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Faraday Discussions

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The "Parade Blue": effects of short-term emission control on aerosol chemistry

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The strict control on emissions implemented in Beijing, China, during the 2015 China Victory Day Parade (V-day Parade) to commemorate the 70th Anniversary of Victory in World anti-fascist War, provided a good opportunity to investigate the relationship between emission sources and aerosol chemistry in a heavily polluted megacity. From August 11 to September 3, 2015, an Aerosol Chemical Speciation Monitor was deployed in urban Beijing, together with other collocated instruments, for the real-time measurement of submicron aerosol characteristics. The average PM1 mass concentration was 11.3 (± 6.7) µg/m³ during the V-day Parade, which was a reduction of 63.5% compared with that before the V-day Parade. Different from the relatively smaller decrease of organics (53%), secondary inorganic aerosols (sulfate, nitrate and ammonium) showed significant reductions of 65%-78% during the V-day Parade. According to the positive matrix factorization results, primary organic aerosol (POA) from traffic and cooking emissions decreased by 41.5% during the parade, whereas secondary organic aerosol (SOA) presented a much greater reduction (59%). The net effectiveness of emission control measures was investigated further under comparable weather conditions before and during the parade. By excluding the effects of meteorological parameters, the total PM1 mass was reduced by 52%-57% because of the emission controls. Although the mass concentrations of aerosol species were reduced substantially, the PM1 bulk composition was similar before and during the control period as a consequence of synergetic control of various precursors. The emission restrictions also suppressed the secondary formation processes of sulfate and nitrate, indicated by the substantially reduced SOR and NOR (molar ratios of sulfate or nitrate to the sums of the sulfate and SO₂ or nitrate and NO₂) during the event. The study also explored the influence of emission controls on the evolution of organic aerosol using the mass ratios of SOA/POA and oxygen-to-carbon ratios. The results showed that for northwesterly airflows, emission restrictions during the V-day Parade also reduced the oxidation degree of organic aerosol.

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Introduction

Aerosol particles are of great importance not only because of their direct and indirect radiative forcing on climate but also because of their adverse effects on health. They can be emitted directly as particles from natural and anthropogenic sources, or formed in the atmosphere through gas-to-particle conversions.¹ According to Seinfeld and Pandis,² considerable amounts of aerosols are anthropogenic in origin, especially those with diameters <1 μ m. Anthropogenic emissions of air pollutants in China are much greater than in European or North American countries, which intensifies China's severe air pollution.³ Therefore, it is essential to understand how anthropogenic sources affect the aerosol load before implementing clean-air measures.

Beijing, the capital city of China, has suffered frequent haze episode events since the early 2000s.⁴ In 2014, the city had a residential population of 21.52 million and the total number of motor vehicles exceeded 5.3 million.⁵ Moreover, air quality in Beijing can be affected significantly by its surrounding regions, especially the heavily industrialized cities in Hebei and Shanxi provinces.⁶

To improve the air quality for the 2015 Victory Day Parade, held on September 3, 2015, the Chinese government implemented a number of strict control measures to reduce anthropogenic emissions in Beijing and the surrounding areas (e.g. Tianjin, Hebei,

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Inner Mongolia, Shanxi, Shandong and Henan). The number of motor vehicles allowed on the roads of Beijing between August 20 and September 3, 2015 was reduced by half. In addition, more than 10,000 enterprises across all 7 municipalities and provinces were suspended or ordered to limit production during this period, and various construction activities were also forbidden. Consequently, the air quality in Beijing during the event was improved significantly and dubbed the "Parade Blue". The control measures implemented during the V-day Parade were much stricter than during the 2008 Olympic Games and 2014 Asia-Pacific Economic Cooperation (APEC) summit. Thus, this event served as a realistic "natural atmospheric chamber"¹ and provided a good opportunity to improve our understanding of the complex relationship between emission sources and aerosol chemistry to guide future control strategies.

Air pollution levels are affected not only by emissions but also by meteorological conditions. Various studies have indicated that air quality in Beijing depends strongly on weather conditions, especially the local wind speed and wind direction.^{7,8} According to research focusing on air quality improvement during the 2008 Olympic Games and 2014 APEC summit, favorable meteorological conditions also played an important role in reducing PM levels in addition to emission reductions. Thus, it is not sufficient to simply compare aerosol concentrations prior to and during emission controls to evaluate the efficiency of reduction measures. A popular strategy to distinguish possible meteorological effects is to use comprehensive air quality models to simulate the aerosol formation processes under different emission and meteorological scenarios. Using emission inventories of June 2008 (without emission reductions) and August 2008 (with emission reductions), Wang et al.⁹ simulated day-to-day PM_{2.5} concentrations with the Community Multiscale Air Quality (CMAQ) model and they found that more than 60% of the PM_{2.5} reduction during the Olympic Games was due to emission controls. However, model predictions could be influenced strongly by the accuracy of the incorporated chemical mechanisms as well as the emission inventories, especially for PM_{2.5}, a complex mixture of chemical species.¹⁰ As presented by Wang et al.,⁹ the correlation coefficient between modeled and observed data was 0.7 for August 2008. With the application of remote sensing and satellite technology, an alternative approach is the development of statistical models based on pollution level and meteorological parameters. Cermak and Knutti¹¹ took aerosol optical depth (AOD) as a surrogate for pollution level and developed a neural network to relate log (AOD) to the wind vector, precipitation and relative humidity (RH). They predicted log (AOD), assuming no emission controls, using meteorological observations obtained during the Olympic Games and then compared them with the observed values. However, they also highlighted that the AOD used in their approach might not be representative of surface conditions. Liu et al.¹² developed a nonlinear statistical model based on both ground and satellite observations. They estimated groundlevel $\mathsf{PM}_{2.5}$ concentrations using satellite AOD and local meteorological parameters, and found that 70% of the temporal variability in PM2.5 could be explained by the fitted model. Their model results indicated that emission controls during the Olympic Games resulted in an approximate 27%-33% reduction in PM_{2.5} concentrations. In addition to the unexplained variability in $PM_{2.5}$

View Article Online DOI: 10.1039/C6FD00004E

concentrations, their small sample size might also have been a limitation of their approach considering such short-term political measures.

