMS operation and data analysis have been reported elsewhere (Zhang et al., 2014). The standard ToF–AMS data analysis software packages, SQUIRREL version 1.50 and PIKA version 1.09, both downloaded from the ToF-AMS-Resources webpage (http://cires.colorado.edu/jimenez-group/ToFAMSResources), were used to generate unit and high-resolution mass spectra from the V-mode and W-mode data, respectively. Middlebrook et al. (2012) suggested that the collection efficiency (CE) should be composition-dependent with influences of high aerosol acidity, high relative humidity, and high ammonium nitrate mass fraction (ANMF, >0.4). In this study, a silica gel diffusion dryer was introduced to keep the relative humidity in the sampling line below 40%, and the aerosol was close to being neutralized (Fig. S2). Therefore, aerosol acidity and relative humidity are expected to have minor effects on the CE. However, the ANMF at times was higher than 0.4 (Fig. S3). Therefore, the variable CEs based on a higher ANMF condition were applied (i.e., $CE_{dry} = \max(0.45, 0.0833 + 0.9167 \times ANMF)$). In addition, positive matrix factorization (PMF) analyses (Paatero and Tapper, 1994) were performed on the high-resolution mass spectra data, that is to say the ion-spectiated W-mode spectra, by using the PMF Evaluation Toolkit (PET) v2.05 (Ulbrich et al., 2009) to interpret the organic aerosol (OA) constituents within PM$_1$. The literature of Ulbrich et al. (2009) and Zhang et al. (2014) present the technical details of PMF analysis. In the present study, we considered only ions up to m/z 100 because larger ions had a low signal-to-noise ratio (S/N) and were more biased due to insufficient mass resolution. Isotopes were systematically constrained in PIKA but were removed from the data and error matrices because their presence would have given excess weight to the parent ions in the PMF analysis (Setyan et al., 2012). Ions with a S/N ratio <0.2 were removed from the high-resolution mass spectrometer (HRMS) data and error matrices before PMF analysis. The “good” ions with S/N between 0.2 and 2 were downweighted by increasing their errors by a factor of 2 (Paatero and Hoppyle, 2003; Ulbrich et al., 2009).

Upon comparison of the mass spectral profiles, the optimal solution for this analysis was determined to be the five-factor solution including low-volatility oxygenated OA (LV–OOA), semi-volatile oxygenated OA (SV–OOA), cooking emission-related OA (COA), hydrocarbon-like OA (HOA) and biomass burning OA (BBOA). The PMF diagnostic discussion and related plots are given in the supplementary material (Part A and Figs. S4–S7).

Light extinction of the PM$_1$ constituents was estimated by using a modification of the Interagency Monitoring of Protected Visual Environments (IMPROVE) method, the details of which can be found in Wang et al. (2015). All of the data presented here are reported at ambient temperature and pressure conditions in Beijing Standard Time.

3. Results and discussion

3.1. Chemical composition and organic aerosol factors

The time-resolved variation in the mass concentrations of all species of PM$_1$, including organics, nitrate, sulfate, ammonium, chloride, and BC, showed that a series of pollution events occurred between 17 October and 12 November, 2014 (Fig. 1a). These pollution events displayed strong asymmetric “sawtooth cycles” in which the cycles began after a cold front, rose progressively in approximately three to five days, and then fell rapidly with the next cold front (Jia et al., 2008). The highest PM$_1$ mass concentration during the entire period was 312 μg m$^{-3}$, and the mean mass concentration was 75.7 ± 69.3 μg m$^{-3}$.

Although two or three pollution events occurred during the APEC conference period (Fig. 1a, gray background), the pollution intensity was reduced significantly from that before the APEC conference period (Fig. 1a, white background). The average mass concentrations of PM$_1$ in the two sub-periods were 101 ± 73.8 μg m$^{-3}$ and 36.9 ± 36.7 μg m$^{-3}$, respectively. Of all the inorganic species and BC, nitrate decreased the most in terms of both mass concentration, from 25.5 to 7.4 μg m$^{-3}$, and relative contribution, from 21% to 14%, as a result of the control measures on vehicles within Beijing and the reduction of industrial emissions in the surrounding areas. Moreover, although no obvious decrease was noted in the relative contributions of sulfate (1%) or...
ammonium (2%), their mass concentrations were lowered by 9.5 and 8.5 $\mu$g m$^{-3}$, respectively.

