



Evaluating the Effects of Springtime Dust Storms over Beijing and the Associated Characteristics of Sub-Micron Aerosol

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ABSTRACT

In order to understand the characteristics, sources and processes of non-refractory submicron particles (NR-PM₁), an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was deployed to acquire observational data during the spring (April 1 to 30) in Beijing, China, in 2012. Based on PM₁₀, PM_{2.5} and NR-PM₁ mass concentrations observation, satellite images and the back trajectory analysis, one haze and dust storm episodes were recorded during the campaign, in addition, one clean episodes was also added to the comparison as a reference. The NR-PM₁ mass concentration was 97 μg m⁻³ during the haze episodes, while it was approximately 12 times and 1.7 times that on the clean and dust episodes, respectively. In addition, the secondary inorganic aerosol (sulfate, nitrate and ammonium) contributed the largest fraction of NR-PM₁ (69%) during the haze episodes. The dust storms originated from the northwestern caused the PM₁₀ peaking at 826 μg m⁻³, with an average of 364 ± 186 μg m⁻³ and higher than the haze episodes (241 μg m⁻³). In addition, compared to the clean episodes (the NR-PM₁ mass was 8 μg m⁻³), the dust storms caused the average NR-PM₁ mass reaching 56 μg m⁻³, corresponding to the secondary components significantly increased, including sulfate (9.5 μg m⁻³), nitrate (8 μg m⁻³), ammonium (6 μg m⁻³) and OOA (6 μg m⁻³). The backward trajectory clustering analysis indicated the air mass from the southeast (at a frequency more than 30%) contained the higher NR-PM₁ concentration (more than 80 μg m⁻³) corresponding to the higher sulfate, nitrate and ammonium contributions.

Keywords: NR-PM₁; Organic aerosols; Dust storm; Springtime; Beijing.

INTRODUCTION

Fine particles (PM_{2.5} and PM₁, defined as particulate matter with an aerodynamic diameter of less than 2.5 μm and 1 μm, respectively) have significantly impacted climate change and visibility and also threaten human health (Guo *et al.*, 2014). As the political, economic and cultural center of China, Beijing frequently encountered severe haze pollution

as a result of the high concentrations of fine particles (Sun *et al.*, 2013b; Guo *et al.*, 2014). Because fine particles are a complicated mixture of various species, a deep understanding of the variations in the chemical properties of fine particles is essential for source identification and pollution control (Huang *et al.*, 2011).

Vehicle emissions, cooking and the secondary formation of aerosols from anthropogenic precursors have all been identified as important sources of fine particulate in the Beijing area (Huang *et al.*, 2010; Sun *et al.*, 2010; Sun *et al.*, 2013b; Zhang *et al.*, 2014; Hu *et al.*, 2016). Dust storms are also an important source of fine particles and can cause adverse health effects for humans (Wang *et al.*, 2013). Therefore, it is very important and meaningful to study the chemical composition and the processes associated with dust particles. The Gobi Desert, located in south Mongolia and north China, is one of the major source regions of dust storms (Arimoto *et al.*, 2006). In spring, the surface dust of the Gobi Desert can internally mix with secondary compounds through coagulation and heterogeneous reactions while dust

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particles are transported (Tobo *et al.*, 2010; Zamora *et al.*, 2011; Wang *et al.*, 2012a).

Most of the previous studies about particles rely on filter sampling followed by laboratory analysis, a method that has some drawbacks, such as the long amount of time necessary to collect particulate matter, laboriousness, low resolution (Huang *et al.*, 2011) and poor capacity for deep analysis of organic aerosols (Hildebrandt *et al.*, 2010). In recent years, high-resolution time-of-flight aerosol mass spectrometers were widely used to characterize the main species of submicron aerosols (Canagaratna *et al.*, 2007; Jimenez *et al.*, 2009; Huang *et al.*, 2010). In particular, based on the high resolution characteristics of the HR-ToF-AMS, multiple organic aerosol (OA) sources have been identified and recognized by combining the positive matrix factorization (PMF) model with the high-resolution OA mass spectral matrix (Ulbrich *et al.*, 2009). Although many studies have been conducted in Beijing to evaluate the composition of submicron particles using HR-ToF-AMS, these observations have mainly been carried out in the summer, autumn and winter (Huang *et al.*, 2010; Sun *et al.*, 2013b; Zhang *et al.*, 2014; Chen *et al.*, 2015; Xu *et al.*, 2015; Zhang *et al.*, 2016). Although Sun *et al.* (2015) used Aerosol Chemical Speciation Monitors (ACSM) to analyze the variation of submicron particles in spring, the elemental composition and source apportionment of the organic aerosol were not studied. More studies are needed, especially to analyze the characteristics, the elemental compositions and source apportionment of submicron particles in the springtime. In addition, the frequent dust storms occurring in spring could impact the submicron particles.

The objective of this work is to contribute to the chemical characterization, elemental composition and source apportionment of submicron particles and to characterize the relative humidity effects on submicron particles. This work also aims to investigate how dust storm episodes could influence the chemical composition of submicron particles in an urban site, such as Beijing.

EXPERIMENTAL METHODS

Sampling Site and Sampling Period

This study was carried out in the courtyard of the Institute of Atmospheric Physics (IAP, 39.97°N, 116.37°E) during April 2012. The site was located between the north 3rd and 4th ring road in Beijing. It is approximately 1 km from the 3rd ring road, 200 m west of the G6 Highway (which runs north-south) and 50 m south of Beitucheng West Road (which runs east-west). The HR-ToF-AMS instrument was installed inside the two story laboratory building, and the ambient air sampling port was installed approximately 12 m above the ground. This site was surrounded by heavy traffic, restaurants, residential areas, and research institutions, and the local environment is typical of urban pollution in Beijing (Liu *et al.*, 2016)

Instrumentation and Sampling

An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was introduced by DeCarlo

et al. (2006). The HR-ToF-AMS was operated in the sensitive V-mode and the high mass resolution W-mode, alternating every 5 min. In V-mode, the aerosol mass spectrometer (AMS) cycled through mass spectrum (MS) mode and particle time-of-flight (PToF) mode every 30 s. No PToF data were sampled in W-mode because of the low signal-to-noise (S/N) ratio. The HR-ToF-AMS was calibrated for inlet flow, ionization efficiency (IE) and particle sizing at the beginning and end of the study following the standard protocols (Jayne *et al.*, 2000; Jimenez *et al.*, 2003). The detection limit (DL) of the HR-ToF-AMS is related to the resolution of the instrument, the signal-to-noise ratio, the vaporization temperature and the ionizer background (DeCarlo *et al.*, 2006). The ionizer background, with influence on the DL, includes measurements of elevated aerosol mass concentrations, short-term instrument history and long-term instrument contamination (Drewnick *et al.*, 2009). In this study, the DL of each individual species is taken as three times the standard deviation of the corresponding signal of particle-free air (DeCarlo *et al.*, 2006; Sun *et al.*, 2009). The 5-min DL of organics, nitrate, sulfate, ammonium and chloride were determined to be 0.056, 0.006, 0.008, 0.04 and 0.014 $\mu\text{g m}^{-3}$, respectively. In addition to the HR-ToF-AMS, a Thermo TEOM1405 (Filter Dynamic Measurement System) was used to measure the mass concentrations of PM₁₀ and PM_{2.5}. Meteorological data, such as temperature (T), relative humidity (RH) and wind speed/direction (WS/WD), were also available from an automatic meteorological observation instrument (Milos520, Vaisala, Finland).