A more straightforward strategy is to regard the atmosphere as a natural laboratory and to estimate the influence of emission reductions using measured changes in air quality under comparable weather conditions. Cheng et al.¹ used source conditions, local meteorological parameters and regional transport characteristics as the selection criteria to distinguish the effects of weather conditions on air quality. Under similar local and regional meteorological factors, they estimated that traffic restrictions imposed during the 2006 Sino-African Summit in Beijing reduced the number concentrations of particles in the Aitken and accumulation modes by 20%-60%. Several studies have applied the real-time aerodyne aerosol mass spectrometer (AMS) to explore the changes of aerosol chemistry due to emission restrictions during the 2008 Olympics and the 2014 APEC in Beijing. 13,14,15,16 These studies largely compared the aerosol loading during the emission control period with that of a pre-control period or the same period in previous years. However, meteorological conditions (e.g. wind and precipitation) can be significantly different between these periods. Thus the link between emission controls and aerosol chemistry is still not clearly understood.

In the present study, we conducted real-time measurements of submicron aerosol composition in urban Beijing, both before and during the V-day Parade (August 11-19 and August 20 to September 3, 2015, respectively), using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) and other collocated instruments. The changes of aerosol chemical species and organic aerosol (OA) sources prior to and during the control period were investigated in detail. In particular, data populations with similar local and regional meteorological conditions before and during the parade were selected. Under comparable weather conditions, the net effectiveness of emission restrictions on aerosol chemistry was elucidated by comparing the changes before and during the event.

Experimental methods

Sampling site

The field measurements were conducted on the campus of Tsinghua University (THU site: 40.0°N, 116.3°E), which is situated in the northwestern urban area of Beijing. Beijing is located at the northern tip of the North China Plain, with Tianjin municipality on its eastern border and Hebei province on its other three sides. Topographically, Beijing is characterized as a semi-basin region, bordered by the Yanshan Mountain to the northeast and the Taihang Mountain to the west. The basin-like topography plays an important role in the regional airflow of this area.¹⁷ Sampling was performed approximately 10 m above ground level on the roof of a three-story building. Local emission sources within 1 km of the THU site included vehicles and fuel combustion for cooking. No major industrial sources are located in the locality.

Online instrumentation

Journal Name

The chemical composition of non-refractory PM₁ was measured in situ from August 11 to September 3, 2015, using an ACSM.¹⁸ The ACSM uses the same particle lens and vaporizer as a research grade AMS; however, no size information is obtained because of the lack of a fast data acquisition and particle beam chopper system. Before sampling into the ACSM, a PM_{2.5} cyclone (model URG-2000-30ED) was used to remove coarse particles (>2.5 μ m), and a silica gel diffusion dryer was supplied to dry the aerosol particles. After passing through a 100-µm-diameter critical aperture, aerosol particles between 30 nm and 1µm were focused into a narrow particle beam via an aerodynamic lens. Particles were then transmitted directly into the detection chamber, where nonrefractory particulate materials were flash vaporized at the oven temperature (~600°C) and ionized by 70eV electron impact. In this study, the applied scan rate of the ACSM was 200 ms per amu from m/z 10 to 150. The time resolution of chemical species concentration was approximately 15 min, by alternating 14 cycles between the filter and sample modes. The ionization efficiency of the ACSM was calibrated at the beginning, in the middle and at the end of the field observations. A detailed description and calibration procedure of ACSM has been given in Ng et al.¹⁸

Because ACSM can only measure the chemical concentrations of non-refractory species (organic, sulfate, nitrate, ammonium and chloride), a multi-angle absorption photometer (MAAP; model 12, Thermo Electron Corporation) was deployed to obtain the concentration of refractory black carbon (BC). The MAAP^{19,20} was operated at an incident light wavelength of 670 nm, with a PM1 cyclone and a drying system incorporated in front of the sampling line. Simultaneously, PM₁ mass was measured based on the β-ray absorption method using a PM-714 Monitor (Kimoto Electric Co., Ltd., Japan).²¹ Other collocated instruments included a suite of commercial gas analyzers from Thermo Scientific to measure the gaseous species (CO, O_3 , NO, NO_2 and SO_2), and an automatic meteorological observation instrument (Milos520, VAISALA Inc., Finland) to monitor temperature, RH, precipitation, wind speed and wind direction. The height of the PBL (planetary boundary layer) was obtained from the ARL (Air Resources Laboratory) at the NOAA website (http://www.arl.noaa.gov/index.php).

ACSM data analysis

The ACSM data analysis were processed within Igor Pro (WaveMetrics, Inc., Oregon USA) using the standard ACSM data analysis software (v.1.5.3.0). To obtain the chemical concentration of NR-PM₁ species, the default relative ionization efficiencies (RIEs) of 1.4 for organics, 1.08 for sulfate, 1.1 for nitrate, and 1.3 for chloride were used in this study. For ammonium, the RIE of 7.16 was derived from pure ammonium nitrate calibration. In most previous field studies, a constant collection efficiency (CE) value of 0.5 has been used to account for the incomplete detection of aerosol particles. However, Middlebrook et al.²² proposed that the CE appeared significantly influenced by high aerosol acidity, high RH

and high ammonium nitrate mass fractions (ANMF). In this study, RH plays a minor role in affecting the CE because a silica gel diffusion dryer was incorporated with the system to maintain RH < 40%. The aerosol particles were almost neutralized during the entire study, as indicated by the value of $NH_4^+_{measured}/NH_4^+_{predicted}$ (Fig. S1a). However, occasionally, high ammonium nitrate was observed with ANMF higher than 0.4 (Fig. S1c). Thus, variable CEs were applied based on the equation proposed by Middlebrook et al.²² (CE_{dry} = max (0.45, 0.0833 +0.9167 × ANMF)). As presented in Fig. S1b, the mass concentration of NR-PM₁ plus BC using variable CEs correlated strongly with the total PM₁ mass measured by the PM-714 Monitor (r²=0.90).

The ACSM mass spectra was processed using the PMF2.exe algorithm combined with the positive matrix factorization (PMF) Evaluation Tool (PET) to explore various sources of OA.²³ We considered only ions up to m/z 100 given the large interferences of the internal standard of naphthalene at m/z's 127-129 and the low signal-to-noise ratio of larger ions. The PMF analysis was performed for 1 to 8 factors and for FPEAK values between -1 and +1 (step: 0.1). The result were evaluated further following the procedures detailed in Zhang et al.²⁴ A summary of the PMF diagnostic discussion and related plots is presented in Figs. S2 - S5 in the Supplement. Finally, a 3-factor solution with FPEAK = 0 was chosen. The three factors were identified as hydrocarbon-like organic aerosol (HOA), cooking-related organic aerosol (COA), and oxygenated organic aerosol (OOA), based on the interpretation of the mass spectral signatures, the temporal and diurnal variation patterns and their correlations with external tracer compounds (see Sect.3.1.2 for details).

