Size-resolved source apportionment of particulate matter in urban Beijing during haze and non-haze episodes

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Abstract: Additional size-resolved chemical information is needed before the physicochemical characteristics and sources of airborne particles can be understood; however, this information remains unavailable in most regions of China due to lacking measurement data. In this study, we report observations of various chemical species in size-segregated particle samples that were collected over one year in the urban area of Beijing, a mega city that experiences severe haze episodes. In addition to fine particles, high concentrations of coarse particles were measured during the period of haze. The abundance and chemical compositions of the particles in this study were temporally and spatially variable, with major contributions from organic matter and secondary inorganic aerosols. The contributions of organic matter to the particle mass decreased from 37.9% to 31.2%, and the total contribution of sulfate \( \text{SO}_4^{2-} \), nitrate \( \text{NO}_3^- \) and ammonium \( \text{NH}_4^+ \) ions increased from 19.1% to 33.9% between non-haze and haze days, respectively. Due to heterogeneous reactions and hygroscopic growth, the peak size distributions of the organic carbon, copper (Cu) and \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \), \( \text{NH}_4^+ \), chloride (Cl\(^-\)) and potassium (K\(^+\)) ions shifted from 0.43-0.65 μm on non-haze days to 0.65-1.1 μm on haze days. Although the size distributions of lead (Pb), cadmium (Cd) and thallium (Tl) were similar during the observation period, their concentrations increased by a factor of more than 1.5 on haze days compared with non-haze days. We observed that \( \text{NH}_4^+ \), which has a size range of 0.43-0.65 μm, \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \), which have a size range of 0.65-1.1 μm, calcium ions \( \text{Ca}^{2+} \), which have a size range of 5.8-9 μm, and the meteorological factors of relative humidity and wind speed were responsible for haze pollution when the visibility was
Source apportionment using positive matrix factorization showed six PM$_{2.5}$ sources and seven PM$_{2.1-9}$ common sources: secondary inorganic aerosol (25.1% for fine particles vs. 9.8% for coarse particles), coal combustion (17.7% vs. 7.8%), biomass burning (11.1% vs. 11.8%), industrial pollution (12.1% vs. 5.1%), road dust (8.4% vs. 10.9%), vehicle emissions (19.6% for fine particles), mineral dust (22.6% for coarse particles) and organic aerosol (23.6% for coarse particles). The first four factors and vehicle emissions were higher on haze days, while the contributions of road dust and mineral dust were higher on non-haze days. The sources generally increased as the size decreased, with the exception of mineral dust. However, two peaks were consistently found in the fine and coarse particles. In addition, the contributing sources varied with the wind direction, with coal and oil combustion products increasing during southern flows. This result suggests that future air pollution control strategies should consider wind patterns, especially during episodes of haze. Furthermore, the findings of this study indicated that the PM$_{2.5}$-based dataset is insufficient for determining source control policies for haze in China and that detailed size-resolved information is needed to characterize the important sources of particulate matter (PM) in urban regions and better understand severe haze pollution.

**Keywords:** Source apportionment; Size distribution; Haze episodes; Particulate matter; Beijing

**Introduction**

Particulate matter (PM) is among the most important atmospheric pollutants that negatively affect human health and visibility. In addition, PM plays a significant role in global climate change through its direct and indirect affects and ecosystem cycling (Huang et al., 2014; McFiggans, 2014; Pan et al., 2013). Due to rapid industrialization and urbanization in recent decades, China has become one of the most significant source regions for anthropogenic atmospheric emissions in the world (Guo et al., 2014). The Chinese capital of Beijing, a megacity with approximately 21 million inhabitants (Beijing statistical yearbook 2013), is experiencing extreme haze events...
From November 30 to December 2 and December 7 to December 8, 2004, the highest concentration of PM$_{2.5}$ (particulate matter with aerodynamic diameter lower than 2.5 μm) over 6 hours was 329.8 μg m$^{-3}$ (Sun et al., 2006). During the haze episode in January 2013, the highest instantaneous five-minute PM$_{2.5}$ concentration was 770 μg m$^{-3}$ at 20:48 on January 12, 2013. Moreover, the highest instantaneous PM$_{2.5}$ concentration reached 1000 μg m$^{-3}$ in some heavily polluted areas of Beijing (Quan et al., 2014). Although previous studies have provided valuable information regarding the physical and chemical characteristics of PM in urban Beijing and its surrounding areas (Li et al., 2013; Du et al., 2014; Song et al., 2006; Chan et al., 2005; Schleicher et al., 2013; Sun et al., 2004), the factors that influence haze formation remain unclear due to its complexity (Yang et al., 2014; Jing et al., 2014). In addition, previous studies have primarily focused on single particle fractions, such as PM$_{2.5}$, and have neglected size-resolved chemical information, especially for coarse particles, which also play an important role in haze events (Tian et al., 2014; Sun et al., 2013).

Knowing the size distributions and associated chemical species is crucial for evaluating the effects of PM on human health, visibility, and regional radiative forcing, and for determining the sources, formation mechanisms and conversion processes of the particles (Pillai and Moorthy, 2001; Duarte et al., 2008; Liu et al., 2008; Contini et al., 2014). Typically, mass distribution of PM is dominated by three modes (or sub-modes): the condensation (~0.1- 0.5 μm), droplet (~0.5- 2 μm) and coarse (> 2 μm) modes (Wang et al., 2012; Guo et al., 2010). Thus, to simplify mass distribution calculations in this study, the particle modes were divided. The sizes of the condensation mode particles were between 0.43 and 0.65 μm, and the sizes of the droplet-mode particles were between 0.65 and 2.1 μm. Recent results have suggested that secondary sulfates and nitrates primarily form fine particles, with elevated concentrations in the droplet mode during haze days (Sun et al., 2013; Wang et al., 2012). During the extreme haze events in urban Beijing in early 2013, the peak mass...
concentration of particles shifted from 0.43-0.65 μm on clear days to 0.65-1.1 μm on lightly polluted days and 1.1-2.1 μm on heavily polluted days due to the hygroscopic growth of submicron particles and the formation of secondary particles, including organic carbon (OC) and sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$) and ammonium (NH$_4^+$) ions (Tian et al., 2014). Because long-term observations are lacking, it is unclear whether the peak shifts occurred during other periods or whether this phenomenon only occurred during the extreme haze events in early 2013.

In addition, source apportionment based on size-fractionated PM data would provide additional insights regarding aerosol sources, especially during haze events (Pant and Harrison, 2012). For example, receptor models have been successfully used to identify coarse aerosol sources separately of fine aerosol sources (Karanasiou et al., 2009; Titos et al., 2014). Source apportionment studies have shown that the sources of PM$_{10}$ (particulate matter with aerodynamic diameter lower than 10 μm) and PM$_{2.5}$ are different. Meanwhile, the features of sources and dominant sources during different periods are different (Karanasiou et al., 2009; Vecchi et al., 2008), and understanding the sources of size-resolved chemical species (i.e., OC, SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$) is important for strategy-makers to effectively control and manage pollution (Hou et al., 2011; Zhang et al., 2014a; Fisher et al., 2011).