Data Analysis

The standard ToF-AMS data analysis software packages SQUIRREL version 1.50 and PIKA version 1.09, 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 (He *et al.*, 2011; Zhang *et al.*, 2014). A previous study proposed that the collection efficiency (CE) is affected by high aerosol acidity, high relative humidity and a high ammonium nitrate mass fraction (ANMF > 0.4) (Middlebrook *et al.*, 2012). In this study, a silica-gel desiccant was used to keep the relative humidity below 40% in the sampling line, and the aerosol acidity was nearly neutral. The ANMF was at times higher than 0.4. Therefore, a variable CE, based on the higher ANMF value, was applied, $CE_{\text{dry}} = \max(0.45, 0.0833 + 0.9167 \times \text{ANMF})$. The default relative ionization efficiency (RIE) values, 1.1, 1.3 and 1.4, were applied to calculate the mass concentration of nitrate, chloride and the organic components, respectively. RIE values of 3.9 and 1.0 were used to calculate ammonium and sulfate, respectively. These two values were determined from IE calibrations using ammonium nitrate and ammonium sulfate particles. The elemental analysis of the organic components identified by positive matrix factorization (PMF) was carried out using previously described methods (Aiken *et al.*, 2007, 2008).

Positive matrix factorization (PMF) was used to analyze the high-resolution mass spectra (HRMS) (m/z 10–120) obtained using HR-ToF-AMS to identify the major organic

components (Reff *et al.*, 2007). The HRMS data and error matrices were generated as outlined in DeCarlo *et al.* (2010). Data and error matrices used as inputs for the PMF analysis were generated with the default fragmentation waves in PIKA. The noise values were calculated as the sum of the electronic and Poisson ion-counting errors for the relevant high-resolution ion fragment (Allan *et al.*, 2003; Ulbrich *et al.*, 2009). Ions with a S/N ratio < 0.2 were removed from the HRMS data and error matrices before the PMF analysis. Weak ions ($0.2 < \text{SNR} < 2$) were downweighted by a factor of 3, and bad ions ($\text{SNR} < 0.2$) were removed from the analysis (Paatero and Hopke, 2003). Solutions for one to eight factors were explored with varying rotational parameters ($-1 \leq \text{FPEAK} \leq 1$, in increments of 0.1). Finally, the 3-factor was chosen as the optimal solution for this analysis.

RESULTS AND DISCUSSION

Aerosol Components by Positive Matrix Factorization

In this sampling campaign, positive matrix factorization analysis of the high resolution mass spectrometer (HRMS) data identified three organic aerosol components: oxygenated organic aerosol (OOA), cooking organic aerosol (COA) and hydrocarbon organic aerosol (HOA) (Fig. 1). Previous studies noted that OOA formed from secondary organic aerosol through a gas-to-particle conversion (Huang *et al.*, 2011, 2012; Zhang *et al.*, 2014). The O/C ratio of the OOA identified in this study was 0.79 (Fig. 1(a)), higher than the O/C ratios of OOA reported in other districts, including winter in Beijing (0.62) (Zhang *et al.*, 2014), summer in Beijing (0.47) (Huang *et al.*, 2010), and autumn in Kaiping (0.52) (He *et al.*, 2011). The high-resolution mass spectra of OOA were characterized by prominent $\text{C}_x\text{H}_y\text{O}_z$ fragments, especially CO_2^+ (m/z 44) and CO^+ (m/z 28). The time series trend of OOA typically correlated well with tracer indicators ($\text{NO}_3 + \text{SO}_4$) (Fig. 1(a1)), and the OOA had the best correlations with sulfate ($R^2 = 0.76$) and nitrate ($R^2 = 0.58$),

consistent with the results from a study conducted in Fresno, CA (Ge *et al.*, 2012).

Cooking activity (including fuel and food materials in cooking) accounts for a significant fraction of the organic aerosol at all urban sites (Chow *et al.*, 2007; Huang *et al.*, 2010; Sun *et al.*, 2010; Zhang *et al.*, 2014). The mass spectra of the COA were characterized by the prominent ion series of C_xH_y^+ , especially $\text{C}_n\text{H}_{2n}^+$, including m/z 41 and m/z 55 (Zhang *et al.*, 2014; Hu *et al.*, 2016; Zhang *et al.*, 2016). This result indicates a significant presence of unsaturated organic compounds (e.g., unsaturated fatty acids) and is consistent with the MS characteristics of primary emissions from Chinese cooking (He *et al.*, 2010). The COA showed correlations with a few $\text{C}_6\text{H}_{10}\text{O}$ ions ($R^2 = 0.48$) (Fig. 1(b1)). These ions were tracer indicators of the spectral sources of cooking emissions and could be used as spectral markers for COA (Zhang *et al.*, 2014).

Previous studies reported that HOA can typically be attributed to fossil fuel combustion (Lanz *et al.*, 2007; Zhang *et al.*, 2007; Ulbrich *et al.*, 2009). Gasoline and diesel fuel combustion emissions consist mainly of n-alkanes, branched alkanes, cycloalkanes and aromatics (Canagaratna *et al.*, 2004), leading to a high signal for ion series $\text{C}_n\text{H}_{2n}^+$ and $\text{C}_n\text{H}_{2n-1}^+$ in the HRMS. Higher m/z (57) and lower O/C ratios (< 0.2) are typically used to identify HOA; nearly all exhaust aerosols from diesel trucks and gasoline vehicles have their most prominent peaks at m/z 57 (Mohr *et al.*, 2009). In this study, the HOA was characterized by prominent hydrocarbon ion peaks at m/z 41, 43, 55, and 57 (Fig. 1(c)). The O/C ratio (0.14) was dramatically higher than the value of 0.03, which was measured during the characterization of emissions from a motor vehicle (Mohr *et al.*, 2009). Sun *et al.* (2011b) deployed an AMS on two high-traffic highways in New York City and found the O/C ratios were only 0.04. However, the O/C ratios measured in Beijing (0.17) (Huang *et al.*, 2010) and Shanghai (0.16) (Huang *et al.*, 2012) were similar to the result of this study. The HOA and NO_x were