Results and discussion

General description

Submicron aerosol and meteorology. Figure 1 depicts the time series of submicron aerosol composition and meteorological parameters for the entire study period. The concentrations of both PM₁ and the chemical species clearly decreased on August 20, when emission control measures were first implemented in Beijing. Relatively low ambient levels were maintained until September 3, during which far stricter emission reductions were imposed both in Beijing and its surrounding areas. Comparatively, the total PM₁ mass (=NR-PM1+BC) was reduced by 63.5% during the parade period. The average PM₁ concentration (11.3 μ g/m³) was much smaller than that during the 2008 Olympics (61.3 μ g/m³) and 2014 APEC (41.6 μ g/m³) in Beijing, indicating a greater improvement of air quality during the V-day Parade because of the more stringent controls of emissions.^{13,14} In fact, the good air quality during the parade (known as the "Parade Blue") could more or less mirror that observed over a 19-month period in northern central Oklahoma, USA (7.0 μ g/m³) and that reported in an urban background site in London, UK (9.9 µg/m³).^{25,26}

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Figure 1. Temporal variations of (a) T, RH and precipitation, (b) WS and WD, (c) PBL, (d) mass concentrations, and (e) mass fractions of chemical species in PM_1 .

Compared with the sharp decline of inorganic species during the parade, changes of OA were relatively smaller. Correspondingly, the concentrations of sulfate, nitrate and ammonium (SNA), decreased by 65%-78% during the emission control period, whereas organics showed a relatively smaller reduction of 53%. Different behaviors of inorganic and organic species also led to the variation of aerosol chemical composition before and during the parade. Although organics accounted for >50% of the total PM₁ mass during the parade, the contribution of SNA declined from 51.0% to 37.7%, possibly indicating their different responses to emission controls.¹⁴

In addition to the effect of emission controls, a detailed investigation of the meteorological variables and time series of aerosol species revealed that local wind direction might also play a dominant role in the variation of submicron aerosol characteristics. As indicated in Fig.1, local meteorological parameters of temperature, RH, wind speed and the PBL height, showed no obvious changes during the entire study period, except for variations on August 31, which were influenced by accumulated precipitation; however, local airflow varied significantly. Although local weather conditions were dominated by southerly winds (56%) before the parade, the frequency of southerly wind was only 18% during the parade. Previous studies have found that high PM concentrations in Beijing usually correspond to southerly wind, while low PM concentrations generally correspond to the opposite wind direction.^{6,17} This was further verified in our study by the back trajectory (BT) analysis (Fig. S6), which displayed that as the wind direction changed from southerly to northerly, the total PM1 concentration decreased from 27.0 to 8.7µg/m³. These results

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suggested that favorable weather conditions helped considerably in the improvement of air quality during the parade. Moreover, we found that the variations of aerosol chemical composition were also closely related to changes of local wind direction. As shown in Fig. 1, the southerly airflow was always accompanied by a rapid increase of SNA, which was consistent with the fact that high concentration air masses from source locations south of Beijing area had more abundant secondary aerosol species.¹³ The BT clustering analysis also revealed that different PM₁ species showed different BT dependence. While SNA dominated the aerosol composition by 54.9% in southerly air masses, its contribution showed a gradual decrease as the wind direction changed from southerly to northwesterly and then to northeasterly. For the northeasterly BT group, SNA only accounted for 23.6% of the total PM₁ mass. Thus the influence of meteorological conditions, especially local wind directions, on submicron aerosol behavior is



Figure 2. Mass spectra and time series of (a) HOA, (b) COA and (c) OOA. Also shown are the time series of external tracers and their correlation coefficients with OA factors.

Investigation of OA sources. The PMF analysis of OA mass spectra measured during the entire study period allowed the identification of three organic components, HOA, COA, and OOA. These components were examined for their mass spectral signatures, and then for their correlation with other tracers, their diurnal variations and other characteristics.^{23,27,28} Figure 2 shows the mass spectra profiles of the three components and their time series during the campaign.

The HOA mass spectrum was characterized by the ion series of m/z 27, 41, and 55, belonging to cycloalkanes, and m/z 29, 43, and 57, belonging to alkanes.²⁹ The time series of HOA correlated moderately well with BC ($r^2 = 0.45$), consistent with the results of previous studies that HOA was linked chiefly to primary combustion emissions, e.g., gasoline and diesel exhausts.³⁰ Compared with the large diurnal peak at night, HOA only presented a tiny rush hour peak in the morning, which may be significantly decreased by the enhanced PBL height (Fig.4). The same phenomenon has been observed and discussed by several studies in Beijing.^{16,29,33} The results showed that HOA identified in our study might be associated mainly with traffic emissions, especially considering the minor contribution of coal combustion in Beijing during this season.

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However, relatively high fractions of ions at m/z 44 were observed in HOA mass spectrum, indicating the presence of some oxygenated compounds in HOA. This could be attributed to the fact that a fraction of HOA was aged OA transported from regional sources, similar to the results conducted in Shanghai and Lanzhou, China.^{13,28,31}



Figure 3. (a) Diurnal variations of mass concentrations and mass fractions of HOA, COA and OOA, Scatterplots of (b) $f55_{OOA, sub}$ vs. $f57_{OOA, sub}$, and (c) f44 vs. f43. The measured OA data points are colored by time of the day. And the shaded ovals indicate regions of LV-OOA and SV-OOA reported in Ng et al.³⁶

The most abundant ions of COA mass spectrum (MS) were similar to those of HOA. However, consistent with the MS characteristics measured for primary Chinese cooking emissions, significantly larger peaks at m/z 41 and 55 were observed from the mass spectra of COA, indicating the large presence of unsaturated organic compounds (e.g. unsaturated fatty acids).³² Another unique distinction between COA and HOA is their diurnal profiles. Unlike the morning and evening rush hour peaks of HOA, COA presented a small peak at noon and a large peak in the evening, corresponding to the lunch and dinner times of local residents (Fig. 3a). According to previous studies, the relative ion intensities of m/z 55 and 57 in the organic mass fragments could also be used to distinguish COA from HOA. $^{\rm 29,33,34}$ Compared with other POA components, COA was generally characterized with a higher ratio of m/z 55/57. The average ratio of m/z 55/57 of the COA factor in this study was 2.4, close to the values observed previously in Beijing.^{29,33} Mohr et al.³⁴ developed a V-shaped plot for distinguishing and quantifying HOA and COA, based on f55_{00A,sub} and f57_{00A,sub} (the mass fraction of m/z 55 and 57 after subtracting the interferences of OOA factors). The dashed lines in Fig. 3b corresponded to the edges of COA and HOA factors from several urban AMS data sets.³⁴ The COA and HOA

factors determined in this study were well separated in the scatter plot of Fig. 3b, with COA located on the left side and HOA on the right side of the V-shape region.³¹ Some recently published work has attributed COA to some other sources such as agricultural practices and animal husbandry activities.⁴⁴ However, as the observation data is limited, we cannot identify if they are influential during this period.

