



Carbonaceous and Ionic Components of Atmospheric Fine Particles in Beijing and Their Impact on Atmospheric Visibility

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ABSTRACT

Ground-based observation of fine particulate matter (PM_{2.5}) in Beijing was carried out continuously in 2006. The carbonaceous and ionic components, as well as their distribution characteristics and seasonal variation, were obtained. The annual mean mass concentration of PM_{2.5} was $176.6 \pm 100.3 \mu\text{g}/\text{m}^3$. Long-range transport dust and local dust raised by strong wind during the spring made a considerable contribution to PM_{2.5} mass concentration. There was significant seasonal variation in carbonaceous and water-soluble ionic components associated with diverse emission sources, varying meteorological conditions during different seasons, and different mechanisms of formation for secondary aerosol ions. Comparing studies under different synoptic conditions suggested that PM_{2.5} pollution was mainly caused by transportation of particulates from remote sources, whereas hazy synoptic conditions are caused by local pollution. PM_{2.5} and visibility were negatively correlated, and the relationship between the concentrations of NH₄⁺, SO₄²⁻, and NO₃⁻ with PM_{2.5} concentration during winter can be described using power function fitting.

Keywords: PM_{2.5}; OC; EC; Ion; Visibility.

INTRODUCTION

Because of the increasing concern about the environment, during recent decades variation and properties of atmospheric pollutants have been investigated by scientists around the worldwide (Arimoto *et al.*, 1996; Brook *et al.*, 1997; Carmichael *et al.*, 1997). The concentration of atmospheric particles is one of the most important indices for assessing air pollution and its sources (Chow *et al.*, 1995). Many studies have shown the considerable impact of PM_{2.5} on human health (Dockery *et al.*, 1993; Pope *et al.*, 1995; Samet *et al.*, 2000), global climate change (Penner and Novakov, 1996; Haywood and Boucher, 2000) and visibility reduction (Sloane *et al.*, 1991; Malm and Pitchford, 1997).

The 29th Summer Olympic Games were held in Beijing during August of 2008 and the air quality situation has attracted worldwide attention. It typically polluted by emissions from the burning of coal and exhaust from vehicles (Zhu *et al.*, 2005; Song *et al.*, 2006), dust storms pollution in and local dust events enhance the complexity of air Beijing

(Zhang *et al.*, 2010). Both the dynamic variation of pollutant emission and the need for a clear sky in Beijing for the 29th Olympic Games, suggest that it is very important to understand the characteristics and sources of atmospheric fine particulate pollution, which are very significant for the establishment and improvement of controls on pollutant emissions.

In the present study, ground-based observation of carbonaceous and ionic components of PM_{2.5} in Beijing was carried out continuously in 2006. The characteristics and seasonal variation of carbonaceous and ionic components as well as the sources of components were identified and discussed. The contributions of NH₄⁺, SO₄²⁻, and NO₃⁻ to PM_{2.5} as well as their effects on visibility were also investigated. The study of chemical composition was a better understanding of the effects of particles (Ning and Sioutas, 2010).

EXPERIMENTS AND METHODS

Location and Sample Collection

Sampling instruments were located at the top of a two-floor building between the third ring road and the fourth ring road (50 m south of the 325 m meteorological tower of the Institute of Atmospheric Physics (39°58'N, 116°20'E)), which represent a typical urban area in Beijing. PM_{2.5}

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samples were collected for 24 hours at 5 L/min with a mini-vol sampler (Airmetrics, Springfield, OR, USA) on 47 mm Whatman quartz-fiber filters (QM-A, Whatman, Clifton, NJ, USA). PM_{2.5} samples were collected every 24 hours during the periods from March 16th to April 6th, July 19th to August 31st, October 23th to November 13th, and from December 6th to December 29th, representing spring, summer, autumn and winter, respectively.

Mass Analysis

Quartz-fiber filters were analyzed gravimetrically for mass concentrations on a Sartorius MC5 electronic microbalance with a $\pm 1 \mu\text{g}$ sensitivity (Sartorius, Göttingen, Germany) after 24-hour equilibration at temperature between 20°C and 23°C and RH between 35% and 45%. Each filter was weighed at least three times before and after sampling, and the net mass was obtained by subtracting the difference between the averaged pre- and post-sampling weights.

Organic Carbon and Elemental Carbon Analyses

A 0.526 cm² punch from each quartz filter was analyzed for organic carbon (OC) and elemental carbon (EC) by the IMPROVE thermal/optical protocol (Chow *et al.*, 1993, Fung *et al.*, 2002, Watson *et al.*, 2005) using a Desert Research Institute (DRI, Reno, NV, USA) Model 2001 thermal/optical carbon analyzer (Atmoslytic Inc., Calabasas, CA, USA). Quality assurance/quality control (QA/QC) procedures are as described by Cao *et al.* (2003).

Ion Analysis

A 25% section of the filter was excised and extracted in 10 ml of high-purity water. Eleven major ionic species (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, F⁻, Cl⁻, Br⁻, NO₂⁻, NO₃⁻, and SO₄²⁻) were measured by DX600 ion chromatography (Dionex Inc., Sunnyvale, CA, USA) (Chow and Watson, 1999). A CS12 column (150 × 4 mm) and an AS14 column (150 × 4 mm) were used for cation and anion analysis, respectively. Field blank levels were averaged and subtracted, and standard deviations were propagated to the measurement precisions.

Meteorological Data Collection

The meteorological data used in the study were obtained from the Data Collection of the China Surface Climate, provided by China Meteorological Administration. The air pollution indices (API) for SO₂ and NO₂ can be obtained from Beijing Public Net for Environment Protection (www.bjee.org.cn).

