Characteristics of Aerosol Optical Properties and Their Chemical Apportionments during CAREBeijing 2006

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ABSTRACT

Field campaigns monitoring the aerosol optical properties and chemical components of PM₁₀ were carried out in Beijing in 2006 summer. The average light extinction coefficient bₚₑₓᵗ, dry aerosol scattering coefficient bₛₚ and aerosol absorption coefficient bₐₚ were 895.0 ± 820.8 Mm⁻¹, 364.0 ± 324.3 Mm⁻¹ and 57.8 ± 31.1 Mm⁻¹, respectively. bₚₑₓᵗ, bₛₚ and bₐₚ had the similar increasing trend during the formation process of haze. Pronounced diurnal cycles were observed for ω₅₅₀ (aerosol single scattering albedo at 550 nm), bₛₚ, bₐₚ and bₚₑₓᵗ. The dry bₛₚ was elevated during the daytime with a maximum mean value of 475.8 Mm⁻¹ (LST 06:00). bₒₓₚ, PM₂.₅ mass concentration and PM₂.₅/PM₁₀ ratio increased at night due to continuous emissions of pollutants to the lower nocturnal boundary layer, and decreased during the daytime due to convective mixing. bₐₚ increased at night, and decreased during the daytime and reached the minimum (37 Mm⁻¹) at LST 16:00. The single scattering albedo reached its maximum (0.87) at LST 11:00. This trend was consistent with the SNA (sulfate, nitrate, and ammonium)/PM₁₀ ratio and was contrary to the BC (black carbon)/PM₁₀ ratio, which demonstrated that secondary pollution largely influenced the scattering ability of aerosols. Ammonium sulfate, ammonium nitrate, organic mass, elemental carbon and coarse mass contributed 26.5%, 15.2%, 21.8%, 16.1% and 20.4% to the total extinction coefficient during clean days, and 44.6%, 22.3%, 13.6%, 10.8% and 8.7% during hazy days. The fractional contributions of ammonium sulfate and ammonium nitrate were significantly higher during the hazy time than those during the clean days. While the fractional contributions of organic mass, elemental carbon and coarse mass were lower during the haze time than those during the clean days.

Keyword: Optical properties; Diurnal variations; Chemical apportionment; Beijing.

INTRODUCTION

Atmospheric aerosols, consisting of liquid and solid particles suspended in the air, are important components of atmosphere. Aerosols play a significant role in visibility reduction (Watson, 2002), regional air quality (Molina and Molina, 2004), and climate change (IPCC, 2007). Components of airborne aerosols, such as sulfate, nitrate, ammonium, black carbon (BC), particulate organic matter (POM), and other chemical species can scatter and absorb the incident light and therefore lead to atmospheric dimming and horizontal visibility degradation (Liu et al., 2009). Several key aerosol optical properties (AOPs), including atmospheric aerosol burden, single scattering albedo (ω), upscatter fraction and the mass scattering and absorption efficiencies must be measured or estimated to evaluate the local or regional aerosol pollution (Chylek and Wong 1995). To fully understand the aerosol optical properties, extensive sets of both in situ and remote measurements are required (Alados-Arboledas et al., 2008). Several observational networks of aerosol optical properties have been established internationally including AERONET (AErosol RObotic NETwork), SKYNET (SKY Network), AEROCAN (Canadian Sunphotometer Network), RIMA (Red Ibérica de Medida de Aerosoles), AGSNet (Aerosol Ground Station Network) and others (Holben et al., 1998; Bokoya et al., 2001; O’Brien and Mitchell, 2003; Uchiyama et al., 2005; Campanelli et al., 2007; Goloub et al., 2008).