OOA factor has shown to be a good surrogate for SOA.^{35,36} Its mass spectrum was characterized by a prominent peak of m/z 44 (CO₂⁺) (20.0% of the total OOA signal), which was mainly from the di- and poly-carboxylic acid functional groups. Two subtypes of OOA, SV-OOA and LV-OOA, have been identified in many ambient datasets, and LV-OOA is more oxidized than SV-OOA.²⁴ The OOA factor identified in this work tended to be highly aged according to the similarities between its spectral pattern and that of the highly oxidized LV-OOA. This was further evidenced by the better correlation of OOA with less volatile sulfate ($r^2 = 0.74$) than with semi-volatile nitrate ($r^2 = 0.61$). Ng et al.³⁶ developed a triangle plot of f44 (mass fraction of m/z 44 to total organic signal) versus f43 (defined similarly) to characterize the evolution of OOA components. In the well-defined triangular region, the less aged SV-OOA generally occupies the broader base while highly aged LV-OOA is concentrated in the narrowing top region of the triangle. The OOA factor determined here showed a higher f44 value but lower f43 value, close to the ambient LV-OOA (Fig. 3c). Data points colored by time of day also revealed that photochemical processes would increase the oxidation degree of OA.

On average, HOA, COA and OOA accounted for 22.2%, 21.0% and 56.8% of the total OA during this campaign, respectively. Because of the strict emission controls implemented after August 20, 2015, the concentrations of all these components decreased significantly, with HOA from 2.3 to $1.4\mu g/m^3$, COA from 2.3 to $1.3\mu g/m^3$, and OOA from 7.0 to $2.9\mu g/m^3$, separately. The significant reduction of COA was mainly associated with the banning of open charcoal grills during the parade. And this control measure was also adopted during the 2014 APEC period. As presented by Zhang et al., the concentration of COA decreased by 33.3% during APEC, from 7.8 to $5.2\mu g/m^{3.16}$ The sum of HOA and COA could be regarded as POA, and the OOA corresponded to aged SOA. In general, POA and SOA were reduced by 41.5% and 59.0% respectively during the parade period.

Segregation of possible meteorological effects

The variation pattern of air pollution level reflects the combination of emissions, meteorological conditions, and secondary formation processes of PM.¹ Previous studies have indicated that air pollution variability in Beijing could be affected significantly by local weather conditions, e.g. temperature, RH, precipitation, wind speed and wind direction. Thus, it is insufficient to simply compare the pollution levels prior to and during the V-day Parade when evaluating the efficacy of emission reduction measures.

Figure 1 depicts the time series of local meteorological parameters during the entire study period. In general, there were not obvious changes in the local temperature, RH, wind speed and PBL height

before and during the parade, except for August 31, 2015, when accumulated precipitation strongly decreased the temperature and PBL height, and increased the RH. To better concentrate on the influence of emission control strategies on air quality, it is necessary to exclude possible meteorological effects by comparing pollution levels before and during the control period under similar weather conditions and similar regional transport characteristics.³⁷ To select comparable data populations, the following procedures were adopted. First, we removed the data points on 30-31 August and 1 September, 2015 to eliminate the interference of accumulated precipitation. While the other meteorological factors were much similar before and during the parade after that step, the local wind direction remained markedly different as indicated by different colors in Fig. 1. We then used the BT analysis to select comparable conditions of wind direction and regional air mass transport. The 72-h BTs at 500 m above ground level were calculated every hour for the entire campaign and the trajectories were afterwards clustered using the HYSPLIT4 software according to their similarity in spatial distribution.³⁸ A three-cluster solution was adopted to



better characterize the total spatial variance, as displayed in Fig. S6. Although cluster 2 largely dominated the parade period, it showed no contribution before the parade. Thus, only cluster 1 and cluster 3 were chosen as two types of situations both of which covered data points before and during the emission control period. Finally, other meteorological parameters prior to and during the parade, including temperature, RH, wind speed and PBL height, were compared in detail under cluster 1 and cluster 3 cases respectively. As shown in Figure 4, weather conditions during the parade were much similar to those before the parade for both cluster 1 and cluster 3, and their data points were distributed uniformly throughout a 24-h day.

Figure 4. Diurnal patterns of T, RH, WS and PBL height before and during the V-day Parade for **(a)** cluster 1 and **(b)** cluster 3.

Therefore, according to the above selection procedures, data populations with similar weather conditions before and during the parade were formed for cluster 1 and cluster 3 cases. Here, we defined B-1 and D-1 as periods before and during the V-day Parade respectively under cluster 1, and B-3 and D-3 were named similarly under cluster 3. The discussions that follow are based on these two cases.

Influence of emission restrictions excluding the effects of weather conditions

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chemical composition. Under Mass concentrations and comparable weather conditions of cluster1 and cluster3 cases separately, the net effectiveness of emission control measures was estimated quantitatively for both PM1 and its major chemical species (Fig. 5). Following the strict emission restrictions during the parade, the total PM1 mass concentration was reduced by 57% and 52% respectively, for cluster 1 and cluster 3. Compared with the non-control period, secondary inorganic aerosol (sulfate, nitrate and ammonium) also showed significant decreases of 42%-67% because of the measures imposed during the parade period. The reductions of organics during the parade were 48% and 50% respectively under cluster 1 and cluster 3. Our results show that regional-scale control of precursor emissions is effective in improving air quality in northern China. However, it is worth noting that the magnitude of the restriction measures was different during different stages of the V-day Parade. As the event approached, the government continued to strengthen the control strategies to reduce the emissions of air pollutants. The days covered by D-1 and D-3 during the control period (20 August to 3 September, 2015) are listed in Table1. As D-3 included days only in the early stage of the event, the reduction for cluster 3 case might underestimate the effectiveness of control measures.