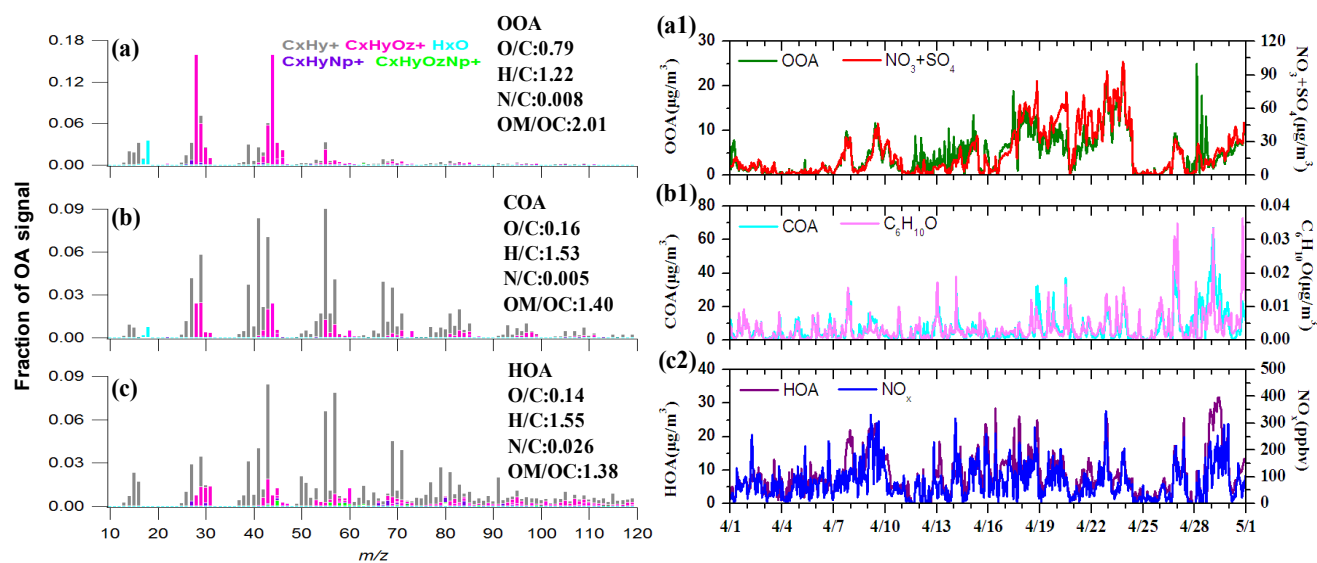


Fig. 1. The HRMS profiles of the (a) OOA, (b) COA and (c) HOA identified by PMF and the time series of (a1) the OOA and $\text{NO}_3 + \text{SO}_4$; (b1) the COA and $\text{C}_6\text{H}_{10}\text{O}$; (c1) the HOA and NO_x .

well correlated ($R^2 = 0.60$) and had pronounced peaks during the morning and night, corresponding to traffic emissions (Fig. 1(c1)). These facts indicate that HOA is likely a surrogate for the combustion of primary organic aerosol (POA), a conclusion reached in many other studies (Aiken *et al.*, 2009; Ulbrich *et al.*, 2009).

Characteristics of NR-PM₁

Mass Concentrations, Composition and Size Distribution of NR-PM₁

Total non-refractory submicron particle (NR-PM₁) mass concentration ranged from 0.3 to 209.5 $\mu\text{g m}^{-3}$, with an average of $49.7 \pm 40.2 \mu\text{g m}^{-3}$ (Fig. 2(d)). This mean value was lower than previously reported values of NR-PM₁ mass concentrations measured using an AMS in the Beijing district. For example, the mean mass concentrations during the summers of 2006 and 2008 were $80.0 \mu\text{g m}^{-3}$ (Sun *et al.*, 2010) and $63.1 \mu\text{g m}^{-3}$ (Huang *et al.*, 2010), respectively; the mean mass concentrations during the winters of 2011 and 2012 were $66.8 \mu\text{g m}^{-3}$ (Sun *et al.*, 2013b) and $89.3 \mu\text{g m}^{-3}$ (Zhang *et al.*, 2014), respectively. However, values in this study approached the mean mass concentrations found during the spring of 2012 in Beijing ($52 \mu\text{g m}^{-3}$) (Sun *et al.*, 2015). Compared with other districts, this result is much higher than other urban districts, such as New York City ($11.0 \mu\text{g m}^{-3}$) (Sun *et al.*, 2011a) and Pittsburgh ($14.8 \mu\text{g m}^{-3}$) (Zhang *et al.*, 2005); NR-PM₁ mass concentrations were 10–30 $\mu\text{g m}^{-3}$ in Europe (Kubelova *et al.*, 2015). In some atmospheric background areas in China, the NR-PM₁

mass concentrations were much lower than in the urban areas; for example, Du *et al.* (2015) measured mass concentration of $11.9 \mu\text{g m}^{-3}$ which at a national background monitoring station in the Tibetan plateau.

As mentioned in Section 3.1, OA components (OOA, COA, HOA) were identified using the PMF model. The OOA concentration varied within the range of 0.01–24.99 $\mu\text{g m}^{-3}$, with an average value of $4.65 \mu\text{g m}^{-3}$, and accounted for 23% (Fig. 3(b)) of the OA. The HOA varied between 0.01 $\mu\text{g m}^{-3}$ and 31.7 $\mu\text{g m}^{-3}$, with an average of $8.5 \mu\text{g m}^{-3}$, and contributed 42% (Fig. 3(b)) to the OA, which indicates this research district was influenced by the fossil fuel combustion during the observation period. The COA varied within the range of 0.02–66.9 $\mu\text{g m}^{-3}$, with a mean value of $7.2 \mu\text{g m}^{-3}$, and accounted for 35% (Fig. 3(b)) of the OA. This result was higher than most reported values; for example, the COA accounted for 20% of the organic aerosol observed in the winter in Beijing (Zhang *et al.*, 2014) and 24.4% of the organic aerosol observed in the summer (Huang *et al.*, 2010). The COA accounts for 16% of organic aerosol in New York City (Sun *et al.*, 2011a) and 17% of organic aerosol in Barcelona (Mohr *et al.*, 2012).

The average chemical composition of NR-PM₁ was showed in Fig. 3(a). The organics accounted for 51% of the NR-PM₁ components, followed by sulfate (18%), nitrate (16%), ammonium (12%) and chloride (3%). Compared with previous studies on the average contribution of organics, the organics contribution value (51%) measured in the present study was higher than those observed during the

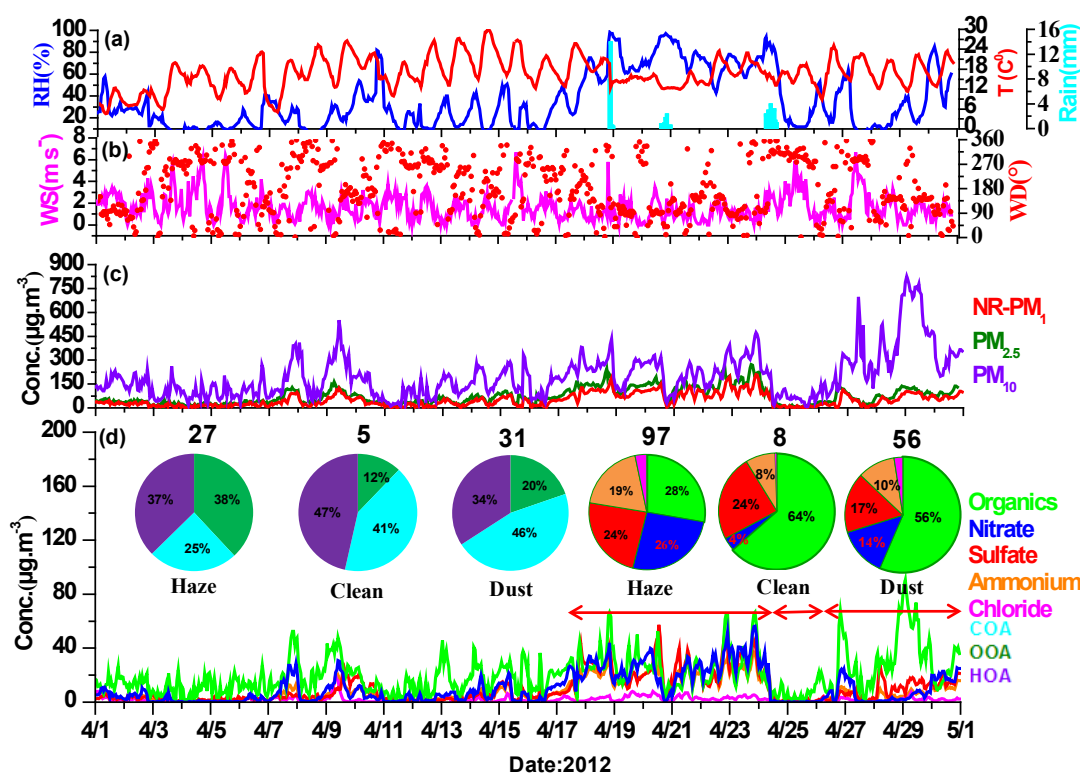


Fig. 2. Temporal evolution of (a) ambient temperature, relative humidity and rainfall; (b) wind direction and wind speed; (c) NR-PM₁, PM_{2.5} and PM₁₀ mass concentrations; (d) NR-PM₁ species concentrations and the pie charts in (d) showed the average chemical composition during the haze, clean and dust episodes.