RESULTS AND DISCUSSION

Meteorological Conditions during Observational Period

Fig. 1 presents the variations of relative humidity (RH), pressure, wind speed and precipitation in Beijing during the observational period in 2006. RH was relatively low during spring and relatively high in the summer, with a mean value of 30% and 71%, respectively. During autumn and winter, RH was in the levels between spring and summer and exhibited considerable variation. Wind speeds during the spring were strong but were weaker during the summer,

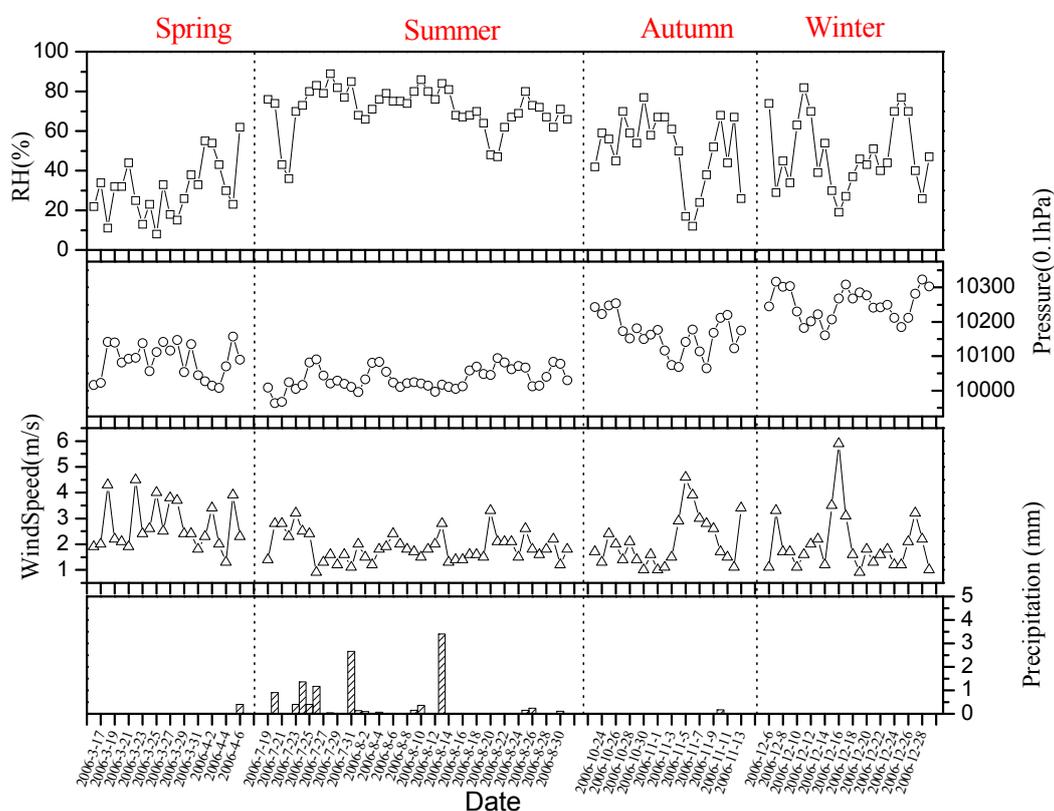


Fig. 1. Meteorological variation in Beijing during observation period in 2006.

with mean values of 2.8 m/s and 1.9 m/s respectively. The wind speed in autumn and winter rapidly increased in conjunction with strong cold fronts. Therefore, the amplitude of wind speed in autumn and winter was considerable. The precipitation in Beijing was concentrated in the summertime. The amount of precipitation in summer accounted for about 95% of the total precipitation observed during the entire observational period. Fig. 1 also shows that the atmospheric surface pressure was higher in winter and lower in summer. Surface inversion layers occur frequently and inhibited the turbulent and vertical motion in the atmosphere. In summer, however, Beijing was dominated by low pressure system, with significant turbulence. Therefore, summer weather conditions were favorable for pollutant dispersion; while just the opposite was true during the winter (Xia, 2004).

Variations in $PM_{2.5}$ Mass Concentration

Fig. 2 shows variation in $PM_{2.5}$ mass concentration during the four-seasons: the minimum value was $39.5 \mu\text{g}/\text{m}^3$, which occurred on August 13th, 2006, while the highest concentration was $504.1 \mu\text{g}/\text{m}^3$, which occurred on March 26th, 2006, about 12-fold the minimum concentration observed. The annual mean value of $PM_{2.5}$ mass concentration was $176.6 \pm 100.3 \mu\text{g}/\text{m}^3$. Katzman *et al.* (2010) investigated $PM_{2.5}$ of 18 cities across the Midwestern USA that the annual average PM concentration is no more than $20 \mu\text{g}/\text{m}^3$. It indicated that developing countries achieve the economic development at the cost of environment pollution. For a given particle size distribution, the main factors influencing the atmospheric aerosol concentration are emission source and meteorological condition (wind speed and direction, atmospheric stability, and precipitation). In Beijing, atmospheric particles sources consisted of vehicle exhaust, coal-burning emissions, blowing dust, and dust in suspension. Vehicle exhaust is a continuous annual pollutant emission source, while coal burning became

significant during seasonal energy generation. Dust events, including dust in suspension, blowing dust and dust storm were evident. The categories of dust events are defined on the basis of horizontal visibility, that is, the horizontal visibilities for dust in suspension, blowing dust and dust storm are less than 10 km, 1 to 10 km, less than 1000 m, respectively (Ho *et al.*, 2010). During the spring observation period, two suspended dust events (March 17th and March 24th, 2006) and one dust storm (March 26th–27th, 2006) occurred; accordingly, $PM_{2.5}$ concentrations during those events were $461.9 \mu\text{g}/\text{m}^3$, $458.2 \mu\text{g}/\text{m}^3$, $504.1 \mu\text{g}/\text{m}^3$, respectively. These observations indicated that the $PM_{2.5}$ concentration was highest in spring, followed by the concentration observed in autumn and winter, and the lowest value was in summer. The ratio of the days with $PM_{2.5}$ concentration greater than the annual mean value to all spring sampling days was 86%, due to the frequent strong spring wind accompanied by locally raised dust. The second highest $PM_{2.5}$ concentration occurred during autumn, and was probably related to biomass-burning and locally blowing dust (for instance, high $PM_{2.5}$ concentrations occurred in November 3rd–6th, 2006 and were caused by dust-blowing weather with strong winds of grade 3–5). During the winter, when many heating systems were run by burning coal, particle emission increased. In winter, Beijing weather was usually influenced by high pressure systems, which cause formation of inversion layers that can inhibit pollutant dispersion. Therefore, the $PM_{2.5}$ concentration in winter was relatively high. However, in winter, days with relatively strong wind were more frequent, often during the winter sampling period. Daily mean winter wind speed was 5.9 m/s, surface inversion intensity is weak relative to during synoptically calm conditions, and high winds favor pollutant transport. These factors resulted in lower $PM_{2.5}$ concentrations in winter than in autumn. In contrast, the $PM_{2.5}$ concentration was low in summer, because (a) Beijing