The significant reductions of secondary aerosol species were consistent with the heavily reduced emissions of their precursors. For example, under the cluster 1 case, the regional emissions of the southern Hebei, where the airflow of cluster 1 came from, was reduced by 61%-77% for SO₂, 48%-57% for NO_x and 58%-66% for VOCs during the parade, which were more proportional to reductions in their secondary species. However, the primary pollutant (e.g. POA), mainly influenced by local emissions, was not observed to decline as much as secondary species. This is consistent with the fact that our monitoring site is located tens of kilometres away from the sources impacting cluster 1.

Table 1. Days covered by D-1 and D-3 during the V-day Parade.

Periods	Days covered
D-1	Aug 22-23, 2015
	Aug28-29, 2015
	Sep 3, 2015
D-3	Aug 20-22, 2015



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Figure 5. Estimated influence of emission controls on mass concentrations of PM_1 and its major chemical species.

Figure 6 displays the aerosol composition before and during the parade for cluster 1 and cluster 3. Under comparable weather conditions, the bulk PM1 composition was relatively similar between the control and non-control periods, with only a small increase of organics contribution and a little decrease of sulfate contribution during the parade. The mass fractions of nitrate and ammonium remained almost stable. Although the mass concentrations of aerosol species were reduced substantially, these results highlighted that emission controls during the parade in itself did not significantly affect the aerosol bulk composition, consistent with the conclusions of an APEC case study focusing on the aerosol characteristics above the 260m urban canopy.¹⁵ One possible explanation for this is the synergetic control of various precursors such as SO₂, NO_x and VOCs. According to the Beijing Municipal Environment Protection Bureau (Beijing EPB, http://www.bjepb.gov.cn/), emissions of SO₂, NO_x and VOCs decreased by 36.5%, 49.9% and 32.4% separately, due to emission strategies implemented during the event.



Figure 6. Average composition of PM_1 before and during the V-day Parade for cluster 1 and cluster 3 respectively. Also shown are the average mass concentrations of PM_1 , and the average ratios of SNA and organics.

The reduced emissions of various precursors also suppressed the secondary formation process of aerosol. The SOR and NOR (molar ratios of sulfate or nitrate to the sum of sulfate and SO₂ or nitrate and NO₂) have been used as indicators of the secondary transformation of sulfate and nitrate.²¹ In addition to the gas-phase oxidation by OH radicals, sulfate could also have been formed through heterogeneous reactions of SO₂ with dissolved H₂O₂.^{2,39} The formation of nitrate is dominated by the gas-phase oxidation of NO₂ with OH radicals during daylight, and the heterogeneous reactions of nitrate radical (NO₃) during nighttime.² During the parade period, the SOR and NOR decreased substantially during both day and night, clearly demonstrating the abated secondary

formation of sulfate and nitrate due to emission control measures (Fig. 7a and b). In addition, the mass ratio of NO₃^{-/}SO₄²⁻ could to some extent indicate the relative importance of mobile versus stationary sources.^{40,41} A higher NO₃^{-/}SO₄²⁻ ratio likely reveals the predominance of mobile sources over stationary sources of



pollutants. Figure 7c shows the daytime and nighttime mass ratios of NO_3^{-1}/SO_4^{-2} before and during the parade under similar meteorological conditions. Overall, NO₃⁻/SO₄²⁻ fluctuated around 1, indicating the comparable importance of nitrate and sulfate to air pollution. Interestingly, we observed a significant decrease of the daytime NO_3^{-}/SO_4^{-2} during the emission control period, possibly due to the strict odd-even traffic control regulations. However, no such change occurred in the nighttime NO_3^{-1}/SO_4^{-2} . The ratio of NO_3^{-1}/SO_4^{-2} remained relatively stable or even slightly increased during the parade. This is consistent with the oxidation mechanisms of nitrate at night, when NO_3 radical production is not very sensitive to NO_2 varying between 10ppb to 20ppb with O₃ lower than 50ppb.⁴⁵ For cluster 1, the mixing ratio of NO₂ decreased from 23ppb to 13ppb, and that of O3 decreased from 53ppb to 49ppb, which lied in the above range. This resulted in little changed conversion of NO₃ to nitrate via heterogeneous reactions. Consequently, the nighttime NO_3^{-}/SO_4^{-2-} instead slightly increased during the control period under cluster 1.

Figure 7. Daytime and nighttime (a) SOR, (b) NOR, (c) $NO_3^{-7}SO_4^{-2}$, and (d) SOA/POA before and during the V-day Parade for cluster 1 and cluster 3 respectively. The mean (pentagram), median (horizontal line), 25th and 75th percentiles (lower and upper box), and 10th and 90th percentiles (lower and upper whiskers) are shown for each bin.

Evolution of organic aerosol. Based on the PMF results of this study, OA was apportioned into HOA, COA and OOA. Here, we regarded the sum of HOA and COA as total POA, and OOA as aged SOA to investigate the influence of emission controls on OA characteristics. Under similar weather conditions of cluster 1, the mass concentrations of POA and SOA showed the same reduction of 48% during the control period (Fig. 5). However, for cluster 3 case, SOA showed a higher reduction of 54% compared with the 40% reduction of total POA. We explored the relative importance of primary versus secondary sources of OA further by considering the mass ratio of SOA/POA. As indicated in Fig. 7d, the average SOA/POA ratios were >1 both before and during the parade, indicating the dominance of secondary sources of organics during the entire study period. However, under cluster 3, the mass ratio of SOA/POA decreased slightly during both daytime and nighttime of

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the parade period, reflecting the reduced contribution of secondary organic sources due to emission controls for northwesterly airflows over Beijing.

The oxidative properties of OA correlate closely with its density and water solubility, which could be characterized by the atomic oxygen-to-carbon (O: C) ratios.^{42,43} According to Aiken et al.,⁴² O: C ratio of ambient OA can be estimated from f44 (the ratio of m/z 44 to total signal in the component mass spectrum) through a linear parameterization. Here, we calculated the O: C ratios following the least-squares fit of Aiken et al.⁴² based on the *f*44 of ACSM mass spectrum (Fig. 8). Consistent with the results of SOA/POA, the O: C ratios were similar both before and during the parade for cluster 1. However, for the northwesterly airflows of cluster 3, the O: C ratios showed a slight decrease during the control period. Similar results have also been observed by an APEC emission control study, where the average O: C level reduced from 0.43 to 0.36 during the control period.¹⁴ This indicates that in addition to the large reduction of organic mass concentrations, emission control measures could also influence the oxidation degree of OA.