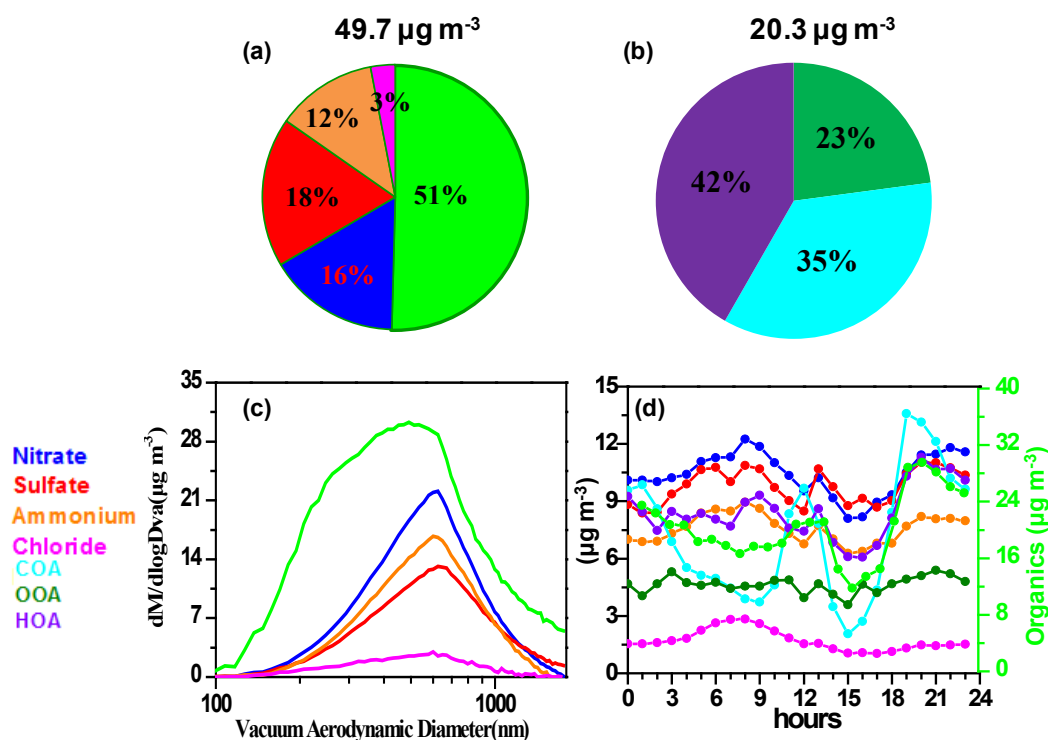


Fig. 3. The mean NR-PM₁ (a) and OA compositions (b); (c) the average mass size distributions of NR-PM₁ species; (d) the average diurnal variation of NR-PM₁ species.

summer in Beijing in 2006 (35%) (Sun *et al.*, 2010) and 2008 (39%) (Huang *et al.*, 2010) but approximated those measured during the winter in Beijing in 2011 (52%) (Sun *et al.*, 2013b) and 2012 (50%) (Zhang *et al.*, 2014).

Organic aerosol showed a broader distribution and appeared in accumulation mode, peaking around 500–550 nm in vacuum aerodynamic diameter (D_{va}), whereas inorganic species (sulfate, nitrate and ammonium) peaked at 600 nm (Fig. 3(c)). The organics also had a smaller ultrafine mode (peaking < 150 nm), this mode was dominated by HOA, which generally is non-hygroscopic with low scavenging rates (Sun *et al.*, 2011a).

The Diurnal Variation of NR-PM₁

The diurnal variation in organics was characterized by two pronounced peaks at noon (12:00–13:00; $21 \mu\text{g m}^{-3}$) and at night (19:00–20:00; $29 \mu\text{g m}^{-3}$) (Fig. 3(d)). The noon peak is related to cooking emission; the evening peak is derived from a combination of cooking and traffic emissions (Huang *et al.*, 2010; Zhang *et al.*, 2014; Sun *et al.*, 2015). The OOA showed a mostly stable diurnal signal, and the highest and lowest values occurred at night ($5.37 \mu\text{g m}^{-3}$) and at noon ($3.57 \mu\text{g m}^{-3}$) (Fig. 3(d)), respectively. The COA showed pronounced diurnal variation with peaks corresponding to meal times appearing at noon (12:00) and in the evening (20:00), having values of $13.1 \mu\text{g m}^{-3}$ and $9.7 \mu\text{g m}^{-3}$, respectively (Fig. 3(d)). This phenomenon indicated that the local cooking-related emission sources play a very important role. The HOA showed a clear diurnal variation pattern. The highest and lowest values occurred in the afternoon (16:00) and at night (20:00), with values of

$6.0 \mu\text{g m}^{-3}$ and $11.3 \mu\text{g m}^{-3}$, respectively. The HOA always increased between 16:00 and 20:00, similar to the COA (Fig. 3(d)).

Sulfate showed significant diurnal variation and appeared as three small peaks throughout the day. The sulfate concentrations during the peak periods were 10.8 , 10.6 and $11.0 \mu\text{g m}^{-3}$, corresponding to the morning (8:00), noon (13:00) and the evening (20:00), respectively (Fig. 3(d)). The morning and evening sulfate peaks depended on the dilution effect of the planetary boundary layer and traffic emission; the noon sulfate peak was related to daytime photochemical sulfate production (Sun *et al.*, 2015). Nitrate concentrations continuously increased throughout the morning, peaking at 8:00 ($12.2 \mu\text{g m}^{-3}$). Nitrate was also characterized by a pronounced evening peak (20:00–21:00), corresponding to $11.4 \mu\text{g m}^{-3}$ (Fig. 3(d)). The diurnal variation in ammonium was similar to sulfate. Ammonium appeared as two small peaks: one in the morning (8:00) and one in the evening (20:00), where the corresponding concentrations were $8.9 \mu\text{g m}^{-3}$ and $8.2 \mu\text{g m}^{-3}$, respectively (Fig. 3(d)). The diurnal variations of sulfate and ammonium were different from others studies. For example, Huang *et al.* (2010) found the diurnal variation of sulfate and ammonium to be a relatively flat trend, except for a small increase in the afternoon during summer. Zhang *et al.* (2014) found that the sulfate, nitrate and ammonium mass concentrations obviously decreased in the morning during winter. These seasonal differences likely impact the gas-to-particle partitioning and aqueous-phase processing, and the planetary boundary layer plays a significant role in spring. The chloride concentration appeared peak in the morning

(Fig. 3(d)); this phenomenon was similar to a study conducted in the spring by Sun *et al.* (2015) and a study conducted in the summer by Huang *et al.* (2010) but was different from a study conducted in winter by Zhang *et al.* (2014).