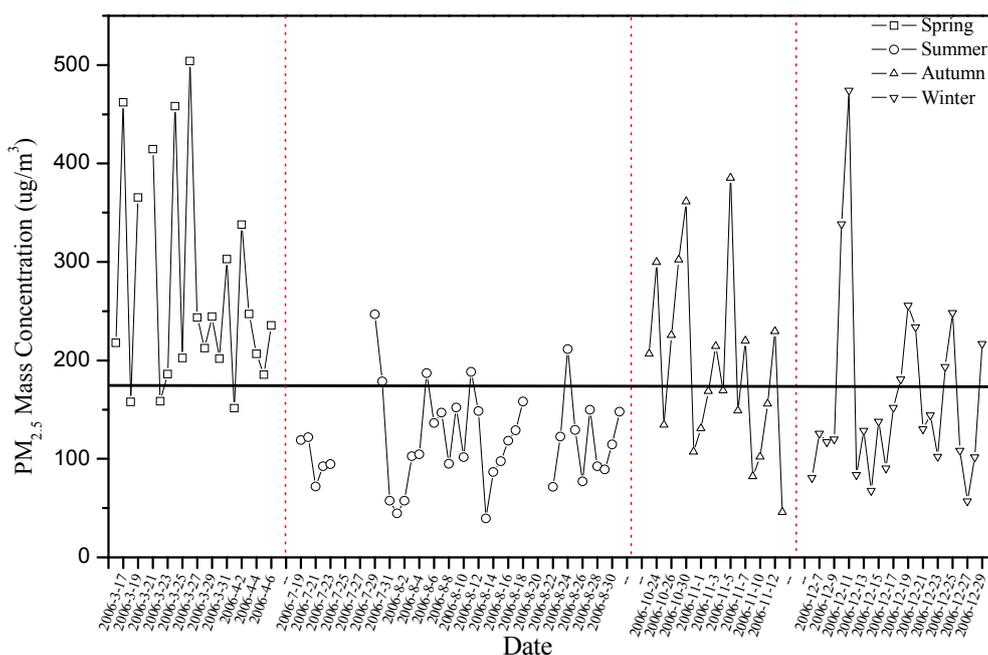


Fig. 2. The sequence of variation in $PM_{2.5}$ mass concentration during the observation period.

was often under low pressure systems; (b) temperatures were high and convection was strong, which favors particle dispersion; (c) precipitation was relatively abundant, which washes particulates downward; and (d) No coal combustion for heating which is a main PM_{2.5} source in winter in Beijing

Characteristics of Carbonaceous and Water-Soluble Species

Carbonaceous Species

Table 1 presents that the annual mean concentrations of the OC and EC components in PM_{2.5} were $25.9 \pm 15.8 \mu\text{g}/\text{m}^3$, and $6.1 \pm 3.4 \mu\text{g}/\text{m}^3$, respectively. The order of seasonal variation in OC concentration was: winter > autumn > spring > summer. The mean value for OC concentration in winter was about 2.5-fold that in summer. The seasonal variation in EC level was: autumn > winter > spring > summer, distinct from what was observed for OC. The mean value for EC in autumn was about 2-fold that in summer. The differences in seasonal variation between OC and EC suggest that emission sources for OC and EC are probably different.

Turpin *et al.* (1990) explained that the sources of carbonaceous aerosols can be determined by investigating the relationship between OC and EC concentrations. Once the correlation coefficient between OC and EC is significant, it suggests that OC and EC originated from the same pollution sources. In the present study, the correlation coefficient between OC and EC in PM_{2.5} was 0.89 ($p < 0.0001$), suggesting that the OC and EC originate from similar emission sources. Fig. 3 shows the correlation coefficients between OC and EC during all four seasons: the correlations were very high in autumn and winter ($R = 0.98$), high in spring ($R = 0.89$) and low in summer ($R = 0.64$). The main sources contributing to autumn may be vehicle exhaust and biomass burning, and coal burning in winter. Although dust events in Beijing were evident, the contents of OC and EC in these dust events were low, suggesting that the impact of dust on the OC/EC R value was small in spring. The low R value in summer indicated a significant effect of the formation of secondary organic carbon.

Fig. 3 also reveals that the slope of EC compared with OC was the largest in winter (5.6) and the smallest in summer (1.6), close to the value of 1.1 obtained by Watson *et al.* (2001) was obtained by investigating the OC/EC ratio for only vehicle exhaust, which suggests that the pollution source in summer in this study was mainly vehicle exhaust. The high slope in winter resulted from, aside from vehicle

exhaust, winter heating system emissions from burning coal. The intercept of the fitting lines were 9.0 and 8.3 for spring and summer, respectively, indicating the existence of other non-combustion pollutant sources. The reasons for a high intercept value in spring seem to include that during dust events in spring, samples contained carbonate. During the IMPROVE thermal/optical reflectance (IMPROVE_TOR) used to analyze samples, carbonate in the samples releases CO₂ upon oxidation at 400–500°C, increasing the OC concentration. Secondly, PM_{2.5} dust can include fine biomass particles, which influences the OC concentration. High temperatures and strong sunshine which result in the formation of secondary OC aerosol were responsible for the high value of the intercept in summer. The low value of the intercept in autumn and winter indicated that during these two seasons' coal burning, vehicle exhaust, and biomass burning were the main sources of OC and EC, while the contribution from other sources was very small.