Previous studies showed that sulfate and organic mass are the main chemical components contributing to light
extinction and visibility degradation (Cheung et al., 2005; Yuan et al., 2006; Yang et al., 2007; Tao et al., 2009; Liu et al., 2012). Though gas pollutants can also reduce visibility through light extinction, this influence is generally weak (Chan et al., 1999). Moreover, meteorological parameters also contribute to visibility degradation, especially relative humidity (Malm and Day, 2001; Liu et al., 2008; Liu et al., 2013a, b). Many studies on chemical compositions of PM$_{10}$ (particulate matter with aerodynamic diameter less than 10 µm) and PM$_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5 µm) in Beijing have been carried out during last decade (He et al., 2001; Yao et al., 2002; Yang et al., 2005; Sun et al., 2006). These studies indicated that the water soluble inorganic ions and carbonaceous aerosols were major components of aerosols. There are also studies focusing on pollution levels and chemical compositions such as water soluble inorganic ions, carbonaceous fractions, and trace elements (He et al., 2001; Ye et al., 2003; Duan et al., 2006; Gu et al., 2011), however, studies on the relationship between aerosol chemical composition and optical properties remain limited. Thus, it is necessary to study the characteristics of aerosol optical properties and their chemical apportionments to understand the cause of visibility degradation. In this study, we analyzed the chemical components and optical properties of aerosols from 18 August to 8 September 2006 in the urban area of megacity Beijing, and studied the relations between aerosol optical properties and their chemical components.

EXPERIMENT

Experiment Site
The CAREBeijing 2006 campaign (Liu et al., 2009) was carried out in urban and rural site of Beijing, China in the summer of 2006. By the end of 2006, Beijing had a population of 15.8 million with a population density of 963 people per square kilometer (http://www.bjstats.gov.cn/nj/main/2007-tjnj/index.htm). With the rapid economic growth (annual GDP had a growth rate of 12.8% in 2006), the total energy consumption reached 59 million tons of standard coal (http://www.bjstats.gov.cn/nj/main/2007-tjnj/index.htm). The number vehicles also reached 2.8 million in 2006, an increase of 11.9% compared with 2005 (http://www.bjstats.gov.cn/nj/main/2007-tjnj/index.htm). High population density and extensive economic activities had inevitably resulted in heavy emission of air pollutants in Beijing.

Field measurements in urban site of Beijing were carried out from August 18 to September 8, 2006 on the campus of Peking University (39.98°N, 116.35°E), which is located in the north-western of Beijing and is ~600 meters to the north fourth ring road. The observation station was set up on the roof of a 6-floor building (~20 m above ground level). The observation sites are to some extent influenced by local vehicular traffic, combustion of fuels for cooking, local industrial activities and some of transported pollutants (Liu et al., 2009).

Measurement and Method

Instruments used in this study with their model and manufacturer information are listed in Table 1. Mass concentrations of PM$_{10}$ and PM$_{2.5}$ were measured by the dust monitors & counters (Grimm M265, USA). Water-soluble ionic components (WSIC) including cations (Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$) and anions (Cl$^–$, NO$_2^–$, NO$_3^–$, SO$_4^{2–}$) in PM$_{10}$ were measured by an in-situ particle-into-liquid sampler (PILS) system (Orsini et al., 2003). Atmospheric extinction coefficient b$_{ext}$, aerosol scattering coefficient at dry conditions b$_{sc}$, aerosol absorption coefficient b$_{abs}$, and RH were measured by transmissiometer (Malm and Persha, 1991), integrating nephelometer (Anderson and Ogren, 1998), multi-angle absorption photometer (MAAP) (Petzold and Schonlinner, 2001), and automatic meteorological station, respectively. It should be noted that the wavelengths that the optical instruments used were different. As a result, all parameters were scaled to values at the wavelength of 550 nm by using power-law wavelength dependence (Liu et al., 2012). Elemental carbon (EC) and organic carbon (OC) were monitored by a semi-continuous OC/EC analyzer with the thermal-optical transmittance method (Kondo et al., 2006). Mie scattering LIDAR (light detection and ranging), being