The main source apportionment methods can be divided into three categories: emissions inventory, diffusion model and receptor model. Among these categories, receptor models have been widely used because the methods are not limited by pollution discharge conditions, weather or terrain factors. The receptor models based on chemical analysis can be divided into two categories: one in which source profiles are needed, such as the Chemical Mass Balance (CMB) method; and one in which source profiles are not needed, such as the Positive Matrix Factorization (PMF) method. Because it is difficult to build large and accurate source profiles, we use the PMF method to perform source apportionment in our study. Previously, source apportionment studies in Beijing have mainly focused on single size fractions (i.e.,
Overall, the results showed that the contributions of major sources to PM$_{2.5}$ mass in Beijing exhibited seasonal and annual variations. The major sources of PM$_{2.5}$ mass in Beijing during 2000 were dust (20%), secondary sulfate (17%), secondary nitrate (10%), coal combustion (7%), diesel and gasoline exhaust (7%), secondary ammonium (6%), biomass aerosol (6%), cigarette smoke (1%), and vegetative detritus (1%) (Zheng et al., 2005). However, the PMF model identified six main sources of PM$_{2.5}$ in 2009-2010: soil dust, coal combustion, biomass burning, traffic and waste incineration emissions, industrial pollution, and secondary inorganic aerosols, with annual mean contributions of 16, 14, 13, 3, 28, and 26%, respectively, (Zhang et al., 2013b). In addition, the PMF method resolved 87 and 80% of the PM$_{2.5}$ in January and August 2004, respectively. The major sources were coal combustion (38% in January and 11% August), secondary sulfate (9% and 24%), secondary nitrate (10% and 8%), biomass burning (15% and 1%), motor vehicle emissions (8% and 15%) and road dust (7% and 8%) (Song et al., 2007). Previous studies regarding the size distributions of PM in urban Beijing have primarily focused on limited chemical species (Sun et al., 2013; Li et al., 2013; Yao et al., 2003) or have been conducted over short periods (Li et al., 2012a; Sun et al., 2010; Gao et al., 2012; Zhang et al., 2014b). To the best of our knowledge, no studies have been conducted on the source apportionment of size-resolved atmospheric particles based on long-term observations in urban Beijing.

To fill this knowledge gap, we observed size-resolved PM in urban Beijing from March 1, 2013 to February 28, 2014. In this study, we report the mass closure of particles based on a size-resolved chemical dataset obtained from haze and non-haze days over four seasons. The PMF method was combined with back trajectory cluster analysis to estimate the relative contributions of sources in different size fractions between haze and non-haze days and among different regional sources. These results will help policy-makers design emission control strategies and can serve as a database for future field measurements and modeling studies.
2. Materials and Methods

2.1. Sampling site

The experiment was performed from March 1, 2013, to February 28, 2014, at the Institute of Atmospheric Physics, Chinese Academy of Sciences (39°58′N, 116°22′E) (Fig. S1). The samplers were placed on the roof of a building approximately 15 m above the ground. The sampling site was located in Northwest Beijing between the 3rd and 4th ring roads. The site was selected to broadly represent the air pollution levels in urban Beijing because it was far from specific point emission sources.

2.2. Sampling collection

Two 9-stage samplers (Andersen Series 20-800, USA) with cutoff points of 0.43, 0.65, 1.1, 2.1, 3.3, 4.7, 5.8, and 9.0 μm, were used to simultaneously collect particles for 48 h (from 10:00 (local time, LT) on Monday to 10:00 LT on Wednesday) every week at a flow rate of 28.3 L min⁻¹. Overall, 52 sets of size-resolved PM samples were collected on quartz fiber filters and cellulose membranes (81 mm in diameter) during the study period. The quartz fiber filters were pre-fired (2 h at 800 °C) to remove all organic material and were weighed before and after sampling using a microbalance with a sensitivity of ±0.01 mg. During the weighing processes, the filters eliminated static. Filters were conditioned in a dryer at 25±3 °C under a relative humidity (RH) of 22±3% for 72 h before each weighing. After re-weighing, the exposed filters were stored in a freezer at −20 °C to limit losses of volatile components loaded on the filters. To prevent the sampler from becoming blocked by particles during sampling, the samplers were cleaned using an ultrasonic bath for 30 min before each sampling. In addition, the sampling flow rates were calibrated before each sample was collected and were monitored using a flow meter during each sampling. Field blanks (a blank quartz filter and a blank cellulose membrane in each sampling) were used to determine any possible background contamination. All of the tools used during sampling and analysis were cleaned, and the operator wore plastic gloves. Meanwhile, the meteorological parameters used in this study, including visibility, temperature, RH,
wind speed (WS) and wind direction (WD), were collected at Beijing Capital International Airport (http://english.wunderground.com) (Fig. S2).

2.3 Chemistry analyses

A quarter of each quartz filter was subjected to extraction in 25 ml of deionized water (Millipore, 18.2 MΩ) in an ultrasonic bath for 30 min. The extraction liquid was filtered and subsequently measured using ion chromatography (DIONEX, ICS-90, USA) to determine the sodium (Na⁺), NH₄⁺, potassium (K⁺), magnesium (Mg²⁺), calcium (Ca²⁺), chloride (Cl⁻), NO₃⁻ and SO₄²⁻ ion concentrations. For ion analysis, the IC was equipped with a separation column (Ionpac CS12A 4×250 mm for cations and Ionpac AS14A 4×250 mm for anions) and a suppressor (CSRS300–4 mm for cations and ASRS 300–4 mm for anions). The eluents used for cations and anions were 22 mmol L⁻¹ MSA and 3.5 mmol L⁻¹ Na₂CO₃/1 mmol L⁻¹ NaHCO₃, respectively. The ions were quantified by external standard curves every week, and one trace calibration standard solution was used to check the curve each day. The limit of detection was less than 0.02 μg m⁻³ for all ions when the injection volume was 100 μL.

Using another quarter of each quartz filter, the concentrations of OC and elemental carbon (EC) were determined using a thermal/optical carbon aerosol analyzer (DRI Model 2001A, Desert Research Institute, USA). Briefly, a punch aliquot (0.495 cm²) of a quartz fiber filter sample was heated stepwise in an oven at 140°C (OC1), 280°C (OC2), 480°C (OC3) and 580°C (OC4) under a pure helium atmosphere to volatilize the OC before heating to 580°C (EC1), 740°C (EC2) and 840°C (EC3) in a 2% oxygen-contained helium atmosphere for EC oxidation. At each stage, the formed CO₂ was catalytically converted to CH₄ by a MnO₂ catalyst, and the resulting CH₄ was measured using a flame ionization detector (FID). The analyzer was calibrated before and after sample analysis by using a standard mixture of CH₄ and CO₂. One sample was randomly selected from every 10 samples to conduct duplicate sample analyses. The measurement errors were less than 10% for TC
(OC+EC), and the OC and EC concentrations in the field blanks were less than 1% of the sample levels and were subtracted from the samples.

A quarter of the cellulose membrane was digested in a mixture of concentrated HNO₃ (6 ml), HCl (2 ml) and HF (0.2 ml) in a closed vessel microwave digestion system (MARS5, CEM Corporation, Matthews, NC, USA). Then, an Agilent 7500a inductively coupled plasma mass spectrometer (ICP-MS, Agilent Technologies, Tokyo, Japan) was used to determine the concentrations of 21 trace elements (TEs) (sodium (Na), magnesium (Mg), Aluminum (Al), potassium (K), Calcium (Ca), Manganese (Mn), Iron (Fe), cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), molybdenum (Mo), cadmium (Cd), Barium (Ba), thallium (Tl), Lead (Pb), thorium (Th) and uranium(U)). A blank filter was analyzed in each batch for quality control. Quantitative analysis was conducted using external calibration standards with concentrations that were similar to those in the samples. In addition, internal standard elements (⁴⁵Sc, ⁷²Ge, ¹¹⁵In and ²⁰⁹Bi) were added online during the metallic element analysis.

The analysis methods, information regarding the instruments used in this study (e.g., precision, calibration and detection limit) and quality control methods are described elsewhere (Li et al., 2012b; Pan and Wang, 2015).

### 2.4 Chemical mass closure

Mass closure was used to discuss the relative contributions of the major components in the PM. The chemical species were divided into the following seven categories: sulfate-nitrate-ammonium (SNA), organic matter (OM), crustal materials (CM), heavy metals (HM), EC, sea salt (SS) and liquid water (LW). The difference between the mass weighted by microbalance and that reconstructed using the above seven components was defined as unidentified matter (UM). The calculation methods of the main components were described in our previous studies (Tian et al., 2014) and are shown in Table S1 for convenience.
2.5 PMF model

PMF is an effective source apportionment receptor model (Karanasiou et al., 2009; Bullock et al., 2008; Paatero and Tapper, 1994; Paatero, 1997). In this study, EPA-PMF 3.0 was applied separately for the fine (the input data included the mass concentrations and chemical species in the particles with sizes of < 0.43, 0.43-0.65, 0.65-1.1 and 1.1-2.1 μm) and coarse (the input data included the mass concentrations and chemical species for particles with sizes of 2.1-3.3, 3.3-4.7, 4.7-5.8, 5.8-9 and > 9 μm) fractions. The numbers of samples analyzed for the fine and coarse fractions were 208 and 260, respectively. The chemical species included Na, Mg, Al, K, Ca, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Ba, Ti, Pb, Th, U, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, NO₃⁻, OC and EC. The uncertainty of the concentration data, which was also the input data, was calculated as shown below.