Water-Soluble Ions

Table 1 presents the seasonal means for main water-soluble ions in PM_{2.5}. The variation in SO₄²⁻ concentration among the four seasons followed the order: summer > winter > autumn > spring. The highest concentration of NO₃⁻ was in autumn with a seasonal mean of $20.5 \pm 17.6 \mu\text{g}/\text{m}^3$. There is little difference between the other three seasons. This result differs from that presented by Wang *et al.* (2005), who showed that SO₄²⁻ concentration was slightly higher in winter ($19.7 \mu\text{g}/\text{m}^3$) than in summer ($18.4 \mu\text{g}/\text{m}^3$) during the period from 2001 to 2003. The annual variation in NO₃⁻ concentration was small and the magnitude of seasonal mean concentrations for NO₃⁻ in the four seasons were as following: $11.9 \mu\text{g}/\text{m}^3$ (spring), $11.2 \mu\text{g}/\text{m}^3$ (summer), $9.1 \mu\text{g}/\text{m}^3$ (autumn), and $12.3 \mu\text{g}/\text{m}^3$ (winter). The highest value for NH₄⁺ concentration was observed in summer, followed by those for spring and autumn, and the lowest level was found in spring. This result also differs from that of Wang *et al.* (2005), which indicated that the NH₄⁺ concentration in PM_{2.5} was relatively low in spring and autumn, and relatively high in summer and winter during the period from 2001 to 2003. Ammonium ion, is usually transformed from ammonia in atmosphere. Agricultural activity has been considered to be the major emission source for NH₃ in atmosphere (Battye *et al.*, 1994; Sutton *et al.*, 1995; Kirchmann *et al.*, 1998). In this study, the highest value for NH₄⁺ concentration was observed during the summer, likely because increases in the NH₃ atmospheric concentration are associated with high

Table 1. The seasonal means of OC, EC, and main water-soluble ions in PM_{2.5}.

$\mu\text{g}/\text{m}^3$	Spring	Summer	Autumn	Winter	Annual mean
OC	27.5 ± 7.7	14.9 ± 3.5	29.6 ± 15.6	37.9 ± 21.5	25.9 ± 15.8
EC	6.7 ± 2.4	4.2 ± 1.4	8.1 ± 4.6	7.0 ± 3.7	6.1 ± 3.4
NH ₄ ⁺	2.9 ± 3.7	9.3 ± 6.6	7.7 ± 6.6	7.3 ± 7.3	7.3 ± 6.7
K ⁺	2.2 ± 1.1	2.1 ± 1.3	3.7 ± 2.7	2.9 ± 2.3	2.6 ± 1.9
Ca ²⁺	5.8 ± 3.1	1.2 ± 1.5	3.3 ± 2.9	2.3 ± 1.9	3.4 ± 3.0
Cl ⁻	4.6 ± 1.9	1.8 ± 1.2	6.1 ± 4.7	7.3 ± 4.9	4.5 ± 4.0
SO ₄ ²⁻	15.2 ± 9.4	29.9 ± 19.7	18.6 ± 12.5	20.3 ± 17.4	22.4 ± 17.0
NO ₃ ⁻	13.8 ± 10.4	15.2 ± 9.3	20.5 ± 17.6	13.3 ± 9.7	15.4 ± 11.7

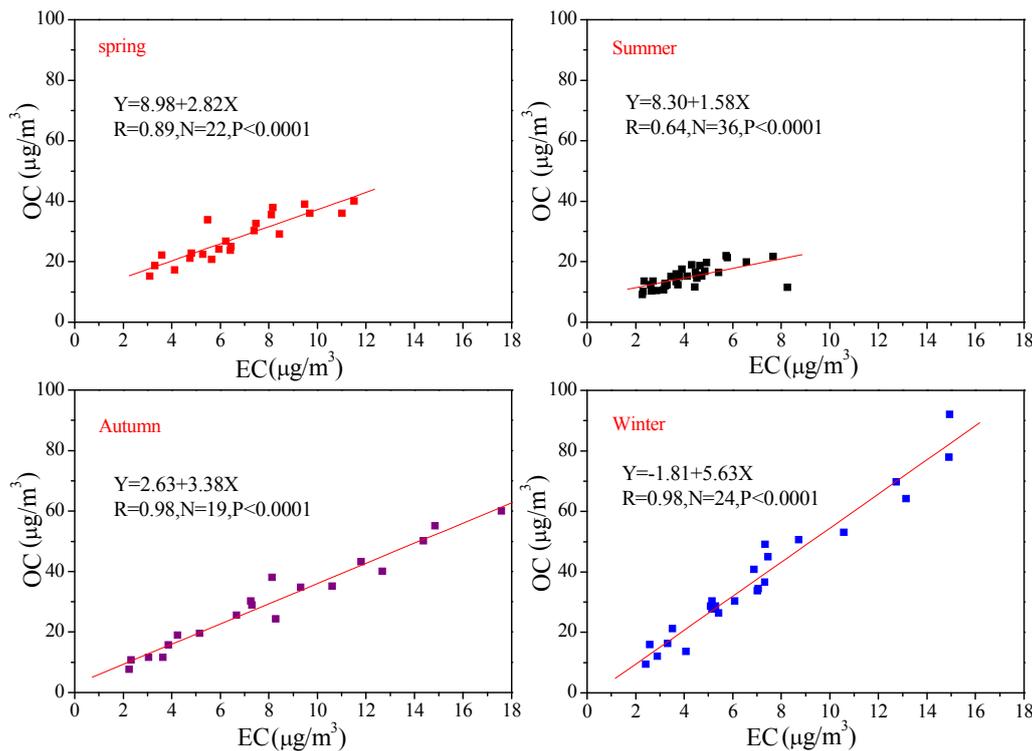


Fig. 3. The correlation coefficients between OC and EC in $\text{PM}_{2.5}$ over Beijing in 2006.

summer temperatures, increased animal activity, and more frequent agricultural activities, including fertilizer application.