<table>
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<tr>
<th>Parameters</th>
<th>Instrument</th>
<th>Model</th>
<th>Calibration</th>
<th>Wavelength (nm)</th>
<th>Resolution</th>
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</thead>
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<tr>
<td>Light extinction coefficient (b$_{ext}$)</td>
<td>transmissiometer</td>
<td>LPV-2 Optec, USA</td>
<td>Before and after the campaign</td>
<td>550</td>
<td>1 min</td>
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<tr>
<td>Aerosol scattering coefficient (b$_{sc}$)</td>
<td>Nephelometer</td>
<td>M9003 Ecotech, Australia</td>
<td>Before and after the campaign</td>
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<td>5 min</td>
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<tr>
<td>Aerosol absorption coefficient (b$_{abs}$)</td>
<td>MAAP</td>
<td>5012 Thermo Scientific</td>
<td>Before and after the campaign</td>
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<td>1 min</td>
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<td>PM$<em>{10}$/PM$</em>{2.5}$ mass concentration</td>
<td>Dust monitors &amp; counters</td>
<td>GRIMM 265</td>
<td>/</td>
<td>/</td>
<td>30 min</td>
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<tr>
<td>Organic carbon/elemental carbon (OC/EC)</td>
<td>Semi-continuous OC/EC analyzer</td>
<td>Sunset Laboratory, Oregon, USA</td>
<td>/</td>
<td>/</td>
<td>1 hour</td>
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<tr>
<td>Water-soluble ions</td>
<td>PILS system</td>
<td>Dionex, USA</td>
<td>Zero check every day</td>
<td>/</td>
<td>15 min</td>
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<td>Height of PBL</td>
<td>LIDAR</td>
<td>Mie Compact</td>
<td>/</td>
<td>532/1064</td>
<td>15 min</td>
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similar to that reported by Sugimoto et al. (2009), continuously monitored the profile of aerosol distribution in troposphere. We used the coefficient of variance ($v$) of LIDAR signals calculated by Eq. (1) to determine the height of the PBL (planetary boundary layer) (Liu et al., 2013b; Strawbridge and Snyder, 2004).

$$v = \frac{\sqrt{\frac{1}{n} \sum_{i=1}^{n} (x_i - \bar{x})^2}}{\bar{x}} \times 100\%$$

where $S$ is standard deviation and $\bar{x}$ is the average of adjacent five LIDAR signals, which were from the normalized backscattering data on 532 nm wavelength channel. The site where its coefficient of variance is the maximum is the height of the PBL.

All of the instruments mentioned above were calibrated according to their manufacturers’ manual. The transmissiometer was installed outdoor, and other instruments were installed in an air-conditioned room.

The light extinction coefficient, $b_{\text{ext}}$, which is wavelength dependent, can be expressed as the sum of scattering ($b_{\text{scat}}$) and absorption ($b_{\text{abs}}$) by Eq. (2).

$$b_{\text{ext}} = b_{\text{scat}} + b_{\text{abs}} = b_{\text{sg}} + b_{\text{sp}} + b_{\text{ag}} + b_{\text{ap}}$$

where $b_{\text{scat}}$ is the sum of scattering by gases $b_{\text{sg}}$ and particles $b_{\text{sp}}$, and $b_{\text{abs}}$ is the sum of absorption by gases $b_{\text{ag}}$ and particles $b_{\text{ap}}$. $b_{\text{sp}}$ is referred to as Rayleigh scattering (approximately 10 Mm$^{-1}$), and $b_{\text{sg}}$, which is the largest contributor to total light extinction in most areas (Malm et al., 1994; Chan et al., 1999), is caused by both fine and coarse particles. $b_{\text{sp}}$ is mainly due to absorption of nitrogen dioxide (NO$_2$), while $b_{\text{sg}}$ is primarily caused by carbon-containing particles.

The approach used in the IMPROVE (The Interagency Monitoring of Protected Visual Environments) program to estimate light extinction for aerosol components assumes externally mixed aerosols. The reconstructed $b_{\text{ext}}$ can then be calculated from the mass concentrations of the aerosol components using Eq. (3), based on the original IMPROVE algorithm (Malm and Hand, 1994; Malm et al., 2007):

$$b_{\text{ext}} = 3f(RH)\times[(NH_4)_2SO_4]+3f(RH)\times[NH_4NO_3]+4\times[POM]+10\times[EC]+1\times[\text{Fine Soil}]+0.6\times[\text{Coarse Mass}] + 0.161\times[NO_2] + 10$$  

$$[(NH_4)_2SO_4] = 0.944\times[NH_4^+] + 1.02\times[SO_4^{2-}]$$

$$[NH_4NO_3] = 1.29\times[NO_3^-]$$

$$[POM] = 1.6\times[OC]$$

$$[\text{Fine Soil}] = 2.49\times[Si] + 2.2\times[Al] + 2.42\times[Fe] + 1.63\times[Ca] + 1.94\times[Ti]$$