If the concentration is less than or equal to the provided method detection limit (MDL), the uncertainty is calculated using the following equation:

\[
\text{Uncertainty} = \frac{5}{6} \times \text{MDL}
\]  

(1)

If the concentration is greater than the provided MDL, the calculation is

\[
\text{Uncertainty} = \sqrt{(\text{Error Fraction} \times \text{concentration})^2 + (\text{MDL})^2}
\]  

(2)

In this study, the error fraction was estimated as 10 (the percent uncertainty multiplied by 100) for all of the chemical species, and the MDLs were similar to those reported in previous studies (Li et al., 2012a; Yang et al., 2009).

The base model was run 20 times with a different number of factors to obtain the best possible solution. During the first run, several species had a large number of absolute scaled residuals greater than 3, which indicated poor observed-predicted correlations. Then, these species were designated as “weak” and the model was rerun. When a reasonable solution was found, the bootstrapping technique was used to obtain the most meaningful results. Overall, 100 bootstrap runs were performed with a minimum \(r^2\)-value of 0.6. Of the 100 runs, the 6 factors were mainly mapped to a base factor in every run, which indicated a stable result.
Several criteria are important for ensuring a good PMF solution. First, the modeled Q's should be within 50% of the theoretical value. Second, the optimum number of factors should be determined by the criterion that each factor has a distinctively dominant grouping of compounds. Third, the model uncertainty produced by bootstrapping should be small. The principles are detailed elsewhere (Liu et al.; Titos et al., 2014; Moon et al., 2008).

2.6 Air mass back trajectory cluster

The three-day backward trajectories arriving at the sampling site were calculated using the National Oceanic and Atmospheric Administration (NOAA) HYSPLIT 4 model with a 0.5°×0.5° latitude-longitude grid. The arrival level was set at 500 m above ground level (a.g.l.). The HYSPLIT model was run four times each day at starting times of 02:00, 08:00, 14:00, and 20:00 UTC during the sampling period. Then, all of the trajectories were divided into different groups based on the horizontal moving speed and direction of the air masses to form the trajectory clusters (Sirois and Bottenheim, 1995; Wang et al., 2006b).

3. Results

3.1 PM mass concentrations and chemical composition

Table 1 describes the concentrations of the size-resolved mass and chemical compositions during different seasons. The annual average concentrations of PM$_{2.1}$ (particulate matter with aerodynamic diameters less than 2.1 μm) and PM$_{9}$ (particulate matter with aerodynamic diameters less than 9 μm) were 67.3 and 129.6 μg m$^{-3}$, respectively. Although the present level of PM$_{2.1}$ is significantly lower than that in 2009-2010 (135 μg m$^{-3}$) (Zhang et al., 2013b), it was more than times higher than the National Ambient Air Quality Standard (NAAQS), which specifies an annual average PM$_{2.5}$ of 15 μg m$^{-3}$ (GB3095-2012, Grade I). In addition, PM$_{9}$ was approximately three times the NAAQS annual average PM$_{10}$ of 40 μg m$^{-3}$ (Grade I). Thus, fine and coarse particles, defined in this study as particles with sizes < 2.1 (PM$_{2.1}$) and 2.1-9.0 μm (PM$_{2.1-9}$), respectively, are important for PM in urban Beijing.
As shown in Table 1, the primary components of PM$_{2.1}$ are OC (24.5% of PM$_{2.1}$), \(\text{SO}_4^{2-}\) (14.7%), \(\text{NO}_3^-\) (11.2%) and \(\text{NH}_4^+\) (9.2%). In contrast, Ca (3.5±1.5 μg m\(^{-3}\)), EC (2.0±1.8 μg m\(^{-3}\)) and other species accounted for approximately 40% of PM$_{2.1}$. The composition of the coarse particles was different from the composition the fine particles (PM$_{2.1}$). In this study the highest contribution to PM$_{2.1-9}$ was Ca (16.3% of PM$_{2.1-9}$), followed by OC (15.5%), \(\text{NO}_3^-\) (4.5%), Fe (4.1%) and \(\text{SO}_4^{2-}\) (3.5%). These species accounted for approximately 44% of PM$_{2.1-9}$. The mass closure of size-resolved particles is discussed in detail below (Sect. 4.2).

3.2 Seasonality

The concentrations of PM$_{2.1}$ were greatest during winter (December to February, 76.8 μg m\(^{-3}\)), followed by spring (March to May), summer (June to August) and autumn (September to November), with concentrations of approximately 65 μg m\(^{-3}\) during the latter three seasons (Table 1). In contrast, the concentrations of PM$_{2.1-9}$ decreased in the following order spring > autumn > winter > summer.

The seasonal dependency varied with species. For most of the species that were enriched in the fine mode (with a PM$_{2.1}$/PM$_{9}$ chemical concentration ratio greater than 0.5, including \(\text{NH}_4^+\), Tl, Cd, Pb, \(\text{SO}_4^{2-}\), \(\text{NO}_3^-\), EC, \(\text{K}^+\), Zn, \(\text{Cl}^-\), OC, Cu, Na, Na$^+$, Mo and K), in the compositions of PM$_{2.1}$ and PM$_{2.1-9}$ exhibited similar seasonal variations, with the PM$_{2.1}$ mass concentration being higher during colder seasons. However, the seasonal dependence of the concentration of certain species in PM$_{2.1}$ differs from the typical seasonal variation. For example, the concentrations of \(\text{SO}_4^{2-}\) and \(\text{NH}_4^+\) in spring and summer were higher than those in autumn and winter. This result was consistent with the seasonal variability of \(\text{SO}_4^{2-}\) and \(\text{NH}_4^+\) in PM$_{2.5}$ in 2009-2010 (Zhang et al., 2013b).

In addition, the OC concentrations in PM$_{2.1}$ decreased as follows: summer (20.2 μg m\(^{-3}\)) > spring (16.5 μg m\(^{-3}\)) > winter (16.2 μg m\(^{-3}\)) > autumn (13.4 μg m\(^{-3}\)). The high OC concentrations during the summer primarily resulted from the photochemical generation of more secondary organic carbon (SOC). This result can be confirmed by
the OC/EC ratios, which exhibited the following seasonal pattern: summer (16.7) > spring (12.7) > autumn (6.7) > winter (4.9). Because EC primarily arises from primary combustion emissions, the OC/EC ratios were used to evaluate the contributions from secondary organic carbon (Cao et al., 2007).

For species enriched in the coarse mode (PM$_{2.1-9}$) (with a PM$_{2.1}$/PM$_{9}$ chemical concentration ratio below 0.5, including Ni, Mn, U, Co, Mg$^{2+}$, Th, Al, Ba, Mg, Ca and Ca$^{2+}$), their PM$_{2.1}$ and PM$_{2.1-9}$ concentrations demonstrated typical seasonal variations, with higher concentrations observed during the spring and autumn (or winter) due to the influences of re-suspended soil dust. Re-suspended soil dust may result from both long transport dust and local anthropogenic sources (construction dust and mechanical abrasion processes). The relatively high wind speed during spring facilitated the ascent of road dust into the atmosphere and resulted in the relatively high value of the species in the coarse mode (Liu et al., 2014a).

### 3.3 Size distribution

The size distributions of the mass concentrations and the chemical species are shown in Fig. 1 and Fig. S3. In each season, the size distribution of the mass concentrations was bimodal. The fine modes commonly showed maxima at 0.65-1.1 μm in spring, autumn and winter and 0.43-0.65 μm in summer. The coarse modes showed maxima at 4.7-5.8 μm in all of the seasons. As shown in Fig. 1, the peak of the fine mode was broader in winter than in the other seasons, indicating the complexity of the emissions in winter (Sun et al., 2013). Emissions from coal combustion for heating are greater during winter, especially for retail coal combustion in surrounding areas, which is difficult to control (Wang et al., 2006a). However, the meteorological conditions in winter are unfavorable for the diffusion of fine particles and precursors (SO$_2$, NOx, VOCs), making secondary particle emissions more complex.