Compared to ammonium, the concentration of Cl^- was relatively low. The highest value occurred in winter with a seasonal mean of $7.3 \mu\text{g}/\text{m}^3$, about 4-fold that the level in summer (which is the season with the lowest concentration $1.8 \mu\text{g}/\text{m}^3$). The mass concentration of Ca^{2+} was relatively high ($5.8 \mu\text{g}/\text{m}^3$), and is related to dry weather, low precipitation and strong winds, which result in both local and long-distance transport dust events. The season with the lowest concentration was summer ($1.2 \mu\text{g}/\text{m}^3$). During the summer sampling period, the Ca^{2+} ion can not be detected on about 80% of sampling days. The seasonal variation in the concentration of K^+ ion was small; the highest value occurred in autumn. Watson *et al.* (1998) indicated that the sources of K^+ ion concentration were closely related to biomass and garbage burning. The contribution from biomass burning was higher than for any other sources, reflecting that biomass burning is common in and around Beijing.

Transformation Mechanism of Sulfate and Nitrate

The primary emissions of sulfate and nitrate tended to be small; they are usually transformed in the atmosphere from sulfur dioxide and nitrogen oxide (air-particle transformation). Eq. (1) and (2) express the oxidation rate for sulfate (SOR) and nitrogen (NOR), respectively, to allow quantification of the amount of SO_2 oxidized to SO_4^{2-} and NO_2 oxidized to NO_3^- , respectively:

$$\text{SOR} = \frac{n - \text{SO}_4^{2-}}{(n - \text{SO}_4^{2-} + \text{SO}_2)}, \quad (1)$$

$$\text{NOR} = \frac{n - \text{NO}_3^-}{(n - \text{NO}_3^- + \text{NO}_2)}, \quad (2)$$

where the units for SO_2 , NO_2 , $n\text{-SO}_4^{2-}$ and $n\text{-NO}_3^-$ are moles, and $n\text{-SO}_4^{2-}$ and $n\text{-NO}_3^-$ stand for non-sea-salt molar value of SO_4^{2-} and NO_3^- , respectively. Eqs. (1) and (2) indicate that higher values of SOR and NOR indicate more SO_2 and NO_2 transformed to $n\text{-SO}_4^{2-}$ and $n\text{-NO}_3^-$, respectively (Pierson *et al.*, 1979; Truex *et al.*, 1980). Therefore, the formation mechanism of sulfate and nitrate can be discussed in terms of the variability in SOR and NOR of $\text{PM}_{2.5}$ samples.

Fig. 4 shows a time series of SOR, NOR, temperature, and RH. In about 94% of the $\text{PM}_{2.5}$ samples, the SOR value was greater than 0.1. This value varied from 0.08 to 0.9, with an annual mean of 0.4, suggesting that sulfate in aerosol over Beijing mainly was a secondary pollutant, formed by transformation. The transformation rate differed considerably among seasons. Generally, the SOR values were 0.7, 0.4, 0.3, and 0.2, in summer, autumn, spring, and winter, respectively, indicating a relatively high value in summer and a relatively low value in winter, resulting from different sulfate formation mechanisms under different atmospheric conditions. Studies (Mcmurry and Wilson, 1983; Seinfeld, 1996) indicated that temperature and RH are the two of most important meteorological elements affecting aerosol components. Fig. 4 shows that variations in SOR are related to temperature and RH, with a correlation coefficient of 0.76 between SOR and temperature, and 0.61 between SOR and RH. In high summer temperature and long photoperiod create optical reaction conditions for photo-chemical oxidation. At the same time, high RH in the summer can increase the

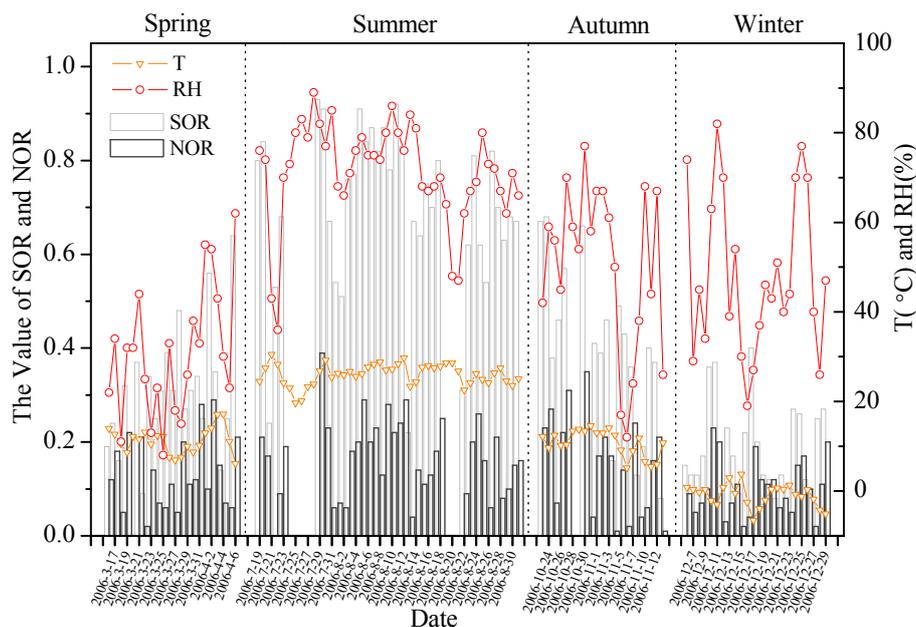


Fig. 4. Time series of SOR, NOR, temperature, and relative humidity.

heterogeneous oxidation reactions involving SO_2 in clouds and fog (Yao *et al.*, 2002). The transformation rate for SO_2 was 1000%/h in clouds (Newman, 1981), but only 1%/h in daytime air-phase oxidation reactions (Tolacka *et al.*, 2001), which makes transformation in clouds and under high humidity important (Pandis and Seinfeld, 1989). About 95% of precipitation in 2006 fell during the summer sampling period, and the average RH is about 71%. The heterogeneous phase oxidation reactions of sulfur dioxide occur easily when high relative humidity. Because the SOR value was very high, correspondingly, SO_4^{2-} concentrations reached their highest levels of the year during this part of the study period.

