



## Chemical Composition and Light Extinction Contribution of PM<sub>2.5</sub> in Urban Beijing for a 1-Year Period

Huanbo Wang<sup>1</sup>, Mi Tian<sup>1</sup>, Xinghua Li<sup>2\*</sup>, Qing Chang<sup>2</sup>, Junji Cao<sup>3</sup>, Fumo Yang<sup>1†</sup>, Yongliang Ma<sup>4</sup>, Kebin He<sup>4</sup>

<sup>1</sup> Key Laboratory of Reservoir Aquatic Environment of CAS, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, China

<sup>2</sup> School of Chemistry and Environment, Beihang University, Beijing 100191, China

<sup>3</sup> Key Lab of Aerosol Chemistry & Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China

<sup>4</sup> State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, School of Environment, Tsinghua University, Beijing 100084, China

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### ABSTRACT

Daily PM<sub>2.5</sub> samples were collected in Beijing across four consecutive seasons from June 2012 to April 2013. Major water-soluble inorganic ions, carbonaceous species and elements were analyzed to investigate their temporal variations and evaluate their contributions to visibility impairment over different seasons and under different pollution levels. The mass concentrations of PM<sub>2.5</sub> ranged from 4.3 to 592.4 μg m<sup>-3</sup>, with an annual average of 112.4 ± 94.4 μg m<sup>-3</sup>. The predominant components of PM<sub>2.5</sub> were secondary inorganic ions (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) and carbonaceous compounds, which accounted for 45.9% and 24.1% of the total PM<sub>2.5</sub> mass, respectively. Distinct seasonal variation was observed in the mass concentrations and chemical components of PM<sub>2.5</sub>. The average mass concentrations of PM<sub>2.5</sub> were the highest in winter, followed by spring, and lowest in autumn. Light extinction coefficients ( $b_{\text{ext}}$ ) were discussed over four seasons. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was the largest contributor (28.8%) to  $b_{\text{ext}}$ , followed by NH<sub>4</sub>NO<sub>3</sub> (24.4%), organic matter (19.5%), elemental carbon (7.4%), and coarse mass (7.2%), while fine soil, sea salt, NO<sub>2</sub> and Rayleigh made minor contributions, together accounting for 12.7% of  $b_{\text{ext}}$ . During the polluted periods, the contributions of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> to  $b_{\text{ext}}$  increased dramatically. Therefore, in addition to control primary particulate emissions, the reduction of their precursors like SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub> could effectively improve air quality and visibility in Beijing.

**Keywords:** Chemical composition; Reconstructed light extinction coefficient; Visibility; PM<sub>2.5</sub>.

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### INTRODUCTION

PM<sub>2.5</sub> in the atmosphere have been found to be responsible for adverse health effects (de Kok *et al.*, 2006; Pope and Dockery, 2006), climate change (Haywood and Boucher, 2000; Tai *et al.*, 2010; Mahowald, 2011) and visibility degradation (Watson, 2002; Chang *et al.*, 2009). The decline of visibility, particularly frequent hazes in megacities like Guangzhou, Chengdu and Beijing during the recent years (Tan *et al.*, 2009; Zhao *et al.*, 2011; Wang

*et al.*, 2013a), has become a major concern for the general public in China.

Visibility degradation is attributed to light absorption and light scattering by both gases and fine particle pollutants (Chan *et al.*, 1999; Watson, 2002). However, fine particles are mostly responsible for the poor visibility, while the light extinction due to gas pollutants usually has a minor influence on urban visibility (Watson, 2002). A few measurements of surface aerosol optical properties have been conducted in polluted cities such as Beijing and Guangzhou (Garland *et al.*, 2009; Jung *et al.*, 2009; Fan *et al.*, 2010). But it is difficult to determine the extinction properties of individual real particles due to their complex shapes and mixtures. At this time, light extinction coefficient ( $b_{\text{ext}}$ ) could, instead, be reconstructed based on the chemical compositions of particles (Pitchford *et al.*, 2007). An empirical formula relating  $b_{\text{ext}}$  to the chemical species of particles was established by the Interagency Monitoring of Protected Visual Environments (IMPROVE) network.

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\* Corresponding author.

Tel.: +86-10-82316160; Fax: +86-10-82314215  
E-mail address: lixinghua@buaa.edu.cn

† Corresponding author.