OA comprised the dominant component of PM$_1$ across the entire time period and within the two sub-periods (Fig. 1b–d); the mass concentration of OA decreased the most during the APEC period, from 40.8 to 18.2 $\mu$g m$^{-3}$. However, the relative contribution of OA actually increased by 5%, associated with the overall larger decrease in PM$_1$ total mass concentration during the APEC period. This result is in agreement with that of previous researches, in which a decrease in PM$_1$ mass concentration corresponded to an increase in the contribution of organics and a decrease in inorganic species (He et al., 2011; Sun et al., 2011a, 2011b). The mass spectrum of OA mostly consisted of prominent CxHyOz fragments, which was low in the MS of SV$_1$OAA at 0.79, which are similar to those measured in Barcelona at 0.32 and 0.75, respectively (Mohr et al., 2012) and Paris at 0.39 and 0.73, respectively (Crippa et al., 2013). LV$_1$OAA strongly correlated with sulfate ($r = 0.946$; Fig. 2a and Table S1), showing that these two species are secondary in nature and mostly driven by regional production. SV$_1$OAA in general correlated with nitrate ($r = 0.907$; Fig. 2b and Table S1), indicating its semi-volatile characteristics. In addition, both strongly correlated with relative humidity and O$_x$ ($r = 0.967$; Ge et al., 2012), and New York city ($r = 0.75$; Ge et al., 2012), indicating that the formation mechanism of SOA in this study includes photochemical oxidation and aqueous-phase processing.

Two typical primary OAs (POAs), HOA and COA, were identified in emissions from traffic and cooking sources, respectively. Therefore, they correlated well with BC and C$_6$H$_{10}$O. ($r = 0.74$ and 0.96; Fig. 2c and d, Table S1), showing a prominent peak in the sources spectra of cooking emissions (Sun et al., 2011b). HOA and COA mass spectra are dominated by the CxHy family, resulting in high hydrogen to carbon ratios (H/C), ranging from 1.78 to 1.81, but low O/C ratios, ranging from 0.09 to 0.12 (Fig. 2c and d); this result is consistent with previous studies in urban sites such as at Fresno, California ($O/C = 0.09–0.11$; Ge et al., 2012), and New York city ($O/C = 0.06–0.18$; Sun et al., 2011b). The most important distinction between these factors is the diurnal profile. The diurnal patterns of

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**Fig. 1.** (a) Time series of the mass concentrations of submicron aerosol particle (PM$_1$) species and the average mass concentration and composition of PM$_1$ (b to d) and organic aerosols (OA; e to g) before (b and e) and during (c and f) the Asia–Pacific Economic Cooperation (APEC) conference period, (d) and (g) represent the entire experimental period. The gray background in (a) represents the APEC conference period.
COA showed two peaks, one at noon and one in the evening, corresponding to the lunch and evening meal times of the local residents. However, those of HOA showed a prominent peak in the morning near rush hour and a second, higher peak at night, consistent with actual traffic conditions in Beijing (Fig. 3). The mass spectrum of BBOA is characterized by prominent signals at ion \(\text{C}_2\text{H}_4\text{O}_2^+\) (m/z 60; Fig. 2e), which is known to be produced by levoglucosan and formed from the breakdown of cellulose in biomass burning (Schneider et al., 2006). The BBOA had an O/C of 0.24, which fits in the ranges of 0.18–0.4 reported for primary biomass burning aerosols generated in laboratory (Aiken et al., 2009; He et al., 2010). In Beijing and its surrounding areas, harvest occurs in late September through October for corn, during which time biomass burning also presents high contributions to fine PM (Yu et al., 2013). In addition, the PMF factors and wind speed (WS) showed a negative correlation (Table S1), indicating the important role of wind during the scavenging process.

In the present study, the relative contribution of the two types of SOA identified, LV—OOA and SV—OOA, decreased from 61% to 50% as a result of the APEC–ECMs; this decrease occurred because of a reduction in the concentrations of SOA precursors such as a 34% decrease in volatile organic compounds (VOCs) in the atmosphere (http://www.bjepb.gov.cn/bjepb/332423/332446/416697/index.html) owing to the controls on vehicle and industrial pollution. Accordingly, the relative contributions of the POA factors either increased, as in the cases of COA and BBOA, or only decreased slightly, as in that of HOA with a 1% decrease. However, the actual concentrations of all POA factors did show decreases. The most
significant increase in relative contribution occurred in COA, from 19% to 29%, because almost no restrictive measures were imposed on the catering industry during the APEC period whereas the sources of all other OA factors were controlled. Although the relative contribution of HOA decreased only 1% from that before the APEC conference, the mass concentration of HOA decreased from $6.5 \pm 7.3$ to $3.3 \pm 4.9$ $\text{mg/m}^3$. All of these results reflect the significant role of the APEC-ECMs.