Relative Humidity (RH) Effects on Chemical Components

The mass concentrations of the NR-PM₁ species appeared to increase as function of relative humidity and reached their highest values at the 60%–70% RH level. When the RH was more than 70%, the mass concentration decreased slightly (Fig. 4(a)). The OA components (OOA, COA and HOA) showed a different dependence on RH (Fig. 4(b)). The mass concentrations, chemical compositions and rate of increase appeared at different RH levels. At low RH (< 50%), the average NR-PM₁ and OA mass concentrations were 34.4 μg m⁻³ and 18.5 μg m⁻³, respectively. Organics dominated the NR-PM₁ composition, accounting for 58% of NR-PM₁, and showed the largest mass concentration rate increase (8.5 μg m⁻³/10% RH) among all the NR-PM₁ components. POA (COA+ HOA) dominated the OA composition at low RH, accounting for 81% of OA (Fig. 4(c)). At high RH (> 50%), the average NR-PM₁ and OA mass concentrations were 88.1 μg m⁻³ and 24.6 μg m⁻³, respectively, and the secondary inorganic species (nitrate + sulfate + ammonium) dominated the NR-PM₁ composition, accounting for 67% of NR-PM₁, which of nitrate represented 25%, sulfate represented 24%, and ammonium represented 18% (Fig. 4(d)). Nitrate showed the largest mass concentration rate increase (9.8 μg m⁻³/RH 10%), followed by sulfate (6.5 μg m⁻³/10% RH), and ammonium (6.5 μg m⁻³/10% RH), indicating the significant effect of RH on secondary inorganic species. The secondary inorganic species (nitrate, sulfate and ammonium) appeared to

rapidly increase because the atmospheric environment exists at a high RH, and the aqueous-phase oxidation is much faster than gas-phase oxidation processes (Seinfeld and Pandis, 2006). The oxidation state in the aqueous-phase relies on droplet pH and mass concentrations of oxidants (Shen *et al.*, 2012). Similar to NR-PM₁ species, the OA components presented synchronous enhancements at high RH levels, especially the OOA, which accounted for 36% of OA and showed the largest enhancement (from 3.5 μg m⁻³ increased to 8.9 μg m⁻³). RH showed a weaker effect on COA and HOA likely due to their lower degree of oxidation and hygroscopicity (Sun *et al.*, 2013a).

The Effects of Dust on Submicron Aerosol

The weather forecast was gathered from the National Satellite meteorological center and combined with mass concentrations of PM_{2.5} and PM₁₀. This portion of the study was divided into three episodes: (i) Haze episodes (April 17–24); (ii) Clean episodes (April 25th); (iii) Dust episodes (April 26–30) (Fig. 2(d)).

Meteorological conditions were predominant factors during the clean period. As shown in Figs. 1(a) and 1(b), wind speed was consistently enhanced, with an average of 2.7 m s⁻¹, which prevailed from the northwest, while RH continuously decreased and reached low levels (with an average of 33.7%), and temperature varied only slightly. Such meteorological conditions would rapidly obliterate local pollutants, leading to the average NR-PM₁, PM_{2.5} and PM₁₀ mass concentrations being 8, 11 and 54 μg m⁻³, respectively, during the clean episodes (Fig. 1(c)). The organics, nitrate, sulfate and ammonium accounted for 64%, 4%, 24% and 8% of NR-PM₁, respectively (Fig. 1(d)).

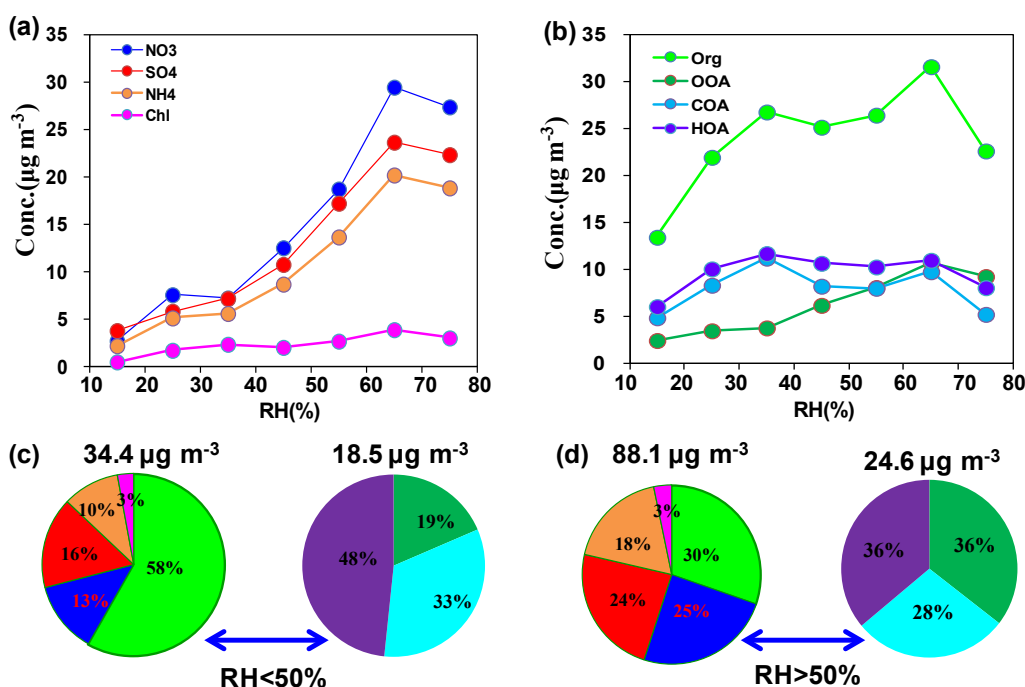


Fig. 4. The variation of mass concentrations of NR-PM₁ species (a) and OA components (b) as a function of relative humidity; (c) the average chemical compositions of NR-PM₁ and OA at low relative humidity (RH < 50%) and high relative humidity (RH > 50%) levels.

The average NR-PM₁, PM_{2.5} and PM₁₀ mass concentrations were 97, 127 and 241 $\mu\text{g m}^{-3}$, respectively, during the haze episodes (Fig. 1(c)). The highest average NR-PM₁ chemical species mass concentration was for the organics (26.8 $\mu\text{g m}^{-3}$), followed by nitrate (25.6 $\mu\text{g m}^{-3}$), sulfate (23.2 $\mu\text{g m}^{-3}$), ammonium (18.7 $\mu\text{g m}^{-3}$), and chloride (3.2 $\mu\text{g m}^{-3}$). In addition, the chemical species composition of NR-PM₁ contained organics, sulfate, nitrate, ammonium and chloride at 28%, 24%, 26%, 19% and 3%, respectively (Fig. 1(d)). Secondary inorganic aerosol (sulfate, nitrate and ammonium) contributed the largest fraction of NR-PM₁ during the haze episodes (66%). Sun *et al.* (2015) indicated that photochemical production, especially higher O₃ and strong solar radiation, plays a dominant role in affecting secondary aerosol formation. In addition, the precursors of NO_x and SO₂ also affect secondary aerosol formation. Pan *et al.* (2016) put forward the nitrogen center theory, indicating that controlling NO_x emissions should be a priority to decrease secondary inorganic aerosol formation in haze pollution. However, heterogeneous formation mechanisms of chemical production that occur primarily in the droplet mode have also been shown to be important contributors of secondary aerosol during fine particles pollution events (Wang *et al.*, 2012b; Sun *et al.*, 2013c). Levy *et al.* (2014) also indicated that the fine particles could undergo rapid hygroscopic growth, and these particles are then characterized by high surface area and low density, which can be easily impacted by the heterogeneous formation mechanisms, leading to more accumulation of secondary aerosol. Therefore, nitrate, sulfate and ammonium were the major contributors to NR-PM₁ during haze pollution.