The chemical species can generally be divided into three groups based on their size distributions. First, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, EC, Zn, Cd, Pb and Tl were abundant in
the fine mode, which exhibited maxima at 0.43-0.65 μm or 0.65-1.1 μm in all four seasons that corresponded to coal and motor vehicle sources (Li et al., 2013). Second, Ca\(^{2+}\), Mg\(^{2+}\), Ba, Mg, Al, Ca, Fe, Co, Ni, Th and U were primarily concentrated in the coarse mode from 4.7 to 5.8 μm, which suggested natural sources from soil dust or mechanical abrasion processes (Sun et al., 2013; Maenhaut et al., 2002a). Third, OC, Cl\(^{-}\), K\(^{+}\), Na\(^{+}\), Na, K, Mn, Cu and Mo exhibited typical bimodal distributions, and the amplitude of the fine mode was well correlated with that of the coarse mode. These species exhibited maxima at 0.43-0.65 μm or 0.65-1.1 μm and peaked at 4.7-5.8 μm in the coarse mode. Cl\(^{-}\) and K\(^{+}\) are good biomass burning tracers (Du et al., 2011), and Mn and Cu are good industrial pollution tracers. Hence, the species in the third group may represent mixed sources from biomass burning and industrial pollution.

The size distribution of the mass concentration and OC peaked at 0.43-0.65 μm in summer and 0.65-1.1 μm in winter. Because the primary organic carbon emissions were relatively stable across the four seasons, the size distribution differences in the fine mode primarily resulted from the generation of SOC (Duan et al., 2005). The difference between summer and winter indicated that the SOC formation in summer was enhanced due to photochemical reactions and primarily accumulated in “condensation mode” (Zhang et al., 2008). However, because photochemistry is typically weak in winter, the SOC generation mainly resulted from the high RH and high precursor concentrations, including volatile organic compounds (VOCs) from biological (such as monoterpene and sesquiterpene) and anthropogenic sources (such as aromatics) (Jacobson et al., 2000). Thus, VOCs primarily accumulated in “droplet mode” (Cao et al., 2007). Previously, our findings indicated that weakening incident solar radiation reduces the formation of SOC formation in the smaller size fraction and that high RH plays an important role in the generation of SOC in larger size fractions (Tian et al., 2014).

### 3.4 Ion balance

We calculated the ion balance for each size fraction, which was used to evaluate
the ion deficiency between cations and anions in the PM (Fig. S4). The average
equivalent ratio of total cations (Na\(^+\), NH\(_4^+\), K\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\)) to total anions (SO\(_4^{2-}\),
NO\(_3^-\) and Cl\(^-\)) ranged from 0.95 to 2.50, with lowest ratio occurring in the 1.1-2.1 \(\mu\)m
size fraction and highest ratio occurring in the 4.7-5.8 \(\mu\)m size fraction. The total
cation to total anion ratio in the fine particles was near unity throughout the year,
which indicated excellent charge balance and high data quality. The slope for the fine
mode particles was mainly greater than 1 because the concentrations of CO\(_3^{2-}\) and
HCO\(_3^-\) were not determined.

Fig. S5 shows good correlations between the NH\(_4^+\) and SO\(_4^{2-}\) concentrations in
the fine particles for the data sets in different seasons, with NH\(_4^+\)/SO\(_4^{2-}\) equivalent
ratios greater than 1 (spring (1.92) summer (1.79), autumn (1.01), winter (1.36)),
revealing the dominance of (NH\(_4\)\(_2\))SO\(_4\). Next, we calculated the molar ratio of NH\(_4^+\) to
[NO\(_3^-\) + SO\(_4^{2-}\)], which was slightly higher than unity in spring (1.25) and summer
(1.33) and indicated the presence of NH\(_4\)NO\(_3\) in the fine aerosols. However, the ratios
were less than one in the autumn (0.78) and winter (0.68), which indicated that NO\(_3^-\)
could be present in chemical forms other than NH\(_4\)NO\(_3\).

For the coarse mode particles, the NH\(_4^+\)/SO\(_4^{2-}\) equivalent ratios in spring (0.78)
summer (0.68) and autumn (0.58) were less than 1 but greater than 0.5, which
indicated the dominance of (NH\(_4\)\(_2\))SO\(_4\) and NH\(_4\)HSO\(_4\). By contrast, the ratio in winter
(1.33) was greater than unity, and the equivalent ratio of NH\(_4^+\) to [NO\(_3^-\) + SO\(_4^{2-}\)] in
winter was less than unity.

4. Discussion

4.1 Size-resolved aerosol compositions on non-haze and haze days

Fig. 2 illustrates the size-segregated PM mass concentrations during the sampling
period. Haze is defined as a weather phenomenon in which a high concentration of
fine particles occur that result in a visibility of less than 10 km at a relative humidity
(RH) of less than 90% (Sun et al., 2006; Tan et al., 2009; Zhuang et al., 2014). Thus,
we used visibility and RH to determine the haze/no-haze days as follows: sampling
days with visibility < 10 km and RH < 90% were defined as haze days and sampling days with visibility > 10 km and RH < 90% were defined as non-haze days. During the observation period, 12 sets of size-resolved PM samples were collected during non-haze days and 19 sets were collected during haze days (marked in Fig. 2). Of the remaining 21 sets, 15 sets were collected during rain, snow or fog days and 6 sets were collected during dust days (visibility < 10 km, RH < 40%). These samples were excluded from the dataset when we discussed the differences between haze and non-haze days.

4.1.1 Concentration enhancement ratios

Table S2 describes the annual average concentrations of the size-resolved mass and chemical compositions on haze and non-haze days over four seasons. The annual average PM$_{2.1}$ and PM$_{2.1-9}$ concentrations on haze days were 86.1 and 72.6 μg m$^{-3}$, which were 2.6 and 1.4 times those on non-haze days, respectively. Therefore, it is evident that fine particles significantly accumulated during the haze pollution period (Wang et al., 2014). In addition, the mass concentration enhancement ratio from non-haze to haze days ($R_{HN}$) was examined during all four seasons.

$$R_{HN} = \frac{C_H}{C_N},$$

$C_H$—Concentration of chemical species on haze days;

$C_N$—Concentration of chemical species on non-haze days.

The $R_{HN}$ for fine particles revealed a typical seasonality, with the highest value occurring in winter (5.6) and the lowest value occurring in the spring (1.8). The $R_{HN}$ for coarse particles was lower than that for fine particles, which ranged from 1.1 to 1.9 and decreased as follows: summer > autumn > winter > spring. The higher $R_{HN}$ values for fine particles further indicated the importance of fine particles in haze pollution.

We calculated the $R_{HN}$ ratios for chemical species in each size fraction. Based on the $R_{HN}$ ratios variations with increasing size fraction, all the species can be divided into three groups. First, OC, NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, K$^+$, Cl$^-$, K, Mn, Ni, Cu, Zn, Pb and
Tl exhibited high $R_{HN}$ ratios in fine mode and a peak value in size fraction 0.65-1.1 μm or 1.1-2.1 μm. Second, $R_{HN}$ ratios of Na$^+$, Mg$^{2+}$, Ca$^{2+}$, Mg and Fe increased with increasing size fraction. Third, EC, Na, Al, Ca, Co, Mo, Cd, Ba, Th and U, $R_{HN}$ ratios of these species first increased and then decreased with increasing size fraction and exhibited highest $R_{HN}$ ratios in size fraction 1.1-2.1 μm, 2.1-3.3 μm or 3.3-4.7 μm.

The annual average $R_{HN}$ of the chemical components in PM$_{2.1}$ ranged from 0.8 to 5.5, with values greater than 2.6 for NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, Pb, Tl and Cd. This finding was consistent with the findings of previous studies (Tian et al., 2014; Sun et al., 2013), indicating that coal and motor vehicle sources played important roles in haze pollution (Li et al., 2013). Regarding the seasonal variations, the particulate mass and most of the species exhibited the highest $R_{HN}$ in winter, which indirectly showed that severe haze events primarily occurred in winter.