$$[\text{Coarse Mass}] = PM_{10} - PM_{2.5}$$

Eq. (3) includes a constant 10 Mm$^{-1}$ which denotes the Rayleigh scattering of clear air. The light extinction coefficients of atmospheric aerosol are in Mm$^{-1}$. The chemical composition concentrations shown in brackets are in unit of µg/m$^3$. Dry efficiency terms are in unit of m$^2$/g; and the hygroscopic growth terms, $f$(RH), are unitless. Elemental carbon (EC) is referred to as light absorbing carbon ($b_{\text{ap}} = 10[EC]$), and the mass extinction coefficient of hygroscopic aerosol implies a RH-dependent scaling factor ($f$(RH)), which represents the relationship between RH and the scattering efficiency. Eqs (4) and (5) assume that SO$_4^{2-}$ and NO$_3^-$ are fully neutralized by NH$_4^+$. Particulate organic matter (POM) was estimated by multiplying the measured OC by a factor (1.6) to compensate for other atoms such as H, O and N in the organic molecule (Turpin and Lim, 2001).

RESULTS AND DISCUSSION

Temporal Variations of Aerosol Chemical and Optical Properties

Temporal variations of the chemical components, optical properties of aerosols and ambient visibility in Beijing from August 18 to September 8 are depicted in Fig. 1. According to the definition of haze (visibility < 10 km and RH < 90%) (Wu et al., 2006), there were four haze episodes observed in Beijing in the time periods of Aug. 18 0:00–Aug. 20 06:00, Aug. 23 1:00–Aug. 28 22:00, Aug. 31 17:00–Sep. 03 11:00 and Sep. 05 22:0–Sep. 08 3:00, and the other days during the campaign could be classified to clean day. $b_{\text{ext}}$, $b_{\text{sp}}$ under dry condition and $b_{\text{ap}}$ had the similar trend to increase during the formation process of haze. The maximum value of $b_{\text{sp}}$(RH) was nearly 5100 Mm$^{-1}$ in the morning of 25th August and the corresponding visibility was as low as 0.8 km. Similarly, the mass concentrations of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and POM also showed an upward trend during the process of haze formation. The average concentrations of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and POM were 49.8, 31.4, 25.8 and 25.0 µg/m$^3$ during the haze episodes in Beijing, which greatly exceeded the overall average of these components during the whole campaign, (34.8, 24.5, 20.7 and 20.9 µg/m$^3$) and even more greater than those during the clean day (11.7, 9.2, 6.3 and 13.9 µg/m$^3$). The mass concentrations of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and POM in hazy days were 4.3, 3.4, 4.1, and 1.8 times of those in clean days. Similar high ratios for NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ in PM$_{2.5}$ between haze days and clean days (6.5, 3.9, and 5.3) have been observed in Guangzhou city of China (Tan et al., 2006).

The atmospheric extinction coefficient, dry aerosol scattering coefficient and aerosol absorption coefficient at 550 nm during CAREBeijing-2006 for $b_{\text{ext}}$, $b_{\text{sp}}$ and $b_{\text{ap}}$ were 895.0 ± 100% Mm$^{-1}$ and $b_{\text{sp}}$,550 = 463 ± 178 Mm$^{-1}$ and $b_{\text{ap}}$,550 = 92 ± 62 Mm$^{-1}$ (Andreae et al., 2008), but are similar to those in the Yangtze
Fig. 1. Time series of the optical parameters ($b_{\text{ext}}$, $b_{\text{sp}}$, $b_{\text{ap}}$), Visibility, and mass concentrations of the chemical components.

delta ($b_{\text{sp}},530 = 353 \pm 202 \text{ Mm}^{-1}$ and $b_{\text{ap}},565 = 23 \pm 14 \text{ Mm}^{-1}$) (Xu et al., 2002) as well as southeast of Guangzhou in Xinken ($b_{\text{sp}},550 = 333 \pm 138 \text{ Mm}^{-1}$ and $b_{\text{ap}},550 = 70 \pm 42 \text{ Mm}^{-1}$) (Cheng et al., 2008). While the current study’s results are larger than a study carried out at a rural site about 150 km northeast of Beijing ($b_{\text{sp}},525 = 174.6 \pm 189.1 \text{ Mm}^{-1}$) (Yan et al., 2008) as well as a study ~60 km northwest of Guangzhou ($b_{\text{sp}},550 = 151 \pm 103 \text{ Mm}^{-1}$ and $b_{\text{ap}},552 = 34.3 \pm 26.5 \text{ Mm}^{-1}$) (Garland et al., 2008). Overall, the average scattering and absorption coefficients observed in this study were higher than reported from other suburban areas but lower than those typically measured in the urban areas of Chinese megacities.