Atmospheric RH in winter tended to be low, so the main source of SO_4^{2-} during this time was air-phase oxidation of SO_2 . Although the winter photoperiod is short, and sunlight is weak, leading to limited SO_4^{2-} from photo-chemical reaction sources, the increased burning of coal for heat releases abundant SO_2 , resulting in relatively high wintertime SO_4^{2-} concentrations.

Fig. 4 illustrates daily variation in NOR value from 0.002 to 0.4. The seasonal means for NOR were 0.17, 0.15, 0.14, and 0.1 in summer, autumn, spring, and winter, respectively, with an annual mean of 0.14. In Beijing, the continual source of NO_2 was vehicle exhaust emission, and variation in the total NO_2 exhaust was slight among seasons. The NO_3^- transformation rate was mainly affected by meteorological factors, such as temperature, RH, and solar radiation intensity, which caused variation in results among sampling seasons. The correlation of NOR with temperature and RH were low ($r = 0.26$ with temperature and $r = 0.42$ with RH), probably due to an interaction between temperature and related humidity. Russell *et al.* (1983) indicated that the atmospheric nitrate occur in a gaseous state when temperatures are greater than 30°C and in a solid state (particle) when temperatures are below 15°C . At temperatures between 15 and 30°C ,

temperature still plays an important role, but RH affects the balance of nitrate existing in the gaseous phase or the solid phase. The ions SO_4^{2-} , NO_3^- , and NH_4^+ can also affect each others' chemical state (Du *et al.*, 2010). In the presence of H_2O , these ions can form a complicated inorganic aerosol system of $\text{SO}_4^{2-}\text{-NO}_3^-\text{-NH}_4^+\text{-H}_2\text{O}$. Seinfeld and Pandis (1998) thought that SO_4^{2-} and NO_3^- competed to combine with NH_3 , but NH_3 prefers SO_4^{2-} to NO_3^- . At high concentrations of SO_4^{2-} , NO_3^- tends to exist in the gaseous state, otherwise NO_3^- tends to be in the solid, particulate state. During the study period, the seasonal mean concentration of SO_4^{2-} in summer was about 1.5-fold that in autumn. The considerable decrease in atmospheric SO_4^{2-} concentration may increase the likelihood of combination for NO_3^- and NH_3 . In autumn, the mean temperature was about 10°C , which favors occurrence of NO_3^- in the solid particulate state. Therefore, the mass concentration of NO_3^- in the summer of 2006 was the highest level observed during the investigation period.

Comparative Study of Pollutant Episodes during Typical Weather Conditions

Table 2 presents the chemical components and meteorological elements typical of events that occurred over Beijing during the investigation period, which is helpful for understanding the relationship between carbonaceous and water soluble ions during various weather conditions (including dust storms, hazy weather, or clear weather).

Clear Weather

In the present study, 13 November 2006 was selected to represent a day with clear sky weather conditions. On that day, precipitation was zero, daily mean wind speed was 3.4/s, RH was 26%, and mixing layer height at noon was 1543.9 m, which suggested that weather conditions favored horizontal and vertical atmospheric mixing. Air quality on that day was grade A, as assessed by the Beijing Environment

Table 2. Chemical components and meteorological elements during typical weather events.

	unit	clear sky	haze	dust storm
Date		Nov. 13	Dec. 11	Mar. 26–27
PM _{2.5}		45.8	474.3	504.1
OM		12.2	147.3	52.3
EC		2.3	14.9	7.5
SO ₄ ²⁻	μg/m ³	4.6	90.0	12.0
NO ₃ ⁻		1.8	42.0	8.2
NH ₄ ⁺		0.1	31.6	0.4
Ca ²⁺		4.7	1.9	10.7
Cl ⁻		0.9	23.1	4.4
K ⁺		0.9	11.1	2.1
Mean wind speed	m/s	1.1	1.6	3.8
Temperature	°C	10.8	-2.9	6.9
Relative humidity	%	26	82	18
Mixing layer height	m	1543.9	472.2	1195.0

Administration. PM_{2.5} mass concentration was low (45.8 μg/m³), as compared to that during the other two types of weather conditions. Only the concentration of Ca²⁺ ions was higher than during hazy weather, while OC, EC and the concentrations of other main water-soluble ions were much lower than their corresponding concentrations during hazy or dusty weather.

Hazy Weather

The PM_{2.5} concentration on December 11th, 2006 was 474.3 μg/m³, slightly higher than the PM_{2.5} concentration during dust storm conditions and about 10-fold that of clear weather conditions. The percentage of organic matter, EC and the main water-soluble ion concentrations to PM_{2.5} mass-concentration was 72.3%. Air quality published daily by Beijing Environment Administration described the air quality grade that day as seriously polluted, and the main pollutants usually found in PM_{2.5}, except for Ca²⁺, were at their highest relative concentration. Organic matter, SO₄²⁻, NH₄⁺, K⁺, and Cl⁻ were at their highest concentrations, while EC and NO₃⁻ concentrations were at their second highest values of the year, from 6.6- to 287-fold the levels observed during clear weather, and from 2- to 73.5-fold the levels measured during dust storms. In the day, the temperature was -3°C, with RH of 82%, and a mixing layer height at noon of 472.2 m. The causes of this pollution episode included increased use of coal-burning boilers for winter heating, which emits more pollutants, and low wind speeds and strong surface inversion that reduce dispersion of accumulated pollutants. High relative humidity also favored formation and increasing the atmospheric concentration of secondary water-soluble ions, such as SO₄²⁻, NH₄⁺, and NO₃⁻, by means of heterogeneous phase oxidation reactions. The values of SOR and NOR on that day were twice than those observed during winter. Atmospheric pollution in hazy weather was attributed by local anthropogenic emissions and the accumulation of pollutants transformation (Shen *et al.*, 2011).