Figure 8. O: C ratios of OA before and during the V-day Parade for cluster 1 and cluster 3.

Conclusions

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In this study, we undertook a detailed investigation of the impacts of emission controls implemented during the 2015 China Victory Day Parade in Beijing on submicron aerosol characteristics. We concluded that emission restrictions implemented during the V-day Parade, which focused mainly on vehicles and industry, were efficacious in reducing the mass concentrations of PM₁ and its chemical species. The average PM₁ mass concentration was 11.3 (\pm 6.7) µg/m³ during the parade, decreased by 63.5% compared with that before the parade. The aerosol composition also changed considerably. Whereas submicron aerosols were dominated by organics (41.3%), followed by sulfate (21.1%) and nitrate (16.4%) prior to the control period, the contribution of organics apparently increased to 53.2% associated with the reduced contribution of SNA during the parade. A detailed characterization of meteorological parameters revealed that in addition to the emission restrictions, the influence of meteorological conditions on aerosol concentration and composition was non-negligible. Thus, the net effectiveness of emission controls was explored further by excluding the effects of weather conditions. Two cases, cluster 1 and cluster 3, resulting from the BT clustering analysis, were formed with similar weather conditions before and during the parade. Under comparable weather conditions, the total PM1 mass concentration was reduced by 52%-57% because of emission controls. However, the bulk submicron aerosol composition was relatively similar prior to and during the parade, possibly owing to the synergetic control of SO₂, NOx and VOCs. The SOR and NOR decreased significantly during the control period both in daytime and nighttime, indicating the suppressed secondary formation of sulfate and nitrate because of emission restrictions. We also investigated the variation of OA composition using the SOA/POA mass ratios, which remained stable for cluster 1 and showed a slight decrease for cluster 3 during the parade. The oxidation degree presented corresponding changes to OA composition, with decreased O: C ratios for cluster 3 during the control period. This result indicated that emission controls implemented during the V-day Parade also reduced the oxidation degree of OA for airflows transported from the northwest of Beijing.

Acknowledgements

This work was supported by the National Science and Technology Support Program of China (2014BAC22B01), by National Natural Science Foundation of China (21107061, 21190054). Authors also thank to Energy Saving and Pollution control Association of East Asia (ESPA), for their helps to the management of the field observation program.

Appendix A. Supplementary material



Figure S1. Scatterplots of (a) measured NH_4^+ versus predicted NH_4^+ and (b) constructed PM_1 mass concentration versus total PM_1 mass measured by PM714 monitor, (c) temporal variations of ammonium nitrate mass fraction (ANMF).

Selection of the optimal PMF solution

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PMF analysis based on the ACSM mass spectra was performed for 1 to 8 factors. Figure S2a showed Q/Q_{exp} as a function of the number of factors P. According to Ulbrich et al.,²³ values of $Q/Q_{exp} > 1$ indicate underestimation of the errors or variability in the factor profiles that cannot be simply modeled as the sum of the given number of components. On the contrary, Q/Q_{exp} <1 means that the errors of the input data have been overestimated. As presented in Figure S2a, Q/Q_{exp} decreased with the increasing number of factors.



In the two-factor solution, $Q/Q_{\rm exp}$ showed a large decrease from 1.37 to 0.88 compared to the one-factor solution, implying that the additional factor explained significantly more of the variation in the data. However, Factor 1 in the two-factor solution appeared to be a mixture of HOA and COA based on its diurnal cycles and mass spectra profiles. Therefore, more OA factors need to be considered. When the factor number increased to three, Factor 1 in the twofactor solution was separated into two new factors, which were identified as HOA and COA. Another factor was characterized as OOA. When the number of factors changed from four to eight, no obvious decrease of Q/Q_{exp} was observed and the mass spectra of new factors could not be well explained. For example, in the fourfactor solution, a new factor which showed only an obvious peak at m/z 43 was separated. No similar mass spectra profile has been observed for organic aerosol from emission sources. Thus the threefactor solution was chosen as the optimal solution. Further, the rotational ambiguity of the three-factor solution was explored by varying FPEAK between -1.0 and +1.0 (step: 0.1). Lower Q/Qexp values can indicate a better fit to the dataset and is used as one criterion for selecting a suitable solution.²³ As shown in Figure 2b, the lowest Q/Qexp was obtained at approximately 0. Therefore, FPEAK = 0 was chosen as the best solution.

Figure S2. (a) $Q/Q_{expected}$, where Q is the sum of the squared scaled residuals over the entire dataset, plotted against the number of factors used in the positive matrix factorization (PMF) solution. (b) Q/Q_{expected} plotted against the rotational forcing parameter (FPEAK) for solutions with three factors.

Figure S3. (a) The box and whiskers plot showing the distributions of scaled residuals for each m/z, (b) Time series of the measured organic mass and the reconstructed organic mass.

Figure S4. Mass spectra profiles of the two-factor solution.



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Figure S5. Mass spectra profiles of the four-factor solution.

Figure S6. The back trajectory clustering analysis associated with the corresponding average PM_1 mass and composition during the campaign. The inserted bar graph shows the directional variation of BTs before and during the Anniversary.

References

- 1 Cheng, Y. F., Heintzenberg, J., Wehner, B., Wu, Z. J., Su, H., Hu, M., and Mao, J. T.: Traffic restrictions in Beijing during the Sino-African Summit 2006: aerosol size distribution and visibility compared to long-term in situ observations, Atmos Chem Phys, 8, 7583-7594, 2008.
- 2 Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: from air pollution to climate change, 2nd Edition, John Wiley and Sons, Inc., Hoboken, New Jersey, 2006.
- Akimoto, H.: Global air quality and pollution, Science, 302, 1716-1719, DOI 10.1126/science.1092666, 2003.
- 4 He, K. B., Yang, F. M., Ma, Y. L., Zhang, Q., Yao, X. H., Chan, C. K., Cadle, S., Chan, T., and Mulawa, P.: The characteristics of



J. Name., 2013, 00, 1-3 | 9

View Article Online DOI: 10.1039/C6FD00004E

PM2.5 in Beijing, China, Atmos Environ, 35, 4959-4970, Doi 10.1016/S1352-2310(01)00301-6, 2001.