The amount of rainfall for the three recorded rainfall events ranged from 0.2 mm to 13.8 mm during the haze episodes. The hourly values, which were higher than 5 mm,

appeared at 20:00 (7.8 mm) and 21:00 (13.8 mm) on the April 18. Although the amount of rainfall was small, NR-PM₁ and its chemical components significantly decreased. Huo *et al.* (2010) showed that with increasing rainfall, the dilution of particulate matter is gradually enhanced. Scavenging of particles through falling precipitation is a major removal mechanism, especially in particles sizes between 0.1 and 10 μm . Rainfall between 1 and 5 mm is most important for washout (Qu  rel *et al.*, 2013). We *et al.* (2015) also studied how rainfall can reduce the fine particle mass concentrations in the atmosphere and found that washing significantly affected the air quality.

Large-scale dust storms with high PM₁₀ levels occurred twice in the Middle East region of Inner Mongolia on the April 26th and 27th, and dust was still heavy in the atmosphere on April 28th during the dust episodes (dust episodes spanned April 26–30). The 72 h backward trajectory indicated that the dust storm air mass arrived over the observation site from the northwest region (Fig. 5). The weather at the observation site was relatively warm (T: $17.4 \pm 3.8^\circ\text{C}$) and dry (RH: $31\% \pm 21\%$). The wind speed ranged from 0.1 to 6.7 m s^{-1} , with an average of $1.5 \pm 1.2 \text{ m s}^{-1}$, and the wind was predominantly from the northwest during the dust episodes (Figs. 1(a) and 1(b)). The dust weather caused the PM₁₀ mass concentration reaching 826 $\mu\text{g m}^{-3}$, with an average value of $364 \pm 186 \mu\text{g m}^{-3}$. Additionally, the NR-PM₁ and PM_{2.5} mass concentrations also increased, and the average mass concentrations were $56 \pm 28 \mu\text{g m}^{-3}$ and $72 \pm 36 \mu\text{g m}^{-3}$, respectively (Fig. 1(c)). Wang *et al.* (2014) indicated that the surface soil in the Gobi Desert and the Loess Plateau contained some fine particles. Previous research on the impacts of dust storms on the chemical species mass concentrations of aerosol found that, in the presence of dust storms, most of the airborne particulate originated

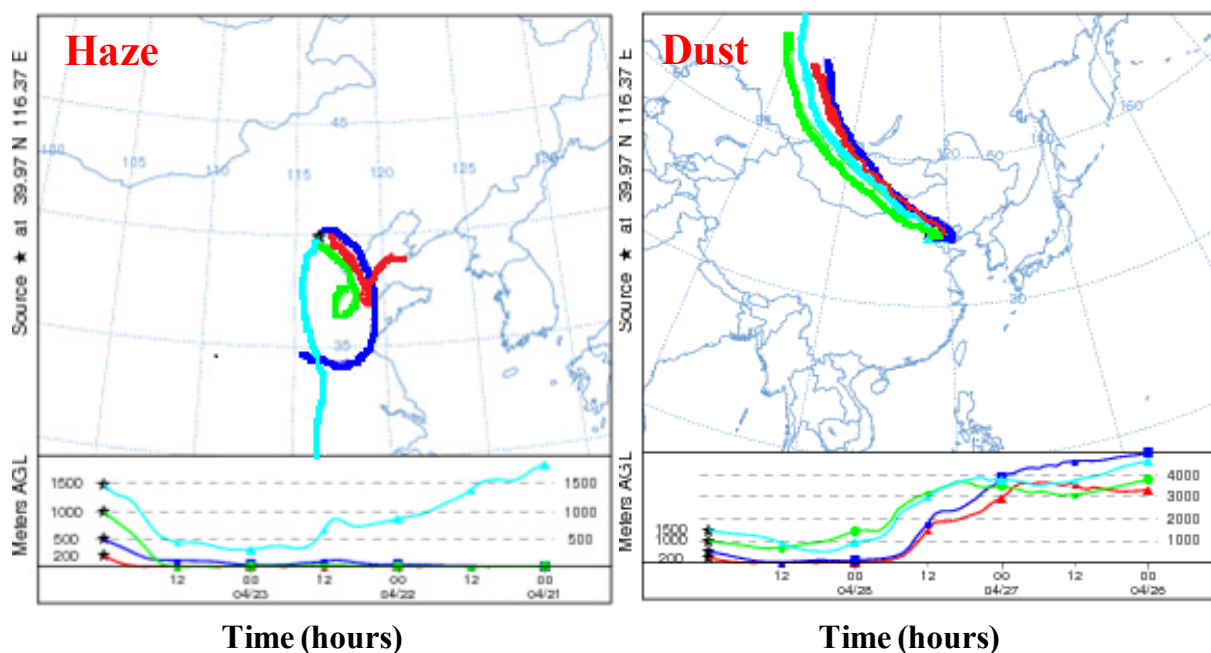


Fig. 5. Backward trajectories of air masses reaching Beijing during the haze episodes (Haze episodes from 17 April to 24 April) and dust episodes (Dust episodes from 26 April to 30 April).

from Gobi Desert soil (Wang *et al.*, 2011, 2013). Compared to the clean episodes (organics, nitrate, sulfate and ammonium mass concentrations of NR-PM₁ were 4.5, 0.2, 1.7, 0.5 $\mu\text{g m}^{-3}$, respectively), the organics, sulfate, nitrate and ammonium mass concentrations reached to 30.7, 8.0, 9.5, 6.0 $\mu\text{g m}^{-3}$, respectively. The organics increased rapidly and accounted for 56% of NR-PM₁ species. This indicates dust aerosol could contribute a large portion of the organics. When dust processes experience high ambient temperatures and low relative humidity, enhanced photochemical oxidation may lead to more production of OOA (6.1 $\mu\text{g m}^{-3}$), the OOA accounted for 20% of OA, and compared to clean period, OOA increased 5.5 $\mu\text{g m}^{-3}$.

Nitrate and sulfate mass concentrations were enhanced during dust episodes but were still much lower than during the haze episodes. This phenomenon can be explained by the formation mechanism and emission sources of sulfate and nitrate during dust process (Wang *et al.*, 2014). Heterogeneous conversion of nitrate and sulfate on dust particles is sensitive to humidity, and their formation efficiency decreases with decreases in humidity (Zhang *et al.*, 1999). Because the humidity was low in the dust episodes (average of 31% \pm 21%), it would have been difficult to form nitrate and sulfate through heterogeneous reactions on the dust particles. The dust particles can absorb sulfuric acid and nitric acid (gas and droplets) formed through heterogeneous reaction of SO₂, NO_x, OH, O₂, H₂O₂ (Wang *et al.*, 2016), leading to the formation of nitrate and sulfate during the dust process. As shown by the backward trajectories (Fig. 5), the heavily polluted and clean air mass originated south and northwest during the haze and dust periods, respectively. Because of the low concentrations of NO_x and SO₂ precursors during the dust process, homogeneous formation of sulfate and nitrate is likely not efficient. During the dust episodes, the average daily mass concentrations of nitrate and sulfate were 7.1, 6.1, 19.2 $\mu\text{g m}^{-3}$ and 3.2, 4.2, 15.3 $\mu\text{g m}^{-3}$ on April 26, 27, 30, respectively; the nitrate mass concentrations were higher than the sulfate concentrations. This phenomenon may be explained as follows: the main formation pathways of nitrate and sulfate during the dust process are photo-oxidation of NO₂ and SO₂ via the OH radical, but the nitrate formation is approximately 10 times faster than the sulfate formation (Wang *et al.*, 2013), yielding higher nitrate concentrations. Furthermore, nitrate, sulfate and ammonium can also be produced in submicron particles as (NH₄)₂SO₄, NH₄HSO₄, NH₄NO₃ during the dust process (Wang *et al.*, 2014).