Simultaneously, the annual average $R_{HN}$ of the chemical components in PM$_{2.1-9}$ ranged from 0.8 to 5.3, which was similar to that for fine particles. The NH$_4^+$, NO$_3^-$, SO$_4^{2-}$, Cd, EC, Cl$^-$, Pb, Tl, Na$^+$, OC, Zn and K$^+$ in the coarse fraction exhibited $R_{HN}$ values greater than 1.4. Among these species, Pb, Cd and Tl had high toxicity. Thus, the mitigation of particles with diameters greater than 2.1 μm cannot be neglected during haze events. Similar to PM$_{2.1}$, most of the species in the coarse fraction exhibited the highest $R_{HN}$ in winter. In contrast, the highest $R_{HN}$ values for Na$^+$, K$^+$ and Cl$^-$ in the coarse fraction were observed in summer, which was similar to the results of the mass concentration. The highest $R_{HN}$ for Na$^+$, K$^+$ and Cl$^-$ in the coarse fraction was observed in summer, mainly due to low concentrations on non-haze days and relatively high concentration of haze days. The lower concentrations of coarse particles in summer were likely related to greater precipitation during this season. High concentrations of K$^+$ and Cl$^-$ in coarse mode on haze days were mainly associated with biomass burning (Du et al., 2011). One of the samples that represented a haze day in summer was collected between June 17 and 19. During this
period, burning wheat straw in the surrounding areas affected both fine and coarse particle pollution in Beijing (Wang et al., 2015; Yan et al., 2015; Cheng et al., 2014). The concentrations of NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ in the fine and coarse particles were higher on haze days than on non-haze days. These species are involved in heterogeneous chemical reactions (Sun et al., 2013). Figs. S6a and b show good correlations between NH$_4^+$ and SO$_4^{2-}$ in fine particles from non-haze and haze days, with an equivalent NH$_4^+$/SO$_4^{2-}$ ratio greater than unity (ranging from 1.5-1.6). This result reveals the dominance of (NH$_4$)$_2$SO$_4$. Next, we calculated the equivalent ratio of NH$_4^+$ to [NO$_3^-$ + SO$_4^{2-}$] (Figs. S6c and d), which was slightly higher than unity on non-haze days and indicated the presence of NH$_4$NO$_3$ in the fine mode aerosols. However, on haze days, the ratios were less than unity, which indicated that NO$_3^-$ may be present in chemical forms other than NH$_4$NO$_3$.

4.1.2 Peak shifts

Fig. 3 compares the annual average mass concentration size distributions on non-haze and haze days, which were considered bimodal, with the peaks corresponding to the fine modes located at 0.65-1.1 μm and those corresponding to the coarse modes peaking at 4.7-5.8 μm. No significant differences in the average size distributions were found between haze and non-haze days in each season (Fig. 3). This result was inconsistent with the results obtained from early 2013, which showed that the peak mass concentration of fine mode particles shifted from 0.43-0.65 μm on clear days to 0.65-1.1 μm on lightly polluted days and 1.1-2.1 μm on heavily polluted days (Tian et al., 2014).

However, in this study, peak shifts from 0.43-0.65 μm on non-haze days to 0.65-1.1 μm on haze days were observed when considering the annual average size distributions of SO$_4^{2-}$, OC, NO$_3^-$, NH$_4^+$, Cl$^-$, K$^+$ and Cd. The peak values of these species at 0.43-0.65 μm in the fine mode on non-haze days correspond to the “condensation mode” due to the transformation of precursors and heterogeneous reactions, while those at 0.65-1.1 μm on haze days correspond to the “droplet mode”,
which likely form in clouds or through aqueous-phase chemical reactions (Sun et al., 2013). The high RH during haze days may facilitate the formation of “droplet mode” particles, and a similar finding was previously reported (Sun et al., 2013; Zhang et al., 2013a). However, this result was slightly different from that observed in early 2013, which showed that the peak concentration of \( \text{NH}_4^+ \), \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) in fine mode at 1.1-2.1 \( \mu \text{m} \) on heavily polluted days resulted from the high RH and high precursor concentrations (Tian et al., 2014).

We also compared size distributions of chemical species between haze and non-haze days in different seasons. The results showed that the peak concentration of OC, \( \text{SO}_4^{2-} \), \( \text{Cl}^- \) and Mn in fine mode particles shifted from 0.43-0.65 \( \mu \text{m} \) on non-haze days to 0.65-1.1 \( \mu \text{m} \) on haze days in spring. However, species exhibited peak shifts in summer were EC, \( \text{K}^+ \), \( \text{NO}_3^- \) and Ni. Besides, in autumn, fine mode peak concentration of EC, \( \text{NH}_4^+ \), \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \), Cd and Cu shifted from 0.43-0.65 \( \mu \text{m} \) on non-haze days to 0.65-1.1 \( \mu \text{m} \) on haze days. Meanwhile, \( \text{NH}_4^+ \), \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \), \( \text{K}^+ \), \( \text{Cl}^- \), Cd, Zn and Pb exhibited fine mode peak shifts from non-haze days to haze days in winter. These indicated that there are different formation mechanisms for haze in different seasons.

4.2 Mass closure studies

4.2.1 Non-haze vs. haze days

Mass closure studies showed that SNA, OM and CM dominated the fine particles, which accounted for 87.7% and 76.6% of the PM_{2.1} mass on non-haze and haze days, respectively (Figs. 4a-d). Generally, the contribution of OM to PM_{2.1} was greater than the contributions of SNA and CM. However, during haze episodes in cold seasons, SNA was more significant than OM because the high RH and precursor emissions (i.e., \( \text{SO}_2 \)) promoted the generation of SNA (Tian et al., 2014). The contributions of SNA to the fine particle mass were significantly higher on haze days than on non-haze days. In contrast, the CM and OM contributions decreased from non-haze to haze days.
High total CM, OM and SNA contributions were also observed in PM$_{2.1-9}$, which accounted for 58.5% and 54.3% of the total PM$_{2.1-9}$ mass on non-haze days and haze days, respectively. The contributions of these species in coarse particles decreased as follows on haze and non-haze days: CM > OM > SNA. However, in fine particles, the order was OM > CM > SNA on non-haze days and OM > SNA > CM on haze days. In summary, the relative contributions of OM and CM to the particle mass decreased from non-haze to haze days, and the relative contribution of SNA increased from non-haze days to haze days.

4.2.2 Differences among size fractions

For different size fractions, the contributions of OM, HM and EC were greatest in the < 0.43 μm fraction (41.3%, 2.2% and 7.0%, respectively). The contribution of SNA, which is primarily formed from precursors via heterogeneous reactions, was greatest in the 0.43-0.65 μm fraction (34.5%), which is within the “condensation mode” (Fig. 4e). The contribution decreased as the size increased, which indicated that these anthropogenic species primarily accumulated in the fine mode. However, the minimal contributions of OM, HM, EC and SNA occurred in the 5.8-9 μm (6.9%), > 9 μm (0.7%), 4.7-5.8 μm (0.9%) and > 9 μm (4.1%) size fractions, respectively. In addition, CM and SS exhibited similar size fraction variations, which increased from < 0.43 μm to 3.3-4.7 μm and then decreased. The highest contributions of CM and SS appeared in the 3.3-4.7 μm fraction and were 35.6% and 4.9%, respectively.

4.2.3 Unidentified mass

The reconstructed PM mass concentrations were compared with the gravimetric values, as shown in Fig. S7. The results were correlated with one another in the different size fractions, with $R^2$ values for PM$_{1.1}$ (particulate matter with aerodynamic diameter lower than 2.5 μm), PM$_{2.1}$, PM$_{9}$ and TSP (total suspended particulate matter) of 0.69, 0.79, 0.70 and 0.60, respectively. In addition, the contributions of the unidentified components ranged from 0.4% to 57.8% and increased as the sizes
increased. The large unidentified components in the coarse particles potentially resulted from underestimating CM (Hueglin et al., 2005; Sun et al., 2004). In this study, Si was estimated as 3.42 times Al, and the ratios were applied to all of the size fractions. This assumption may be underestimated because the Si/Al ratio could increase with size. For example, the contribution of CM to coarse particles reached 42.4% based on the Si/Al ratio of 6.0 in PM$_{2.5-10}$, which was previously reported in Beijing (Zhang et al., 2010). Thus, the contribution of the unidentified components decreased from 38.5% to 25.5% for the total PM$_{2.1-9}$ mass.