During the Beijing Olympics in 2008, a large number of pollution control measures were also implemented in Beijing and its surrounding areas. These measures primarily relate to improvements in the energy structure, reduction in coal burning emissions, regulations on vehicle emission standards (http://www.gov.cn/gzdt/2008-04/14/content_944028.htm). Similar to during the APEC conference, around half of the vehicles were removed from the roads, by an odd/even number plate rule, between 20 July and 20 September 2008. Huang et al. (2010) found that the average PM$_1$ mass concentration during the Olympic campaign was 47 $\text{µg/m}^3$, which is higher than that recorded during the APEC conference (36.9 $\text{µg/m}^3$). These combined results show that implementation of special control measures led to improvements in air quality. However, even with these improvements, the PM$_1$ mass concentration during the Olympic campaign was still significantly higher than that observed in developed countries, such as 11.7 $\text{µg/m}^3$ in New York City in 2009 (Sun et al., 2011b) and 14.8 $\text{µg/m}^3$ in Pittsburgh in 2002 (Zhang et al., 2005). Therefore, more efforts need to be made to control the air pollution in Beijing in the future, particularly because some of the measures imposed during the APEC conference and Beijing Olympics would be difficult to maintain in the long term.

Oxidants ($O_x = O_3 + NO_2$) are critical for the formation of fine particles in the atmosphere. Compared with that prior to the APEC conference period, the $O_x$ concentrations in Beijing during that period decreased by 30% (Fig. S8). In Beijing, nitrogen oxides ($NO_x = NO + NO_2$) are emitted mainly from vehicles in urban areas, and $SO_2$ is transported in mainly from surrounding areas such as Hebei, Shanxi, and Shandong provinces. Correspondingly, the $NO_x$ and $SO_2$ concentrations decreased respectively by 50% and 39% in Beijing during the APEC conference period, when the APEC-ECMs were implemented. In addition, VOCs decreased by 34% (http://www.bjepb.gov.cn/bjepb/332423/332446/416697/index.html).

3.2. Light extinction apportionment of PM$_1$ chemical components

PM$_1$ strongly scatters light due to its size, which is comparable to the wavelengths of visible light (Liou, 2002). Here the chemical components of nitrate, ammonium, and sulfate were identified as ammonium sulfate and ammonium nitrate according to the method reported by Gysel et al. (2007). The aerosol hygroscopic growth curve obtained by Pan et al. (2009) during relative clean periods in Beijing was used to identify the influence of each chemical component on light extinction; details of the methodology can be found in Wang et al. (2015).

An obvious improvement in visibility occurred during the APEC conference period (Fig. 4a); the average visibility before and during the APEC conference was 16 km and 30 km, respectively. The
analysis of the relative contribution of each species to light extinction showed that the relative contribution of ammonium sulfate and ammonium nitrate to light extinction was higher when visibility was reduced, in contrast to that of BC and the OA. OAs were the dominant aerosol components leading to light extinction in both time periods and contributing to 37%–38% of light extinction. Compared with that prior to the APEC conference period, the contributions of ammonium sulfate and ammonium nitrate to total light extinction were decreased substantially, from 13% to 8% and from 24% to 14%, respectively. BC, a material that absorbs light, also had an important role, contributing to 15% of light extinction during the entire experimental period; its contribution increased during the APEC conference period from 13% to 18%. The large reduction in the contribution of ammonium nitrate to light extinction is associated mainly with the strict controls of vehicle numbers in Beijing and controls on industry in the surrounding areas, whereas the reduction in the contribution of ammonium sulfate is the result of controls on industry in the surrounding areas.

3.3. Polycyclic aromatic hydrocarbons

PAHs constitute a well-known class of organic compounds emitted from petroleum-based fuel engines (Eiguren-Fernandez and Miguel, 2012). Many PAHs are highly carcinogenic at relatively low levels; ultrafine forms associated with vehicle emissions have been observed to cause oxidative stress in cells and may be linked to adverse health effects (Li et al., 2002). Dzepina et al. (2007) estimated total particulate PAH concentration by using a quadrupole-based Aerodyne aerosol mass spectrometer (Q-AMS) for the first time. They developed a quantification procedure including a background subtraction method that allows for removal of the interferences from non-PAH organics on m/z values with PAH contributions. They determined that the Q-AMS is capable of measuring particulate PAH in ambient air, with an estimated uncertainty of +35% and –38% through comparisons with laboratory Q-AMS and NIST database spectra of PAH standards. In the present study, due to the availability of the high-resolution (W-mode) data, we directly quantified the PAH-relevant ions in the range of m/z 202 to 328 according to that reported by Xu et al. (2014). Therefore, our results had lower uncertainty and were more reliable than those obtained by the Q-AMS measurement.