The frequency distributions of dry scattering coefficient, extinction coefficient, absorption coefficient and single
scattering albedo in Beijing are shown in Fig. 2. The frequency distributions of absorption coefficient and single scattering albedo $\omega$ (section 3.2) at 550 nm were essentially normal distributed. The mean ($\mu$) and variance ($\delta$) values of absorption coefficient were 54.4 Mm$^{-1}$ and 41.1 Mm$^{-1}$, and corresponding values of single scattering albedo were 0.84 and 0.07. As can be seen from the Fig. 2, nearly 59% of the absorption coefficient values located in the range of 40–100 Mm$^{-1}$, while approximately 82% of the single scattering albedo values focused on the range of 0.7–1.0. In spite of this, the frequency distribution of dry scattering coefficient and extinction coefficient were different, that is, most of the dry scattering coefficient and extinction coefficient was distributed in the lower range. Obviously, there were 68% of the dry scattering coefficient values concentrated on the limits of 0–400 Mm$^{-1}$ and 66% of the extinction coefficient values located in the range of 0–1100 Mm$^{-1}$.

Diurnal Variations of the Optical Properties and Their Chemical Apportionments

Time series of optical properties shown in Fig. 1 already suggested the existence of significant diel trends. These are confirmed further by plots of hourly averages (Fig. 3). Fig. 3 illustrates the diurnal variations of dry $b_{sp}$, $b_{ap}$, $b_{ext}$ and $\omega$, respectively. The dry $b_{sp}$ was elevated during the daytime with a maximum mean value of 475.8 Mm$^{-1}$ (LST 06:00). Then, the mean values descended between LST 08:00 and LST 20:00 with a minimum mean value of 120 Mm$^{-1}$ (LST 20:00). Fig. 3(b) displayed the diurnal cycle of $b_{ap}$, which was even more pronounced than that of dry $b_{sp}$. Apparently, from LST 06:00 to LST 16:00, the mean $b_{sp}$ values continuously declined and reached the minimum (37 Mm$^{-1}$) at LST 16:00 before it began to increase. The maximum mean value of $b_{sp}$ was 80 Mm$^{-1}$ at LST 23:00. For the diurnal variation of extinction coefficient, the first peak of $b_{ext}$ occurred at LST 06:00 and the second peak appeared at LST 18:00, which indicated that the extinction coefficient increased with the deterioration of air pollution during the morning and evening traffic peak. The single scattering albedo, $\omega$, is the ratio of the scattering coefficient over the extinction coefficient at a given wavelength. Here $\omega$ has been calculated at $\lambda = 550$ nm using Eq. (9).

$$\omega_{550} = \frac{b_{sp}}{b_{sp} + b_{ap}}$$

(9)

The single scattering albedo reflects the scattering power of the atmospheric particulate matter. The mean and standard deviation for $\omega_{550}$ for the campaign was 0.80 ± 0.11, which is close to the values reported from other locations in and around Beijing and Guangzhou for the single scattering albedo of dry aerosol particles in the green spectral range [$\omega = 0.82–0.85$ (Li et al., 1993; Bergin et al., 2001; Cheng et al., 2008; Garland et al., 2008; Andreae et al., 2008)]. It indicated a bigger proportion of absorbing particulate matter at the urban site. As shown in Fig. 3(d), there were two peaks and two valleys. The major peak occurred at

![Fig. 2. The frequency distribution of scattering coefficient (b$_{sp}$), extinction coefficient (b$_{ext}$), absorption coefficient (b$_{ap}$) and single scattering albedo (SSA) in Beijing.](image-url)
Fig. 3. Diurnal variations of (a) $b_{sp}$; (b) $b_{ap}$; (c) $b_{ext}$ and (d) SSA (Single Scattering Albedo) in Beijing. The dot is the mean value, the horizontal line in the box is the median, the limits of the boxes are the 25th percentile and 75th percentile, and the vertical lines extend to 5th and 95th percentiles for each 1-hour period after the indicated start time.

LST 11:00, and the other peak was at LST 18:00. The two valley values appeared at LST 05:00 (0.78) and LST 16:00 (0.79), respectively.