4.3 Source apportionment

4.3.1 Fine and coarse particles

Six PM$_{2.1}$ and seven PM$_{2.1-9}$ sources were identified by PMF analysis, respectively. Fig. 5(a) and (b) show the profiles of each source in the fine and coarse fractions, respectively, and the percentages of species apportioned by each source. The sources identified in the fine fraction were named as secondary inorganic aerosol (SIA), coal combustion, biomass burning, industrial pollution, road dust and vehicle emissions. Coarse fraction sources were SIA, coal combustion, biomass burning, industrial pollution, road dust, mineral dust and organic aerosol. Together these sources represented 91.6% and 86.6% of PM$_{2.1}$ and PM$_{2.1-9}$, respectively.

Secondary inorganic aerosol (SIA)

The first source was relevant to secondary inorganic aerosol (SIA), which was identified in both fractions and was typically characterized by significant amounts of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$. SIA contributed 25.1% (16.9 µg m$^{-3}$) and 9.8% (6.1 µg m$^{-3}$) to the fine and coarse particles, respectively. Contributions of SIA to both PM$_{2.1}$ and PM$_{2.1-9}$ followed the order winter (29.5% to PM$_{2.1}$ and to 16.5 to PM$_{2.1-9}$) > spring (27.2% and 9.3%) > autumn (20.3% and 7.8%) > summer (18.1% and 5.7%). The SIA contribution to the fine particles was similar to that in Beijing for 2009-2010 (Zhang et al., 2013b).

Coal combustion
The second source, coal combustion, was also identified in both fractions and was characterized by elevated OC and EC concentrations (Tian et al., 2010; Kang et al., 2011). The contribution of this source to PM$_{2.1}$ was 17.7% (11.9 μg m$^{-3}$), which closely approximates the value of 19% derived in Beijing for 2009-2010 (Zhang et al., 2013b). In addition to its contribution to PM$_{2.1}$, coal combustion significantly contributed to PM$_{2.1-9}$ (7.8%, 4.9 μg m$^{-3}$). The contributions of coal combustion to PM$_{2.1}$ and PM$_{2.1-9}$ exhibited similar seasonal patterns of winter (27.0% to PM$_{2.1}$ and 9.4% to PM$_{2.1-9}$) > autumn (17.5% and 8.9%) > summer (14.5% and 6.6%) > spring (9.6% and 6.4%).

**Biomass burning**

The third source, biomass burning, was also identified in both fractions and was represented by high Cl$^-$ and K$^+$ contents (also K, which is an excellent tracer of aerosols from biomass burning) (Du et al., 2011) and is rich in Na$^+$ (Moon et al., 2008). The contribution in PM$_{2.1}$ was 6.9%, which was significantly higher than the 6.9% contribution in PM$_{2.1-9}$. This finding is expected because biomass burning contributed much more to the fine particles than the coarse particles (Cheng et al., 2014). Its contributions to PM$_{2.1}$ and PM$_{2.1-9}$ demonstrated a typical seasonal variation, with higher concentrations observed in spring (11.1% to PM$_{2.1}$ and 11.8% to PM$_{2.1-9}$) and winter (13.5% and 10.2%).

**Industrial pollution**

The fourth source was industrial pollution, which was also identified in both fractions and was characterized by high Fe, Ni, Co, Mg, Al and Ca contents in fine size fraction and by high Cd, Pb, Tl, Zn and Cu contents in coarse fraction (Karnae and John, 2011). The contribution from this source was 12.1%, which is slightly higher than the 5.1% contribution for coarse particles. Its contributions to PM$_{2.1}$ and PM$_{2.1-9}$ demonstrated a typical seasonal variation, with higher concentrations observed in summer (16.7%) and autumn (14.5%) for fine fraction and with higher concentrations observed in winter (5.7%) and spring (7.9%).
Road dust

The fifth component, road dust, was also identified in both fractions and was related to the high loading of crustal elements, such as Al, Ca (Ca$^{2+}$), Mg (Mg$^{2+}$), Na (Na$^+$) and Co, Ni, Cu (Titos et al., 2014; Vecchi et al., 2008). This source represented 8.4% and 10.9% of the total mass in the fine and coarse fractions, respectively. Contributions of road dust to both PM$_{2.1}$ and PM$_{2.1-9}$ followed the order winter (9.9% to PM$_{2.1}$ and to 18.3% to PM$_{2.1-9}$) > autumn (10.2% and 16.0%) > spring (4.9% and 9.3%) > summer (6.3% and 4.7%).

Vehicle emissions

The sixth source, vehicle emissions, which was only identified in fine fraction and was characterized by high Pb, Cd, Zn, K and EC (Begum et al., 2004; Karnae and John, 2011). EC primarily arises from engines; Zn and K are found in tailpipe emissions; Pb is present in motor and fuel oil combustion (Yang et al., 2013). This source explained 19.6% of PM$_{2.1}$. Contributions of vehicle emissions PM$_{2.1}$ were higher in spring and summer. During 2000 and the period 2009-2010, the contributions from vehicles to the fine particles in Beijing were 7% and 4%, respectively (Zheng et al., 2005; Zhang et al., 2013b), and these values were lower than those reported in this study. The source in previous studies might be primary emissions from vehicles, however, in addition to primary emissions, vehicles also emit large amounts of NO$_x$ precursors, which contributed significantly to the PM via the generation of secondary particles. This important contribution was included in the SIA source but not in the primary emissions factor. Thus, the contributions of traffic emissions to PM will be much higher than the present value if we further consider the secondary formation of NO$_3^-$ from NO$_x$. Besides, vehicles equipped with three-way catalysts are an important source of NH$_3$, which may also contribute to the SIA.

Mineral dust

The seventh component, mineral dust, was only identified in coarse fraction and
was related to the high loading of crustal elements, such as Al, Fe, Ca (Ca$^{2+}$), Mg, K ($K^+$) (Titos et al., 2014; Vecchi et al., 2008). This source might mainly indicate local and long-range transported dust aerosols and represented 22.6% to the total mass in coarse fraction. It exhibited a typical seasonal variation, with higher concentrations observed in spring (36.2%).

**Organic aerosol**

The eighth source was relevant to organic aerosol, which was only identified in coarse fraction and was typically characterized by significant amounts of OC. Organic aerosol contributed 23.6% (14.7 μg m$^{-3}$) to the coarse particles. Its contributions to PM$_{2.1-9}$ demonstrated a typical seasonal variation, with higher concentrations observed in summer (51.3%).

### 4.3.2 Non-haze vs. haze days

Figs. 6a-d illustrate the contributions of the six sources to the fine and seven source to the coarse particles on clear and haze days. On haze days, the contributions of SIA, coal combustion, biomass burning, industrial pollution, road dust and vehicle emissions, were 18.4%, 13.8%, 16.0%, 12.5%, 12.8% and 17.5% to the fine fractions and the contributions of SIA, coal combustion, biomass burning, industrial pollution, road dust, mineral dust and organic aerosol were 13.4%, 8.7%, 7.8%, 5.2%, 8.3%, 24.4% and 19.5% to the coarse fractions. The contributions of these factors on haze days were higher than those on non-haze days, except road dust, and industrial pollution to fine fraction and mineral dust to coarse fraction particles. Additionally, the $R_{HN}$ of the six sources was highest for SIA (6.9 to fine particles vs. 10.1 to coarse particles), followed by vehicle emissions (4.3 to fine particles), biomass burning (2.8 vs. 2.2), coal combustion (1.9 vs. 2.5), mineral dust (1.7 to coarse particles), organic aerosol (1.47 to coarse particles), industrial pollution (1.2 vs. 2.1) and, finally, road dust (0.7 vs. 0.7). The high $R_{HN}$ values indicated that enhanced secondary conversion could occur in the atmosphere during heavy-pollution days. Furthermore, primary particles and gaseous precursors from coal combustion and traffic emissions played
important roles in haze pollution.