The average PAH concentration was determined to be 26 ng m⁻³ during the experimental period, which is consistent with other observations in China such as 24 ng m⁻³ in Guangzhou (Li et al., 2006) and 26 ng m⁻³ in Lanzhou (Xu et al., 2014). In fact, the PAH concentration decreased from 29 to 21 ng m⁻³ during the APEC conference period, in accordance with the change observed in the PM₁ mass concentration. Corresponding to these results, Gao et al. (2011) also reported that the PAH composition differed significantly between haze and non-haze days, indicating a greater potential risk for human health under low-visibility conditions.

In the present study, PAHs and BBOA had the strongest correlation at r = 0.96 (Fig. S9a) and HOA at r = 0.87 (Fig. S9b) and HOA at r = 0.81 (Fig. S9c) were also strong, which is consistent with observations in Lanzhou (Xu et al., 2014). These results suggest that biomass burning and traffic emissions, particularly the former, are important sources of PAHs in Beijing. Although Zhao et al. (2007) determined cooking to
be another potential source of PAHs, the correlation of COA and PAHs in the present study was poor, at r = 0.49 (Fig. S9d). These results indicate that cooking was not a key source of PAHs in Beijing at the time of this study because natural gas is currently the main fuel used for that purpose. The contribution of cooking emissions to ambient PAHs is therefore negligible compared with other sources. In addition, the stepwise multiple linear regressions, which set the PMF factors and BC as predictor variables, also indicated that BBOA and HOA are two important factors for the PAH mass concentration in Beijing. The determination coefficient $r^2$ was 0.94 ($p < 0.001$). However, when other factors were added, the $r^2$ value increased slightly. This result further demonstrates that the PAHs in Beijing are mainly emitted from biomass burning and traffic emissions.

Interestingly, the correlations of PAHs with BBOA and HOA differed before and during the APEC conference periods. The correlation coefficient between PAHs and BBOA was very close in both sub-periods, at 0.97 and 0.96, respectively (Fig. 3b and d). However, that between PAHs and HOA decreased from 0.85 before the APEC conference to 0.73 during that period (Fig. 3c and e). These results indicate that the control measures, which focused mainly on vehicles in Beijing, caused a reduction in PAHs emissions from vehicles.

The sources of PAHs from vehicles have been categorized into gasoline- and diesel-fueled vehicles, which have shown different contributions and intensities to the total PAHs measured (Eiguren-Fernandez and Miguel, 2012; Ho et al., 2009; Zhou et al., 2005). A long-term regulation mandates that heavy-duty diesel trucks are not allowed in Beijing between 06:00 and 23:00 local time. Therefore, to compare the differences in the emissions of PAHs between gasoline and diesel vehicles in the two sub-periods, we defined the period of 06:00–23:00 as the non-diesel-fueled vehicles period (NDP), and the rest of day was classified as the diesel-fueled vehicles period (DP). The correlations were stronger between PAHs and HOA in the DP than that in the NDP in both sub-periods (Fig. 5f–i). This result indicates that the contribution of diesel vehicles to total PAHs was higher than that of gasoline vehicles, which is consistent with the results reported by Eiguren-Fernandez and Miguel (2012) and Ho et al. (2009). Ho et al. (2009) determined that the average PAH emission factor from diesel-fueled vehicles was approximately five times higher than that from non-diesel-fueled vehicles. In addition, the correlations between PAHs and HOA in both the NDP and DP were weaker during the APEC conference period, at 0.70 and 0.81, respectively, than those prior to the period, at 0.83 and 0.92, respectively. Therefore, the control on vehicles in Beijing during the APEC conference decreased PAH emissions from both gasoline- and diesel-fueled vehicles.

4. Conclusions
A series of emission control measures, mainly focused on vehicles and industry, were implemented in Beijing and its surrounding areas to ensure good air quality for the duration of the APEC conference in 2014. Consequently, the average PM$_1$ mass concentration decreased from 101 to 36.9 $\mu$g m$^{-3}$, or 63%, during the APEC period. The relative contribution of inorganic species decreased to different degrees. The decrease in the relative contribution of nitrate to PM$_1$ was particularly large, from 21% to 14%; correspondingly, the contribution of ammonium nitrate to light extinction decreased by 10% during the APEC conference period from the value reported prior to that period. Biomass burning and traffic emissions, particularly the former, were determined to be another potential sources of PAHs in Beijing. Therefore, the control measures, which focused mainly on vehicles in Beijing, caused a significant reduction in PAH emissions from vehicles. Ultimately, a significant decrease in the mass concentration of PM$_1$ and PAHs was shown, with subsequent improvement in visibility, during the APEC conference APEC–ECMs were enforced in Beijing and its surrounding regions.

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Appendix A. Supplementary data
Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.06.049.

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