- 5 State Statistical Bureau China, 2015. Statistical Yearbook of China. China Statistics Press, Beijing
- 6 Gao, Y., Liu, X., Zhao, C., and Zhang, M.: Emission controls versus meteorological conditions in determining aerosol concentrations in Beijing during the 2008 Olympic Games, Atmos Chem Phys, 11, 12437-12451, 10.5194/acp-11-12437-2011, 2011.
- 7 Zhang, Y. M., Zhang, X. Y., Sun, J. Y., Lin, W. L., Gong, S. L., Shen, X. J., and Yang, S.: Characterization of new particle and secondary aerosol formation during summertime in Beijing, China, Tellus B, 63, 382-394, 10.1111/j.1600-0889.2011.00533.x, 2011.
- 8 Wu, Z. J., Hu, M., Lin, P., Liu, S., Wehner, B., and Wiedensohler, A.: Particle number size distribution in the urban atmosphere of Beijing, China, Atmos Environ, 42, 7967-7980, 10.1016/j.atmosenv.2008.06.022, 2008.
- 9 Wang, S. X., Zhao, M., Xing, J., Wu, Y., Zhou, Y., Lei, Y., He, K. B., Fu, L. X., and Hao, J. M.: Quantifying the Air Pollutants Emission Reduction during the 2008 Olympic Games in Beijing, Environ Sci Technol, 44, 2490-2496, 10.1021/es9028167, 2010.
- 10 Zhang, R., Jing, J., Tao, J., Hsu, S. C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., Zhao, Y., and Shen, Z.: Chemical characterization and source apportionment of PM2.5 in Beijing: seasonal perspective (vol 13, pg 7053, 2013), Atmos Chem Phys, 14, 175-175, 10.5194/acp-14-175-2014, 2014.
- 11 Cermak, J., and Knutti, R.: Beijing Olympics as an aerosol field experiment, Geophys Res Lett, 36, Artn L1080610.1029/2009gl038572, 2009.
- 12 Liu, Y., He, K. B., Li, S. S., Wang, Z. X., Christiani, D. C., and Koutrakis, P.: A statistical model to evaluate the effectiveness of PM2.5 emissions control during the Beijing 2008 Olympic Games, Environ Int, 44, 100-105, 10.1016/j.envint.2012.02.003, 2012.
- 13 Huang, X. F., He, L. Y., Hu, M., Canagaratna, M. R., Sun, Y., Zhang, Q., Zhu, T., Xue, L., Zeng, L. W., Liu, X. G., Zhang, Y. H., Jayne, J. T., Ng, N. L., and Worsnop, D. R.: Highly timeresolved chemical characterization of atmospheric submicron particles during 2008 Beijing Olympic Games using an Aerodyne High-Resolution Aerosol Mass Spectrometer, Atmos Chem Phys, 10, 8933-8945, 10.5194/acp-10-8933-2010, 2010.
- 14 Xu, W. Q., Sun, Y. L., Chen, C., Du, W., Han, T. T., Wang, Q. Q., Fu, P. Q., Wang, Z. F., Zhao, X. J., Zhou, L. B., Ji, D. S., Wang, P. C., and Worsnop, D. R.: Aerosol composition, oxidation properties, and sources in Beijing: results from the 2014 Asia-Pacific Economic Cooperation summit study, Atmos. Chem. Phys., 15, 13681-13698, doi:10.5194/acp-15-13681-2015, 2015.
- 15 Chen, C., Sun, Y. L., Xu, W. Q., Du, W., Zhou, L. B., Han, T. T., Wang, Q. Q., Fu, P. Q., Wang, Z. F., Gao, Z. Q., Zhang, Q., and Worsnop, D. R.: Characteristics and sources of submicron aerosols above the urban canopy (260 m) in Beijing, China, during the 2014 APEC summit, Atmos. Chem. Phys., 15, 12879–12895, doi:10.5194/acp-15-12879-2015, 2015.
- 16 Zhang, J. K., L. L. Wang, Y. H. Wang, and Y. S. Wang: Submicron aerosols during the Beijing Asia–Pacific Economic Cooperation conference in 2014, Atmospheric Environment, doi:http://dx.doi.org/10.1016/j.atmosenv.2015.06.049.
- 17 Wang, T., Nie, W., Gao, J., Xue, L. K., Gao, X. M., Wang, X. F., Qiu, J., Poon, C. N., Meinardi, S., Blake, D., Wang, S. L., Ding, A. J., Chai, F. H., Zhang, Q. Z., and Wang, W. X.: Air quality during the 2008 Beijing Olympics: secondary pollutants and regional impact, Atmos Chem Phys, 10, 7603-7615, 10.5194/acp-10-7603-2010, 2010.

- 18 Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass Concentrations of Ambient Aerosol, Aerosol Sci Tech, 45, 780-794, Pii 934555189, 10.1080/02786826.2011.560211, 2011.
- 19 Petzold, A., and Schonlinner, M.: Multi-angle absorption photometry - a new method for the measurement of aerosol light absorption and atmospheric black carbon, J Aerosol Sci, 35, 421-441, 10.1016/j.jaerosci.2003.09.005, 2004.
- 20 Petzold, A., Schloesser, H., Sheridan, P. J., Arnott, W. P., Ogren, J. A., and Virkkula, A.: Evaluation of multiangle absorption photometry for measuring aerosol light absorption, Aerosol Sci Tech, 39, 40-51, 10.1080/027868290901945, 2005.
- 21 Zheng, G. J., Duan, F. K., Su, H., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Poschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions, Atmos Chem Phys, 15, 2969-2983, 10.5194/acp-15-2969-2015, 2015.
- 22 Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Sci Tech, 46, 258-271, 10.1080/02786826.2011.620041, 2012.
- 23 Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos Chem Phys, 9, 2891-2918, 2009.
- 24 Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Ulbrich, I. M., Ng, N. L., Worsnop, D. R., and Sun, Y. L.: Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review, Anal Bioanal Chem, 401, 3045-3067, 10.1007/s00216-011-5355-y, 2011.
- 25 Young, D. E., Allan, J. D., Williams, P. I., Green, D. C., Flynn, M. J., Harrison, R. M., Yin, J., Gallagher, M. W., and Coe, H.: Investigating the annual behaviour of submicron secondary inorganic and organic aerosols in London, Atmos Chem Phys, 15, 6351-6366, 10.5194/acp-15-6351-2015, 2015.
- 26 Parworth, C., Fast, J., Mei, F., Shippert, T., Sivaraman, C., Tilp, A., Watson, T., and Zhang, Q.: Long-term measurements of submicrometer aerosol chemistry at the Southern Great Plains (SGP) using an Aerosol Chemical Speciation Monitor (ACSM), Atmos Environ, 106, 43-55, 10.1016/j.atmosenv.2015.01.060, 2015.
- 27 Zhang, Q., Worsnop, D. R., Canagaratna, M. R., and Jimenez, J. L.: Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: insights into sources and processes of organic aerosols, Atmos Chem Phys, 5, 3289-3311, 2005.
- 28 Huang, X. F., He, L. Y., Xue, L., Sun, T. L., Zeng, L. W., Gong, Z. H., Hu, M., and Zhu, T.: Highly time-resolved chemical characterization of atmospheric fine particles during 2010 Shanghai World Expo, Atmos Chem Phys, 12, 4897-4907, 10.5194/acp-12-4897-2012, 2012.
- 29 Sun, Y. L., Wang, Z. F., Fu, P. Q., Yang, T., Jiang, Q., Dong, H. B., Li, J., and Jia, J. J.: Aerosol composition, sources and processes during wintertime in Beijing, China, Atmos Chem Phys, 13, 4577-4592, 10.5194/acp-13-4577-2013, 2013.
- 30 Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.:

10 | J. Name., 2012, 00, 1-3

This journal is $\ensuremath{\mathbb{C}}$ The Royal Society of Chemistry 20xx

Journal Name

Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, Geophys Res Lett, 34, Artn L13801,10.1029/2007gl029979, 2007.

- 31 Xu, J., Zhang, Q., Chen, M., Ge, X., Ren, J., and Qin, D.: Chemical composition, sources, and processes of urban aerosols during summertime in northwest China: insights from high-resolution aerosol mass spectrometry, Atmos Chem Phys, 14, 12593-12611, 10.5194/acp-14-12593-2014, 2014.
- 32 He, L. Y., Lin, Y., Huang, X. F., Guo, S., Xue, L., Su, Q., Hu, M., Luan, S. J., and Zhang, Y. H.: Characterization of highresolution aerosol mass spectra of primary organic aerosol emissions from Chinese cooking and biomass burning, Atmos Chem Phys, 10, 11535-11543, 10.5194/acp-10-11535-2010, 2010.
- 33 Sun, Y. L., Jiang, Q., Wang, Z. F., Fu, P. Q., Li, J., Yang, T., and Yin, Y.: Investigation of the sources and evolution processes of severe haze pollution in Beijing in January 2013, J Geophys Res-Atmos, 119, 4380-4398, 10.1002/2014JD021641, 2014.
- 34 Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Slowik, J. G., Richter, R., Reche, C., Alastuey, A., Querol, X., Seco, R., Penuelas, J., Jimenez, J. L., Crippa, M., Zimmermann, R., Baltensperger, U., and Prevot, A. S. H.: Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data, Atmos Chem Phys, 12, 1649-1665, 10.5194/acp-12-1649-2012, 2012.
- 35 Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the 1525-1529. Atmosphere, Science. 326. 10.1126/science.1180353, 2009.
- 36 Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prevot, A. S. H., Dinar, E., Rudich, Y., and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmos Chem Phys, 10, 4625-4641, 10.5194/acp-10-4625-2010, 2010.
- 37 Wang, Z.S., Li, Y.T., Chen, T., Li, L.J., Liu, B.X., Zhang, D.W., Sun, F., Wei, Q., Jiang, L., and Pan, L.B.: Changes in atmospheric composition during the 2014 APEC conference in Beijing, J Geophys Res-Atmos, 10.1002/2015JD023652, 2015.
- 38 Draxler, R., Stunder, B., Rolph, G., et al.: HYSPLIT4 user's guide, Version 4.9, http://ready.arl.noaa.gov/HYSPLIT.php (last access:January 2010), 2009.
- 39 Saxena, P., and Seigneur, C.: On the Oxidation of So2 to Sulfate in Atmospheric Aerosols, Atmos Environ, 21, 807-812, Doi 10.1016/0004-6981(87)90077-1, 1987.
- 40 Arimoto, R., Duce, R. A., Savoie, D. L., Prospero, J. M., Talbot, R., Cullen, J. D., Tomza, U., Lewis, N. F., and Jay, B. J.: Relationships among aerosol constituents from Asia and the

North Pacific during PEM-West A, J Geophys Res-Atmos, 101, 2011-2023, Doi 10.1029/95jd01071, 1996.

- 41 Yang, F., Tan, J., Zhao, Q., Du, Z., He, K., Ma, Y., Duan, F., Chen, G., and Zhao, Q.: Characteristics of PM2.5 speciation in representative megacities and across China, Atmos Chem Phys, 11, 5207-5219, 10.5194/acp-11-5207-2011, 2011.
- 42 Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, Environ Sci Technol, 42, 4478-4485, 10.1021/es703009q, 2008.
- 43 Pang, Y., Turpin, B. J., and Gundel, L. A.: On the importance of organic oxygen for understanding organic aerosol particles, Aerosol Sci Tech, 40, 128-133, 10.1080/02786820500423790, 2006.
- 44 Dall'Osto, M., Paglione, M., Decesari, S., Facchini, M. C., O'Dowd, C., Plass-Duellmer, C., and Harrison, R. M.: On the Origin of AMS "Cooking Organic Aerosol" at a Rural Site, Environ Sci Technol, 49, 13964-13972, 10.1021/acs.est.5b02922, 2015.
- 45 Pusede, S. E., Duffey, K. C., Shusterman, A. A., Saleh, A., Laughner, J. L., Wooldridge, P. J., Zhang, Q., Parworth, C. L., Kim, H., Capps, S. L., Valin, L. C., Cappa, C. D., Fried, A., Walega, J., Nowak, J. B., Hoff, R. M., Berkoff, T. A., Beyersdorf, A. J., Olson, J., Crawford, J. H., and Cohen, R. C.: On the effectiveness of nitrogen oxide reductions as a control over ammonium nitrate aerosol, Atmos. Chem. Phys. Discuss., 15, 27087-27136, doi:10.5194/acpd-15-27087-2015, 2015.

This journal is © The Royal Society of Chemistry 20xx