Dust Storm

Dust storm is severe natural disaster in northern China

(Yang *et al.*, 1997), that occur when strong winds scour away soil and destroy vegetation (Zhou *et al.*, 1981). These storms are detrimental to aviation, transportation, and air quality (Wang *et al.*, 2000). According to meteorology announcement, a dust storm occurred in Beijing from March 26th to 27th, 2006. On the afternoon of March 26th, a dust storm began over a wide area covering southeastern Mongolia, inner Mongolia, Gansu Province, and the Ningxia Autonomous Region of China, and the strong winds carried the dust to arriving in Beijing in the midnight.

At the time the dust storm appeared, the weather conditions included strong winds and low RH. During the dust storm event, the daily mean wind speed was 3.8 m/s, with instantaneous winds of grade 5–6, RH of 18%, and a mixing layer height of 1195 m, completely opposite the conditions observed during hazy weather conditions. The concentration of PM_{2.5} during the dust storm was as high as 504.1 μg/m³, about 11-fold that seen in clear conditions, so the air quality grade was serious polluted. The concentrations of organic matter, EC, and the main water-soluble ions accounted for 19.4% of the mass concentration of PM_{2.5}, suggesting that about 80.6% of the mass concentration of PM_{2.5} was soil dust and trace elements transformed by the dust storm. Concentrations of OM, EC and all main water-soluble ions were much lower than those observed in hazy weather, except for the ion Ca²⁺, which was as high as 10.7 μg/m³, the highest value observed during the investigation period, about 5.7-fold that seen in hazy weather and 2.3-fold that seen during clear weather. Wang *et al.* (2000) indicated that concentrations of elemental components of atmospheric particles and soil ion components increased considerably, but that the concentrations of other ions, except for Ca²⁺, decreased considerably during hazy days. Using the rich-factor method, Zhang *et al.* (2003) investigated fine particulate pollution in Beijing under dusty weather conditions and found that the main contributor to the dust pollution over Beijing was dust transported from remote sources.

Impact of PM_{2.5} on Visibility

Visibility is an important index for assessment of urban environmental air quality. Although particle mass

concentration ranged only from about 10 to 100 ppb, a minor part of the atmosphere, it can decrease the strength of visible light by about 65–95% (Horvath, 1993). The impacts of $\text{PM}_{2.5}$, carbonaceous, and water-soluble ions on visibility will be discussed in the section, without reference to the influences of dust events and precipitation on annual visibility.

Table 3 indicates that visibility was negatively correlated with temperature and humidity, but positively correlated with wind speed. Study shows that as the relative humidity increased, lower visibilities occurred more frequently (Xiao et al., 2011). The correlation coefficients between $\text{PM}_{2.5}$ mass concentration and visibility varied across seasons: -0.35 during spring, -0.52 during summer, -0.43 during autumn, and -0.64 during winter while the greatest negative correlation was found. Fig. 5 shows that the data can be best fit using power curve fitting with a correlation coefficient of -0.84 . The impact of atmospheric fine particles on visibility was the largest in winter, followed by summer, autumn, and spring. The atmosphere tends to be most stable in winter, with the frequent appearance of surface inversions and haze, and during the winter, $\text{PM}_{2.5}$ contained more sulfate and nitrate that strongly scatter light. Relatively low correlation coefficients between $\text{PM}_{2.5}$ mass concentration and visibility in spring and autumn are probably related to low RH and related strong wind speeds. In summer, the correlation coefficient was fair, which can be ascribed to the relatively low $\text{PM}_{2.5}$ mass concentration.

Among $\text{PM}_{2.5}$ components, NH_4^+ , SO_4^{2-} , and NO_3^- have the greatest correlation with visibility, with R values of -0.63 , -0.58 , and -0.61 , respectively. The correlation coefficients between visibility and total carbon (TC) and the remaining components of $\text{PM}_{2.5}$ were -0.38 and -0.07 , respectively,

suggesting that the impacts of NH_4^+ , SO_4^{2-} , and NO_3^- on visibility were relatively large. Fig. 6 presented that using power curve fitting was more informative than using linear line fitting. The correlation coefficients between visibility and NH_4^+ , SO_4^{2-} , and NO_3^- were -0.75 , -0.80 , and -0.75 , respectively. Fig. 6 shows that when NH_4^+ was less than about $9 \mu\text{g}/\text{m}^3$, SO_4^{2-} less than about $20 \mu\text{g}/\text{m}^3$, and NO_3^- less than about $13 \mu\text{g}/\text{m}^3$, the correlation coefficients rapidly decreased with increasing concentrations of NH_4^+ , SO_4^{2-} , and NO_3^- . When the concentrations of NH_4^+ , SO_4^{2-} and NO_3^- were larger than these values, visibility became very low, and the decrement in visibility was relatively small with increasing concentrations of NH_4^+ , SO_4^{2-} , and NO_3^- .

CONCLUSIONS

A one-year-long observation of $\text{PM}_{2.5}$ in Beijing was carried out in 2006. Major chemical components and their relationships with visibility were investigated. The annual mean concentration of $\text{PM}_{2.5}$ in Beijing was $176.6 \pm 100.3 \mu\text{g}/\text{m}^3$. The order of concentration levels observed was: spring > autumn > winter > summer, resulting from varying emission sources and meteorological conditions in each season. Dust storms and local dust contributed strongly to $\text{PM}_{2.5}$ mass-concentrations during the spring.

The annual mean concentrations of OC and EC in $\text{PM}_{2.5}$ over Beijing were $25.9 \pm 15.8 \mu\text{g}/\text{m}^3$ and $6.1 \pm 3.4 \mu\text{g}/\text{m}^3$, respectively. The correlation between EC and OC varied among seasons, reflecting the variation in main emission sources for EC and OC during different seasons. NH_4^+ , SO_4^{2-} , and NO_3^- were the main components of $\text{PM}_{2.5}$ in Beijing. SO_4^{2-} and NH_4^+ concentrations were in the highest

Table 3. The impacts of meteorological elements, and $\text{PM}_{2.5}$ and its components on visibility.