Tel.: +86-23-65935921; Fax: +86-23-65935924  
E-mail address: fmyang@cigit.ac.cn

Reconstruction of  $b_{\text{ext}}$  assumes that the particles are externally mixed and the mass extinction efficiency for each species is constant. Although these assumptions were not always satisfied, the reconstruction of  $b_{\text{ext}}$  is still a commonly used approach to identify key factors affecting the  $b_{\text{ext}}$  and ambient visibility (Cao *et al.*, 2012; Zhang *et al.*, 2012; Li *et al.*, 2013a; Tao *et al.*, 2014). Most recent studies have focused on analyzing mass concentrations, different chemical compositions, and sources of fine particles (He *et al.*, 2001; Yao *et al.*, 2002; Yang *et al.*, 2011a; Yu *et al.*, 2013). In addition, the studies in Beijing were mainly conducted during the important events, such as the 2006 Campaign of Air Quality Research and the 2008 Olympics (Li *et al.*, 2012; Li *et al.*, 2013a), or heavy pollution episode during wintertime in 2011–2013, especially in January 2013 (Wang *et al.*, 2013b; Zhao *et al.*, 2013a; Ji *et al.*, 2014; Quan *et al.*, 2014; Sun *et al.*, 2014; Wang *et al.*, 2014), all of which were short-term sampling and analysis. Recently, the seasonal characteristics of the chemical composition of  $\text{PM}_{2.5}$  in Beijing have been determined during the 2009–2010 periods (Li *et al.*, 2013b; Zhao *et al.*, 2013b; Liu *et al.*, 2014), whereas few of these previous studies have reported the contributions of each species to  $b_{\text{ext}}$ . An exception is that reported by Cao *et al.* (2012) for Xi'an. Furthermore, there is no study on reconstructing extinction coefficients based on the chemical compositions of  $\text{PM}_{2.5}$  over four consecutive seasons in Beijing (Jung *et al.*, 2009; Li *et al.*, 2013a; Tian *et al.*, 2014), especially on appointing the contribution of  $\text{PM}_{2.5}$  chemical species to visibility degradation under different pollution levels and over different seasons.

In the present study, water-soluble inorganic ions, trace elements, organic carbon (OC) and elemental carbon (EC) during four different seasons were analyzed, and then seasonal variations of major components were investigated. Moreover, the apportionment of the chemical compositions of  $\text{PM}_{2.5}$  for extinction effects was identified during different pollution levels. Understanding the impact of chemical compositions of  $\text{PM}_{2.5}$  on  $b_{\text{ext}}$  will be very useful for the government agencies in their attempts to improve visibility and human health in Beijing.

## METHODS

### Site and Sampling

Sampling was conducted from 15 to 30 June and 10 to 20 August (representative of summer), 15 September to 21 October (autumn) in 2012, 5 January to 5 February (winter), and 4 March to 2 April (Spring) in 2013 at the campus of Beihang University (referred to as BHU, 39°59'N, 116°21'E) in urban Beijing. This sampling site is surrounded by the educational and residential districts without major industrial source. In addition, the sampling site is about 3.0 km southeast from Peking University and 2.8 km west from the Tower Division of the Institute of Atmospheric physics, which represent the general urban pollution in Beijing (Zhang *et al.*, 2013; Tian *et al.*, 2014).

Daily 23-h integrated  $\text{PM}_{2.5}$  samples were collected using a five-channel Spiral Ambient Speciation Sampler (SASS, MetOne Inc.) with a flow rate of  $6.7 \text{ L min}^{-1}$ . The first channel

was used to collect  $\text{PM}_{2.5}$  with a 47 mm Teflon filter for  $\text{PM}_{2.5}$  mass and elemental analysis. The second channel collected the particles for the analysis of water-soluble inorganic ions with a 47 mm Teflon filter. An MgO honeycomb denuder was set in front of the Teflon filter to reduce the acid gaseous interference. The third channel was used to collect  $\text{PM}_{2.5}$  on quartz fiber filters for OC and EC analyses. The fresh quartz filters were pre-heated at  $450^\circ\text{C}$  in a muffle furnace for 4 h to remove any volatile components before sampling. The filter samples were stored in a freezer at  $-18^\circ\text{C}$  before chemical analysis to minimize the evaporation of volatile components.

Meteorological data including wind speed (WS), temperature, relative humidity (RH) and precipitation were obtained from China Meteorological Data Sharing Service System (<http://cdc.cma.gov.cn/home.do>).

### Gravimetric and Chemical Analysis

Before and after each sampling, the Teflon filters were conditioned at  $22^\circ\text{C} \pm 5^\circ\text{C}$  in relative humidity of  $40\% \pm 5\%$  for 24 h and then weighed using an electronic balance with a detection limit of  $1 \mu\text{g}$  (Sartorius, Göttingen, Germany). Differences among replicate weights were less than  $5 \mu\text{g}$  for each sample, which represented less than  $\pm 5\%$  of the total aerosol mass of the field samples.

Teflon filter from the second channel was extracted twice in 7.5 ml Milli-Q water via an ultrasonic bath for 20 min. The extracted water-soluble ions were filtered through a  $0.45 \mu\text{m}$  PTFE syringe filter and stored at  $4^\circ\text{C}$  until analysis. Four anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{F}^-$ ) and five cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) were determined by Ion chromatography ICS-1000 (Dionex Corp, Sunnyvale, CA.) with  $2.4 \text{ mmol L}^{-1} \text{ Na}_2\text{CO}_3$  and  $0.3 \text{ mmol L}^{-1} \text{ NaHCO}_3$  as the eluent and Ion chromatography ICS-2000 (Dionex Corp, Sunnyvale, CA.) with  $20 \text{ mmol L}^{-1}$  methanesulfonic acid (MSA) eluent, respectively. Field blank values were subtracted from sample concentrations.