The strong contribution of mineral dust and road dust on non-haze days was primarily due to high wind speeds, which transported large quantities of particles from nearby areas outside of the city. Similarly, the industrial pollution affecting urban Beijing primarily arose from the surrounding areas, and the high wind speeds on non-haze days transported large quantities of industrial emission particles into Beijing from outside areas. However, on haze days, particles from coal combustion, primary emissions from vehicles, biomass burning and secondary formation were important. Thus, strict control over particles and gaseous precursor emissions from coal and oil combustion is required.

4.3.3 Difference among the size fractions

Fig. 7 shows that the relative contributions of each identified source varied substantially among size fractions. Among all the sources, SIA and mineral dust (road dust for fine fractions and road dust plus mineral dust for coarse fractions), which were also identified in the mass closure analyses, exhibited relative orders in the eight size fractions that were similar to those in the mass closure results. However, the contributions of SIA in the eight size fractions were different from the contributions of SNA obtained by mass closure (i.e., 3.2-30.4% for SIA vs. 4.1-34.5% for SNA). The contribution of mineral dust increased with particle size, with the highest contribution found observed in the 3.3-4.7 \( \mu \text{m} \) fraction (37.4%) and the lowest contribution observed in the 0.65-1.1 \( \mu \text{m} \) fraction (5.2%). These results were consistent with the mass closure results, which indirectly verified the reliability of the PMF results.

The contributions of the other sources (coal combustion, biomass burning, industrial pollution) generally decreased with increasing size fraction and were present at high concentrations in the fine and coarse modes. For example, the contributions of coal combustion to the total mass in the different size fractions ranged from 7.2% to 42.2%, with the highest proportion found in the <0.43 \( \mu \text{m} \) fraction.
fraction (42.2%) and a relatively high proportion found in the 3.3-4.7 μm fraction (8.5%). Similarly, the contributions of industrial pollution ranged from 2.4% (5.8-9 μm) to 15.9% (<0.43 μm). The concentrations of biomass burning were approximately 8% with high proportions in the fine (< 0.43 μm) and (1.1-2.1 μm). The complexity of the source apportionment results for different size fractions indirectly verifies that the source apportionment of PM$_{2.5}$ cannot provide comprehensive source information because it neglects the importance of the sources that dominated the coarse size fractions. For example, the highest proportion of industrial pollution was observed in the 3.3-4.7 μm size fraction.

To further examine the importance of source apportionment in the different size fractions, we compared the source apportionment results for the corresponding size sub-fractions within PM$_{2.1}$ and PM$_{2.1-9}$. As shown in Fig. 7, the contributions of each source to PM significantly varied among the size fractions within PM$_{2.1}$ and PM$_{2.1-9}$. The contributions of SIA, coal combustion, vehicle emissions and road dust to the size fractions within PM$_{2.1}$ ranged from 8.9% to 30.4%, from 10.1% to 42.2%, from 11.4% to 27.7% and from 5.2% to 10.5%, respectively. In addition, significant differences were observed among the size fractions within PM$_{2.1-9}$ regarding the contributions of SIA, industrial pollution and organic aerosol, which ranged from 3.2% to 23.6%, from 2.4% to 8.5% and from 13.8% to 27.9%, respectively. This result further indicated the importance of source apportionment for subdivided size fractions within PM$_{2.1}$ and PM$_{2.1-9}$.

4.3.4 Back trajectory cluster analysis

Approximately 34% of PM$_{2.5}$ in urban Beijing can be attributed to sources outside of Beijing, and the contribution increased 50-70% during sustained wind flow from the south Hebei Province (Streets et al., 2007). This modeling result indicated the importance of the regional transport effect on fine particles in urban Beijing, but the; However the source apportionment based on size-resolved chemical measurements was previously unavailable.
To fill this gap, the annual data were subjected to back trajectory cluster analysis to identify the source regions and primary atmospheric circulation pathways that influence the PM concentration and chemical species (Fig. 8). The air masses that reach Beijing follow seven main paths, including four from the northwest (NW, C1, C2, C5 and C7) and one from southwest (SW, C3), one from the southeast (SE, C4) and one from the northeast (NE, C6). Fig. S8 shows the size distributions of the mass concentrations within each trajectory cluster. The size distributions of the mass concentrations reveal large differences between the different trajectory clusters in the fine mode, especially in the peak size fraction (0.65-1.1 μm).

Because regional transport has stronger impacts on fine particles than on coarse particles, with the largest differences observed between trajectory clusters, we only report the identified PM$_{2.1}$ sources associated with different trajectory clusters to determine the effects of the different source regions (Fig. 8). The polluted air mass trajectories are defined as those with PM$_{2.1}$ concentrations higher than the annual mean of 67.3 μg m$^{-3}$.

Although the greatest proportion of the trajectories (approximately 36%) was assigned to the NW cluster, this cluster was associated with the lowest PM$_{2.1}$ concentration of 47.6 μg m$^{-3}$. Thus, this cluster has a weaker effect on PM pollution in Beijing. The long and rapidly moving trajectories were disaggregated into this group, and members of this cluster have extremely long transport patterns in which some parts cross over Mongolia, Inner Mongolia and northwest Hebei. In addition, this cluster was dominated by coal combustion (19%) and SIA (18%).

The SW cluster is the most important transport pathway with a large number of trajectories (approximately 32%) and a high PM$_{2.1}$ concentration (79.9 μg m$^{-3}$). The trajectories belonging to the SW cluster are characterized by the shortest trajectories, which indicate the closest and slowest-moving air masses that are primarily transported from Hebei and south Beijing. Most of the extreme episodes in this group were probably enriched by regional and local emission sources. As shown in Fig. 8,
As shown in Fig. 8, only 15% and 16% of the trajectories were assigned to the SE and NE clusters, respectively. However, these trajectories were associated with high PM$_{2.1}$ concentrations (87.0 and 67.4 μg m$^{-3}$). The SE cluster typically followed a flow pattern over north Jiangsu and Shandong and was dominated by SIA (31%) and vehicle emissions (28%). In addition, the NE cluster, which crossed over the Liaoning Province and Tianjin, was dominated by SIA (25%), vehicle emissions (22%) and coal combustion (20%). These results show that southern flows were dominant in urban Beijing and were associated with higher SIA, vehicle emissions and coal combustion contributions. Because SIA is primarily attributed to the transformation of precursors that originate from oil and coal combustion (i.e., NO$_x$ and SO$_2$), controlling oil and coal combustion in the southern regions is required.

4.4 Reconstructing the visibility

In addition to particle size distributions, various chemical components play significant but different roles in reducing visibility on haze days. To further investigate the effects of the chemical species in the different size fractions and meteorological factors on visibility, correlation analyses were performed and regression model was used. SPSS 16.0 was used for multiple linear regression analysis (Cheng et al., 2011).

In this study, 93 variables were investigated; however, only 7 variables were selected because they had high correlation coefficients (> 0.5) with visibility. Overall, the results (Table S3) showed that visibility had high correlation coefficients (> 0.5) with SO$_4^{2-}$ in the 0.43-0.65 μm and 0.65-1.1 μm size fractions, NH$_4^+$ in the 0.43-0.65 μm and NO$_3^-$ in the 0.65-1.1 μm size fractions and Ca$^{2+}$ in the 5.8-9 μm size fraction as well as the RH and WS. All of the parameters that significantly affected visibility were used as inputs in the multiple linear regression models to simulate visibility. Ultimately, we developed the following regression equation for urban visibility in Beijing (Line 756-757).
Previously, SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ in PM$_{2.5}$ were reported to play important roles in visibility degradation during haze events in Beijing (Zhang et al., 2015). Compared with previous studies, this study provides additional insights into the effects of chemical species in different size fractions on the visibility. In addition, the RH, WS and Ca$^{2+}$ content are important for explaining changes in visibility. High RH is conducive to the hygroscopic growth of particulate matter and the generation of secondary species and reduces the visibility. In addition, Ca$^{2+}$ crucially affects visibility because it associated with dust, which strongly reduces visibility. By contrast, high wind speeds are favorable for the diffusion of fine particles and can improve visibility.