Elemental Composition of the Organic Aerosol

The high-resolution organic mass spectra were used to determine the elemental composition of C, H, O, N and the mass ratios of the OM/OC (the ratio of organic mass/organic carbon mass) of the OA. The H/C and N/C ratios varied within a range of 1.37–1.81 and 0.003–0.026, with mean values of 1.59 \pm 0.1 and 0.01 \pm 0.005, respectively (Fig. 6(a)); the time series of the O/C and OM/OC ratios varied consistently in the ranges of 0.11–0.57 and 1.21–1.93, with mean values of 0.33 \pm 0.09 and 1.55 \pm 0.15, respectively (Fig. 6(a)). The average values of H/C (1.62), N/C (0.02),

O/C (0.41) and OM/OC (1.71) that Aiken *et al.* (2008) found at the ground site in Mexico City were slightly higher than the results of the present study (H/C:1.59, N/C:0.01, O/C:0.33 and OM/OC:1.55). However, the results of the present study were close to those observed using AMS at an urban site in New York City (1.49, 0.01, 0.36 and 1.62) by Sun *et al.* (2011b) and in Beijing (1.44, 0.01, 0.34 and 1.62) by Zhang *et al.* (2014). The elemental ratios are affected by the elemental analysis method calibration, the correction for interferences in ambient air and the improved fragmentation table for ambient organic aerosol (Aiken *et al.*, 2008). The O/C ratio is regarded as a good reference for the oxidation state and photochemical age of the OA (Jimenez *et al.*, 2009; Ng *et al.*, 2010). Hu *et al.* (2016) indicated that the regression slopes between OOA and Ox (O₃+NO₂) in photochemically processed urban emissions provide a metric to investigate the relative efficiency of secondary organic aerosol formation versus O₃ formation during photochemical oxidation. The atmospheric oxidation state and photochemical oxidation processes appeared different during different observation periods and study areas, leading to differences in the composition of the elements (C, H, O, N) in the OOA. Therefore, different seasons should generate different O/C ratios.

Figs. 6(c) and 6(d) showed the average diurnal variations of the H/C, N/C, O/C and OM/OC ratios. The relative organic composition was made up of five major organic matter fragments, including C_xH_y⁺, C_xH_yO_z⁺, H_xO⁺, C_xH_yN_p⁺, C_xH_yO_zN_p⁺, which decide the H/C, N/C, O/C and OM/OC ratios. The diurnal patterns of the atomic ratios were mostly attributed to diurnal changes in the relative importance of the different sources (Zhang *et al.*, 2014). Both the O/C and OM/OC ratios appeared to peak at 15:00 local time; the peak values corresponded to 0.42 and 1.70 for the O/C ratio and OM/OC ratio, respectively. The peak times occurred when the photochemical production enhanced the formation of secondary organic aerosol. It lead to the content of oxygen increasing substantially, which made the O/C ratio reach its highest value. This study found an additional, significantly lower peak at 12:00 noon. This phenomenon may have been caused by cooking activity or motor vehicle exhaust emissions, which both produce primary organic aerosols with a lower O/C ratio. These findings were similar to the results obtained by Zhang *et al.* (2014). The lowest values of the O/C and OM/OC ratios appeared at 19:00, corresponding to 0.21 and 1.37, respectively, and were related to cooking activities and evening rush hour. As expected, the H/C ratio showed a diurnal variation with a trend opposite to that of the O/C and OM/OC ratios, where the maximum (1.67) and the minimum (1.52) values occurred at 19:00 and 15:00, respectively. The N/C ratio's diurnal pattern was similar to the pattern observed for O/C and OM/OC ratios. Fig. 6(e) showed the average organic elemental compositions, with C, H, O, and N composing 72.4%, 7.3%, 16.9% and 3.4% of the total organic matter, respectively.

Back Trajectory Clustering Analysis

The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to analyze the

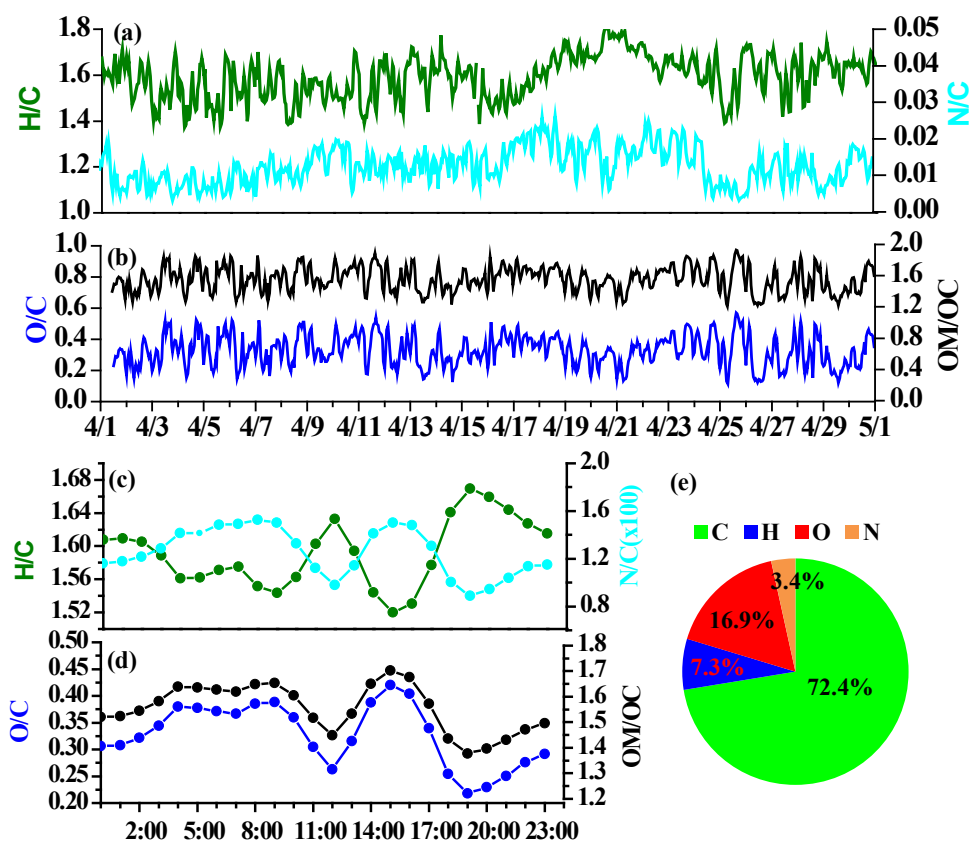


Fig. 6. The time series of (a) H/C and N/C ratios; (b) O/C and OM/OC ratios; the average diurnal variations of (c) H/C and N/C ratios and (d) O/C and OM/OC ratios; (e) the average organics elemental compositions.

influence of air current transport on NR-PM₁ loading and composition. The back trajectory analysis steps are described in detail in a previous study (HYSPLIT4 user's guide, Version 4.9, <http://ready.arl.noaa.gov/HYSPLIT.php>) and are briefly introduced here. First, 72 h back trajectories starting at 200 m (BT1) and 500 m (BT2) above ground level in Beijing (39.97°, 116.37°) were calculated every 6 h (at 0, 6, 12 and 18:00 local time (LT)) throughout the campaign. The back trajectories were then clustered according to their similarity in spatial distribution using the HYSPLIT4 software. As a result, the four-cluster solution was adopted according to the change in total spatial variance (Fig. 7).