For comparison, Fig. 4 displays the diurnal cycles of the PM$_{2.5}$ mass concentration, PM$_{2.5}$/PM$_{10}$ ratio, SNA/PM$_{10}$ ratio, BC/PM$_{10}$ ratio and the height of PBL, respectively. In Beijing, higher PM$_{2.5}$ concentrations were observed in the night and maximum values observed at LST 23:00 and LST 0:00. PM$_{2.5}$ concentrations began to decrease from LST 0:00 to LST 5:00 except a little peak at LST 6:00. PM$_{2.5}$ concentrations kept on decreasing until LST 16:00, then, PM$_{2.5}$ concentrations started to increase. The trend of PM$_{2.5}$/PM$_{10}$ ratio was similar with the PM$_{2.5}$ mass concentrations which corresponding to the diurnal variations of $b_{ext}$. The diurnal cycles of $b_{ext}$ PM$_{2.5}$ mass concentrations and PM$_{2.5}$/PM$_{10}$ ratio were possibly dominated by convective mixing during the daytime, leading to a dilution and thus a decrease. After sunset, the formation of a stable nocturnal boundary layer (BL) in combination with the continued emission or advection of particles and gases throughout the night, leads to an increase in $b_{ext}$ PM$_{2.5}$ mass concentration and PM$_{2.5}$/PM$_{10}$ ratio. Low height of BL would retain the pollutants in the surface layer (Liu et al., 2013). The diurnal variation of the height of PBL is displayed in the Fig. 4(e). The height of PBL rose from LST 8:00 and reached its peak at LST 14:00, then gradually decreased until LST 23:00. Obviously, the diurnal variation of PBL showed an opposite trend with the mass concentration of PM$_{2.5}$. Because the $b_{sp}$ was calculated from the mass concentration of BC, the diurnal variation of BC/PM$_{10}$ ratio was consistent with $b_{sp}$. Lastly, the SNA/PM$_{10}$ ratio was elevated during the daytime with a maximum mean value of 0.5 at LST 12:00. The SNA/PM$_{10}$ ratio increased with the height of PBL rising during noon time, which indicated that secondary transformation of SNA was active in the noon. Both the mean and median values then decreased between LST 12:00 and LST 21:00 with a minimum mean value of 0.38 at LST 21:00. This trend was consistent with the SSA, which implied that secondary pollution would largely influence the scattering ability of aerosols and the chemical composition had an important impact on the optical properties. As for the reason why SSA reached the maximum at midday, it was partly due to the strong photochemical reactions that led to the formation of secondary pollutant with strong scattering and negligible absorption ability. Meanwhile, the lowest value of BC/PM$_{10}$ ratio was observed at midday. The sulfur oxidation ratio (SOR = $n_{SO_4^{2-}}/(n_{SO_4^{2-}} + n_{SO_2})$, where $n$ refers to the molar concentration) and the nitrogen oxidation ratio (NOR = $n_{NO_3^-}/(n_{NO_3^-} + n_{NO_2})$) are good indicators of secondary transformation. The higher values of SOR and NOR
Fig. 4. Diurnal variations of the (a) PM$_{2.5}$ mass concentration; (b) PM$_{2.5}$/PM$_{10}$ ratio; (c) SNA (sulfate, nitrate, and ammonium)/PM$_{10}$ ratio and (d) BC/PM$_{10}$ ratio in Beijing; (e) The height of PBL (m). Symbols are analogous to Fig. 3.

indicated that more gaseous species had been oxidized to secondary aerosol in the atmosphere (Sun et al., 2006). The diurnal variations of SOR and NOR are depicted in Fig. 5, where a small peak of SOR and NOR was observed at LST 11:00 which conformed to the influence of secondary pollutants to SSA.

**Chemical Apportionment of the Aerosol Optical Properties**

Figs. 6(a), 6(b) and 6(c) illustrate the relationship between $b_{sp}$, $b_{ap}$, $b_{ext}$ and the mass concentration of PM$_{2.5}$ in Beijing during the whole campaign, respectively. In Fig. 6(c), $b_{ext}$ showed an strong and positive correlation with PM$_{2.5}$ mass concentration with a correlation coefficient of 0.90. As shown in Fig. 6(b), $b_{ap}$ was also strong correlated ($r = 0.95$) with PM$_{2.5}$ mass concentration. Same strong correlation was observed for $b_{sp}$ and PM$_{2.5}$ mass concentration.