NH$_4^+$ in the 0.43-0.65 μm size fraction, SO$_4^{2-}$ in the 0.65-1.1 μm size fraction, and NO$_3^-$ in the 0.65-1.1 μm size fraction are also among the most important factors that affect visibility. These species primarily accumulated in the submicron particles. Because the SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ in this size fraction primarily originated from gaseous precursors (NH$_3$, NO$_2$ and SO$_2$), regulations that control gaseous emissions of these precursors are important for reducing PM pollution and therefore improving visibility.

Our findings were similar to those reported for Jinan, in which the SO$_4^{2-}$ and water content in the 1.0-1.8 μm fraction and the RH were the most important factors that affected visibility (Cheng et al., 2011). However, in this study, the Ca$^{2+}$ in the coarse particles, which primarily originated from construction dust and dust transported over long distances (Liu et al., 2014a; Maenhaut et al., 2002b), also played an important role in reducing the visibility in urban Beijing. However, the transport of over long distances is not easy to control. Thus, we stress that construction dust must be controlled to improve visibility.
To validate the above equation, datasets from other periods (from March 2012 to February 2013) were used to characterize the relationships between visibility and chemical species (Miao, 2014). As shown in Fig. S9, the estimated visibility was well correlated with the measured visibility ($R^2 = 0.87$, $p < 0.05$). However, the ratio of the estimated visibility to the measured visibility was only 0.78, and discrete points primarily appeared for visibilities greater than 10 km (clear days). After scaling down, i.e., using datasets with visibilities less than 10 km to validate the above equation, the ratio of the estimated visibility to the measured visibility reached 1.15 and $R^2$ reached 0.97. This result indicated that the species that resulted in reduced visibility were different for haze and clear conditions. This result is another indication that the above equation can characterize the relationship between visibility and chemical species during haze periods with a visibility of less than 10 km. This result will be useful for reconstructing the relationships between visibility and particulate matter source and we will do more discussion regarding this topic in the future.

5. Summary and conclusions

The analysis of size-segregated airborne particles collected in Beijing from March 1, 2013 to February 28, 2014 was presented. The annual average mass concentrations of the fine and coarse particles were higher than the National Ambient Air Quality Standard (Grade I) of China. The OC, $SO_4^{2−}$, $NO_3^{−}$ and $NH_4^+$ species were the most abundant in the fine particles, accounting for 24.5%, 14.7%, 11.2% and 9.2% of the PM$_{2.1}$ mass, respectively. In PM$_{2.1-9}$, the primary chemical components were Ca (16.3%) and OC (15.5%). SOC, which formed due to photochemical reactions, primarily accumulated in the “condensation mode”. The size distribution of the OC peaked at 0.43-0.65 μm in summer and at 0.65-1.1 μm in winter.

The dataset excluding extreme weather events (i.e., rain, snow, fog and dust) was categorized into non-haze and haze days. $NO_3^{−}$, $SO_4^{2−}$, $NH_4^+$, Pb, Tl and Cd in PM$_{2.1}$ accumulated heavily during haze periods with $R_{HN} > 2.6$. In coarse particles, the $R_{HN}$ values of $NH_4^+$, $NO_3^{−}$, $SO_4^{2−}$, Cd, EC, Cl−, Pb, Tl, Na+, OC, Zn and K+ were also
greater than unity, indicating that the effect of particles with a diameter larger than 2.1 μm cannot be neglected. The annual average size distributions of \( \text{SO}_4^{2-} \), \( \text{OC} \), \( \text{NO}_3^- \), \( \text{NH}_4^+ \), \( \text{Cl}^- \), \( \text{K}^+ \) and \( \text{Cd} \) exhibited peak shifts from 0.43-0.65 μm on non-haze days to 0.65-1.1 μm on haze days. In addition, a regression equation was developed to characterize the relationship between the visibility and the chemical species concentrations when the visibility was less than 10 km.

The mass closure results showed that OM, SNA and CM dominated the fine and coarse particulate mass concentrations. Although OM dominates in fine particles, it decreased from 37.9% on non-haze days to 31.2% on haze days. In contrast, the contribution of SNA to the \( \text{PM}_{2.1} \) mass increased from 19.1% on non-haze days to 33.9% on haze days, indicating that SNA played a key role in haze formation. Moreover, the SNA, OM, HM and EC contributions decreased as the size increased, whereas those of CM and SS exhibited the opposite trend. Further studies are required to determine the identities of the unidentified components in the larger size fractions.

Six \( \text{PM}_{2.1} \) sources and seven \( \text{PM}_{2.1-9} \) sources were identified using the PMF method based on the annual size-segregated data. The source concentrations varied between non-haze and haze days. The results show that coal combustion, vehicle emissions, industrial pollution, biomass burning and secondary formation were major contributors on haze days. In contrast, mineral dust (road dust) was important source on non-haze days. In addition, the relative contributions of these sources in Beijing varied significantly as the fraction sizes changed. The contributions of all of the sources decreased as the size of the fraction increased with the exception of mineral dust; however, they exhibited relatively high proportions in the fine and coarse modes, indicating the importance of source apportionment for size sub-fractions within \( \text{PM}_{2.1} \) and \( \text{PM}_{2.1-9} \). Combining these findings with the trajectory clustering results, the source regions associated with \( \text{PM}_{2.1} \) in Beijing were further explored. We found that the southern and northeastern flows are associated with greater SIA, vehicle emissions...
and coal combustion contributions, whereas the northwestern flows transport more mineral dust.

Acknowledgements

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Figure captions

Fig. 1 Mass concentration size distributions and that of typical chemical species in different categories.

Fig. 2 Size-resolved mass concentration (distributions that are marked as solid circle and open triangle denote haze and non-haze days, respectively).

Fig. 3 Mass concentration size distributions on haze and non-haze days over the entire sampling period (annual) and by season as well as that of the typical chemical species.

Fig. 4 Contributions of different components to the total masses in (a) PM$_{2.1}$ on non-haze days; (b) PM$_{2.1}$ on haze days; (c) PM$_{2.1,9}$ on non-haze days; (d) PM$_{2.1,9}$ on haze days; (e) different size fractions.

Fig. 5 The profiles of each source in (a) fine and (b) coarse fractions.

Fig. 6 Relative contributions from each identified source to (a) PM$_{2.1}$ on non-haze days; (b) PM$_{2.1}$ on haze days; (c) PM$_{2.1,9}$ on non-haze days; (d) PM$_{2.1,9}$ on haze days and (e) mass concentrations of each source.

Fig. 7 Relative contributions from each identified source to different size fractions.

Fig. 8 Relative contributions from each identified source to PM$_{2.1}$ at different trajectory clusters.
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Figure 3. Mass concentration size distributions on haze and non-haze days over the entire sampling period (annual) and by season as well as that of the typical chemical species.
Fig. 4 Contributions of different components to the total masses in (a) PM$_{2.1}$ on non-haze days; (b) PM$_{2.1}$ on haze days; (c) PM$_{2.1-9}$ on non-haze days; (d) PM$_{2.1-9}$ on haze days; (e) different size fractions.
Figure 5. The profiles of each source in (a) fine and (b) coarse fractions.
Figure 6. Relative contributions from each identified source to (a) PM$_{2.1}$ on non-haze days; (b) PM$_{2.1}$ on haze days; (c) PM$_{2.1-9}$ on non-haze days; (d) PM$_{2.1-9}$ on haze days and (e) mass concentrations of each source.
Figure 7. Relative contributions from each identified source to different size fractions.

Figure 8. Relative contributions from each identified source to PM$_{2.1}$ at different trajectory clusters.
Table 1 Concentrations of different chemical compositions in size-resolved particles during entire sampling period (annual) and four seasons (μg m⁻³).

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<td>PM₂,₁</td>
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