	Temp	RH	WS	$\text{PM}_{2.5}$	TC	NH_4^+	SO_4^{2-}	NO_3^-	Remainder
Visibility	-0.20	-0.53	0.54	-0.42	-0.38	-0.63	-0.58	-0.61	-0.07

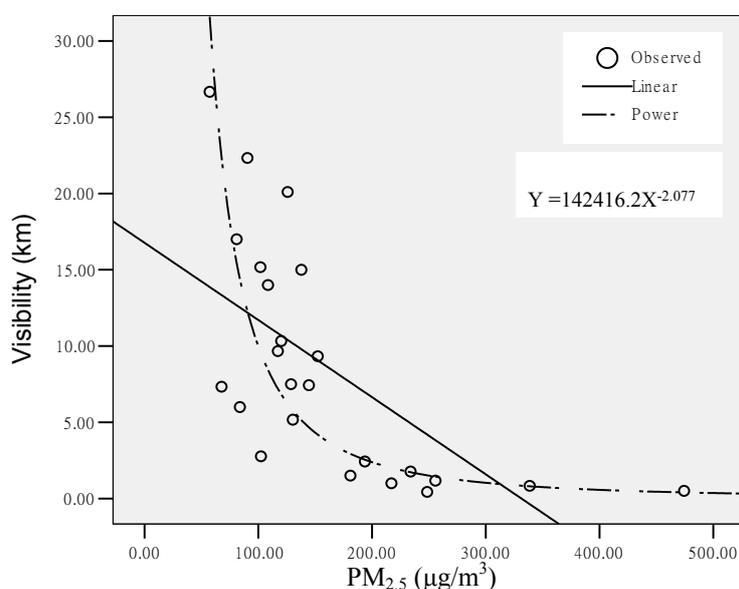


Fig. 5. The linear modeling and curve fitting between visibility and $\text{PM}_{2.5}$ in winter over Beijing.

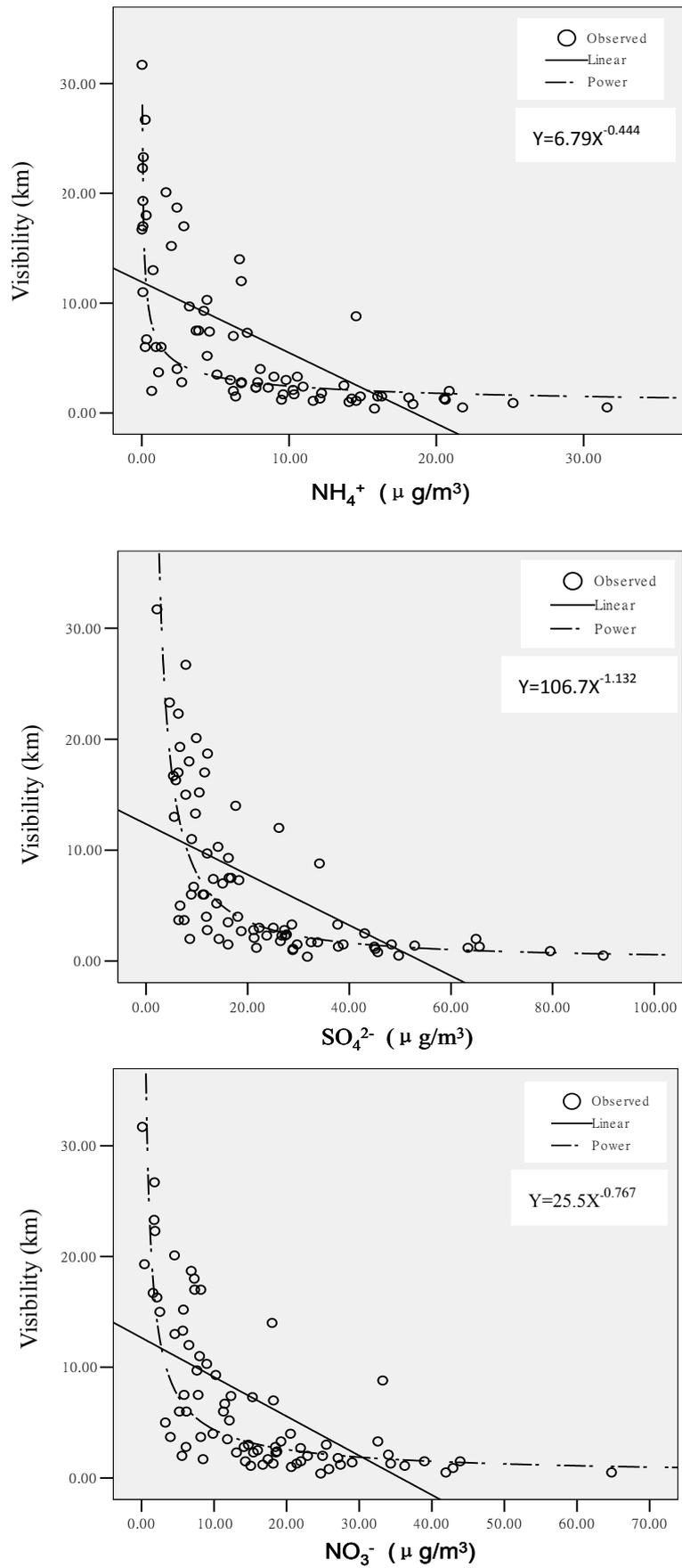


Fig. 6. The linear modeling and curve fitting of visibility, NH_4^+ , SO_4^{2-} and NO_3^- .

in summer, while NO_3^- was in the highest in autumn. The reasons for seasonal variation concentration of different ions included variation in the ion sources on one hand, and variation in secondary aerosol ion formation mechanisms and meteorological conditions on the other hand.

Comparative investigation of various weather conditions revealed that $\text{PM}_{2.5}$ pollution resulted from remote source transportation during dust storms, but came from local pollution during hazy weather. The meteorological characteristics of dust storm conditions included strong wind speed, low relative humidity and high mixing layers, just the opposite of those observed during hazy weather conditions. $\text{PM}_{2.5}$ and visibility were found to be inversely correlated, and the relationships between visibility and NH_4^+ , SO_4^{2-} , and NO_3^- in winter could be best fit using a power curve function.

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