In this study, we mainly studied the extinction effect by fine particles and the contribution of fine soil was excluded in $b_{ext}$ estimation because it only accounted for a small fraction of PM$_{2.5}$ mass (Wang, 2003). Extinction by fine soil could be neglected from the standpoint of light extinction in summer in Beijing (Liu et al., 2009). Thus, the modified IMPROVE algorithm is presented as Eq. (10).

\[
b_{ext} = 3f(RH) \times [(NH_4)_2SO_4] + 3f(RH) \times [NH_4NO_3] + 4 \times [POM] + 10 \times [EC] + 0.6 \times [\text{Coarse Mass}] + 10 \quad (10)
\]
Fig. 5. Diurnal variations of the (a) SOR (sulfur oxidation ratio) and (b) NOR (nitrogen oxidation ratio) in Beijing. Symbols are analogous to Fig. 3.

Fig. 6. Relationship between the mass concentration of PM$_{2.5}$ and (a) b$_{ap}$; (b) b$_{sp}$; (c) b$_{ext}$ in Beijing.

Table 2 summarizes different f(RH) values for (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ in selected relative humidity ranges (Malm and Day, 2001; Liu et al., 2012). Table 3 lists the composite variables for particulate matter proposed by IMPROVE. According to the Eqs. (4), (5), (6), (8) and (10), the calculated b$_{ext}$ can be derived and then compared with the measured b$_{ext}$. As depicted by Fig. 7(a), the measured b$_{ext}$ were slightly larger than the calculated b$_{ext}$ and the deviation between measured values and calculated values was about 18.4%. Fig. 7(b) illustrated that the correlation coefficient between
Table 2. Statistical summary of mean $f$(RH) values for (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ in selected relative humidity ranges.

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<tr>
<td>$f$(RH)</td>
<td>1.06</td>
<td>1.11</td>
<td>1.16</td>
<td>1.21</td>
<td>1.22</td>
<td>1.27</td>
<td>1.33</td>
<td>1.38</td>
<td>1.45</td>
<td>1.55</td>
<td>1.65</td>
<td>1.83</td>
<td>2.10</td>
<td>2.46</td>
<td>3.17</td>
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</table>

Table 3. Composite variables for particulate matter proposed by IMPROVE.

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<thead>
<tr>
<th>Component</th>
<th>Specification</th>
<th>Mass calculation</th>
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<tbody>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>Ammonium sulfate</td>
<td>0.944[$\text{NH}_4^+$] + 1.02[$\text{SO}_4^{2-}$]$^a$</td>
</tr>
<tr>
<td>NH$_4$NO$_3$</td>
<td>Ammonium nitrate</td>
<td>1.29[$\text{NO}_3^-$]</td>
</tr>
<tr>
<td>OMC</td>
<td>Organic mass by carbon</td>
<td>1.6[$\text{OC}$]$^b$</td>
</tr>
<tr>
<td>$b_{abs}$</td>
<td>Absorption coefficient</td>
<td>[EC]</td>
</tr>
<tr>
<td>CM</td>
<td>Coarse mass</td>
<td>[PM$<em>{10}$]−[PM$</em>{2.5}$]</td>
</tr>
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</table>

$^a$ Malm and Day, 2001; Tao et al., 2009.

$^b$ Turpin and Lim, 2001.

Fig. 7. (a) Time series of the measured $b_{ext}$ and the calculated $b_{ext}$ in Beijing; (b) Relationship between the measured $b_{ext}$ and the calculated $b_{ext}$.

measured $b_{ext}$ and calculated $b_{ext}$ was 0.92, which verified the reliability of IMPROVE algorithm. We conclude that IMPROVE Eq. (10) can be used to calculate the chemical apportionment for extinction effects.