BT1 and BT2 showed significant similarities. The BT1-cluster 1 (air mass frequency of 34%) and BT2-cluster 1 (air mass frequency of 33%) represented heavily polluted air mass originating from the Bohai Sea region, east of Beijing, and passed Tianjin, a large industrial city in northern China, before arriving. The corresponding NR-PM₁ mass concentrations were 87 $\mu\text{g m}^{-3}$ and 82 $\mu\text{g m}^{-3}$, for BT1 and BT2, respectively. The secondary components nitrate, sulfate, ammonium and OOA dominated the NR-PM₁ composition, accounting for 25%, 23%, 19% and 10% in BT1-Cluster1 and 24%, 23%, 18% and 10% in BT2-Cluster1, respectively. Previous studies (Huang *et al.*, 2010; Zhang *et al.*, 2014) indicated that high NR-PM₁ mass concentrations were associated with southerly air pollution events.

The other three air mass clusters of BT1 and BT2 all originated from the northwest. BT1-Clusters 2 and 3 were

similar and originated in the clean area of northern Beijing, but the NR-PM₁ mass concentrations showed only small differences because of the differences in the heights of the air masses. BT1-Cluster 2 was always lower than BT1-Cluster 3 before the air mass arrived in Beijing. BT1-Cluster 2 had a shorter transport distance than BT1-Cluster 3; therefore, the air mass carried more pollutants, causing the high concentrations. Long distance transport increases the dilution of the pollutants in the air mass, leading to lower concentrations. Similar results were presented in Zhang *et al.* (2014). However, there was no significant difference in NR-PM₁ mass concentrations between BT2-Cluster 2 and BT2-cluster 3, where the mass concentrations were 38 $\mu\text{g m}^{-3}$ and 35 $\mu\text{g m}^{-3}$, respectively. BT1-Cluster 4 and BT2-Cluster 4 were the cleanest air mass, with corresponding mass concentrations of 22 $\mu\text{g m}^{-3}$ and 23 $\mu\text{g m}^{-3}$, respectively.

CONCLUSIONS

This study systematically investigated the characteristics of submicron aerosol during spring in Beijing and the impact frequent spring dust events could have on submicron aerosol. The high temporal resolution NR-PM₁ mass concentration varied between 0.3 $\mu\text{g m}^{-3}$ and 209.5 $\mu\text{g m}^{-3}$, and with an average concentration of $49.7 \pm 40.2 \mu\text{g m}^{-3}$. Organic matter was the most abundant component, accounting for 51% of the NR-PM₁, followed by sulfate (18%), nitrate (16%), ammonium (12%) and chloride (3%). The spring dust

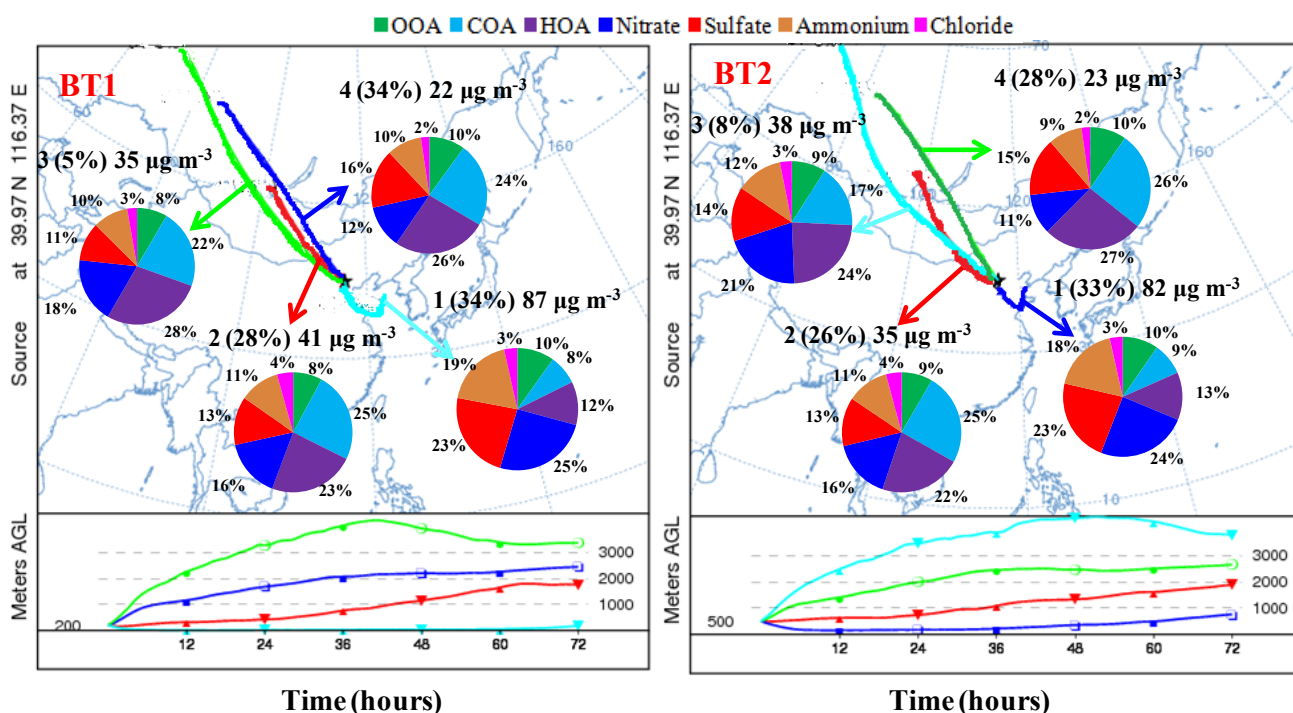


Fig. 7. Back trajectory clusters, and the corresponding mean NR-PM₁ compositions during the campaign.

originating from the northwest may have contributed more fine particles and allowed the average NR-PM₁ concentration to reach 56 $\mu\text{g m}^{-3}$. The spring dust also affected the chemical components of the fine particles, and the secondary species mass concentrations of sulfate, nitrate, ammonium and OOA increased. The measurements of the organic elemental composition indicated that the average C, H, O and N contributions to the total organic matter were 72.4%, 7.3%, 16.9% and 3.4%, respectively, and the average O/C and OM/OC ratios were 0.33 ± 0.09 and 1.55 ± 0.15 , respectively. A PMF analysis performed on the high resolution organic mass spectral data found that OOA, HOA and COA accounted for 23%, 42% and 35% of organic aerosol, respectively. OOA showed a mostly stable diurnal profile, but COA and HOA showed apparent diurnal variation. COA showed peak values at noon and night, which were related to cooking activity; HOA showed higher values at night (20:00), which were related to evening motor vehicle traffic. Back trajectory clustering analysis indicated that the southeast air mass was associated with the highest NR-PM₁ loading, and was rich in oxidized organic aerosol.

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