Fig. 8 shows the averaged proportion of chemical components to extinction coefficient in PM$_{10}$ during the CAREBeijing 2006 campaign under (a) clean and (b) hazy days. Ammonium sulfate, ammonium nitrate, organic mass, elemental carbon and coarse mass accounted for 26.5%, 15.2%, 21.8%, 16.1% and 20.4% of the total extinction coefficient during clean days, and 44.6%, 22.3%, 13.6%, 10.8% and 8.7% during hazy days. Ammonium sulfate, ammonium nitrate and POM accounted for 20.2%, 11.2% and 15.8% of the mass concentration of PM$_{10}$ during clean days, and 34.0%, 19.1% and 13.9% during hazy days (Han et al., 2013). Obviously, ammonium sulfate was the largest contribution to the total extinction coefficient, which was comparable to other cities like Hong Kong (47%) (Cheung et al., 2005), Jinan (41%) (Yang et al., 2007), and Guangzhou (40.1%) (Tao et al., 2009) in China and eastern United States (40%) (Watson, 2002). However, organic mass was the largest contributor to the total extinction coefficient in Xiamen (Zhang et al., 2012). The proportion of ammonium sulfate and ammonium nitrate were significantly higher during the hazy time than that during the clean days. While the contribution of organic mass, elemental carbon and coarse mass were lower during the hazy time than that during the clean days. It was characterized that (NH$_4$)$_2$SO$_4$ + NH$_4$NO$_3$ increased while carbonaceous material decreased from clean days to hazy days (Fig. 8), which implied that the SNA (sulfate, nitrate, and ammonium) pollutants were more important than carbonaceous pollution for haze formation, and the problem of secondary pollution for haze episodes was mainly SNA pollution in Beijing.

CONCLUSIONS

As a part of the CAREBeijing 2006 campaign which was carried out from 18 August to 8 September, 2006, aerosol optical and physical properties as well as the aerosol chemical components were observed simultaneously. In this study, we analyzed the characteristics of the aerosol optical properties and explored the relations to the change of the chemical components.

During haze conditions, the averaged concentrations of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and POM were 49.8, 31.4, 25.8 and
Fig. 8. The averaged fractional contributions to extinction coefficient by chemical components under (a) Clean day, and (b) Hazy day during the CAREBeijing 2006 campaign.

25.0 µg/m³ respectively, which were significantly higher than the overall averaged conditions during the campaign (34.8, 24.5, 20.7 and 20.9 µg/m³), and much higher than that of the clean days (11.7, 9.2, 6.3 and 13.9 µg/m³). Pronounced diurnal cycles were observed for \( \omega_{550} \), \( b_{sp} \), \( b_{ap} \) and \( b_{ext} \). The dry \( b_{sp} \) was elevated during the daytime with a maximum mean value of 475.8 Mm⁻¹ (LST 06:00). Both the mean and median values then fell below one between LST 08:00 and LST 20:00 with a minimum mean value of 120 Mm⁻¹ (LST 20:00). The \( b_{ext} \) value increased at night probably due to the lower nocturnal boundary layer while surface emissions continued, and then decreased during the daytime due to the uplift of the boundary layer. The diurnal variations of PM_{2.5} mass concentration and PM_{2.5}/PM_{10} ratio were consistent with the \( b_{ap} \). The \( b_{ap} \) value increased at night, and decreased during the daytime and reached the minimum (37 Mm⁻¹) at LST 16:00. The single scattering albedo reached its maximum at LST 11:00. This trend was consistent with the SNA/PM_{10} ratio and was contrary to the BC (black carbon)/PM_{10} ratio, which demonstrated that secondary pollution largely influenced the scattering ability of aerosol cluster and the chemical composition had an important impact on the aerosols optical properties. In addition, the diurnal variations of SOR and NOR further confirmed the influence of secondary pollutants on SSA.

The \( b_{ext} \), \( b_{sp} \) and \( b_{ap} \) showed an increasing trend with PM_{2.5} mass concentration and the correlation coefficient were 0.90, 0.95 and 0.98, respectively. The calculated \( b_{ext} \) by the modified IMPROVE algorithm agreed with the measured \( b_{ext} \) and the correlation coefficient between measured \( b_{ext} \) and calculated \( b_{ext} \) was 0.92. Ammonium sulfate, ammonium nitrate, organic mass, elemental carbon and coarse mass accounted for 26.5%, 15.2%, 21.8%, 16.1% and 20.4% of the total extinction coefficient during clean days, and accounted for 44.6%, 22.3%, 13.6%, 10.8% and 8.7% during hazy days. It is obvious that ammonium sulfate was the largest contributor to the total extinction coefficient. The proportion of ammonium sulfate and ammonium nitrate were apparently higher during the hazy time than that during the clean day. While the contribution of organic mass, elemental carbon and coarse mass were lower during the hazy time than that during the clean day, which implied that the SNA (sulfate, nitrate, and ammonium) pollutants were more important than carbonaceous pollution for haze formation, and the problem of secondary pollution for haze episodes was mainly SNA pollution in Beijing.

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REFERENCE


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