A  $0.5 \text{ cm}^2$  punch from each quartz filter was analyzed for OC and EC using a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, USA) following the IMPROVE thermal optical reflectance (TOR) protocol (Chow *et al.*, 2007).

Specific elements from sodium to uranium were analyzed by Energy Dispersive X-ray fluorescence spectrometry (Epsilon 5 ED-XRF, PANalytical company, Netherlands) on Teflon filters. Quality assurance/Quality Control (QA/QC) procedures of the XRF analysis procedure were described by Xu *et al.* (2012a).

### Data Analysis

The mass of  $\text{PM}_{2.5}$  was reconstructed according to the method adopted by Zhang *et al.* (2013) and the revised IMPROVE method (Pitchford *et al.*, 2007).  $\text{PM}_{2.5}$  species were classified into eight major components:  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ , OM, EC, fine soil, sea salt, trace element oxide (TEO), and biomass burning-derived K.

The  $(\text{NH}_4)_2\text{SO}_4$  mass was estimated by the  $\text{SO}_4^{2-}$  mass multiplied by a factor of 1.38, and the  $\text{NH}_4\text{NO}_3$  mass was estimated by the  $\text{NO}_3^-$  mass multiplied by a factor of 1.29. OM was derived from multiplying OC concentrations by a

factor of 1.6 to account for unmeasured atoms, such as hydrogen, oxygen, and nitrogen in organic materials. The factor of 1.6 was employed in this study according to Xing *et al.* (2013), which demonstrated that the calculated OM/OC mass ratio in summer was relatively high ( $1.75 \pm 0.13$ ) and in winter was lower ( $1.59 \pm 0.18$ ) in PM<sub>2.5</sub> collected from 14 Chinese cities.

Sea salt was usually calculated by the Cl<sup>-</sup> mass multiplied by a factor of 1.80 or by the Na<sup>+</sup> mass multiplied by a factor of 2.54. It should be noticed that most Cl<sup>-</sup> may be contributed by coal combustion rather than sea spray in Beijing, especially during the heating period in winter and spring. Thus, we calculated sea salt using Na<sup>+</sup> by a factor of 2.54.

TEO was estimated following Zhang *et al.* (2013). The fine soil component was often estimated by assuming the elements mainly associated with soil be in their oxidized state (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CaO, K<sub>2</sub>O, FeO, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>), which was thus calculated as follows:

$$[\text{Fine Soil}] = 2.20[\text{Al}] + 2.49[\text{Si}] + 1.63[\text{Ca}] + 2.42[\text{Fe}] + 1.94[\text{Ti}] \quad (1)$$

The total  $b_{\text{ext}}$  include the contributions of light scattering by particles ( $b_{\text{sp}}$ ) and gases ( $b_{\text{sg}}$ ), and light absorption by particles ( $b_{\text{ap}}$ ) and gases ( $b_{\text{ag}}$ ), where:

$$b_{\text{ext}} = b_{\text{sp}} + b_{\text{ap}} + b_{\text{ag}} + b_{\text{sg}} \quad (2)$$

The  $b_{\text{ext}}$  can be calculated based on revised IMPROVE algorithm:

$$\begin{aligned} b_{\text{ext}} \approx & 2.2 \times f_s(\text{RH}) \times [\text{Small}(\text{NH}_4)_2\text{SO}_4] \\ & + 4.8 f_L(\text{RH}) \times [\text{Large}(\text{NH}_4)_2\text{SO}_4] \\ & + 2.4 \times f_s(\text{RH}) \times [\text{Small NH}_4 \text{ NO}_3] \\ & + 5.1 f_L(\text{RH}) \times [\text{Large NH}_4 \text{ NO}_3] \\ & + 2.8 \times [\text{Small OM}] + 6.1 \times [\text{Large OM}] + 10 \times [\text{EC}] \\ & + 1 \times [\text{Fine Soil}] + 1.7 \times f_{\text{ss}}(\text{RH}) \times [\text{Sea Salt}] \\ & + 0.6 \times [\text{PM}_{2.5-10}] + 0.33 \times [\text{NO}_2(\text{ppb})] \\ & + \text{Rayleigh Scattering} \end{aligned} \quad (3)$$

The apportionment of the total concentrations of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> into the concentrations of the small and large size fraction in PM<sub>2.5</sub> was calculated according to Pitchford *et al.* (2007). The water growth adjustment term  $f_s(\text{RH})$ ,  $f_L(\text{RH})$  for small and large size distribution (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub>, and  $f_{\text{ss}}(\text{RH})$  for sea salt are used according to the water growth curves provided by Pitchford *et al.* (2007). The coarse mass was calculated by subtracting the PM<sub>2.5</sub> mass from the PM<sub>10</sub> mass. The  $b_{\text{ext}}$  is in Mm<sup>-1</sup>, chemical composition concentrations are in μg m<sup>-3</sup>, dry efficiency terms are in unit of m<sup>2</sup> g<sup>-1</sup>, and  $f(\text{RH})$  is dimensionless.

## RESULTS AND DISCUSSION

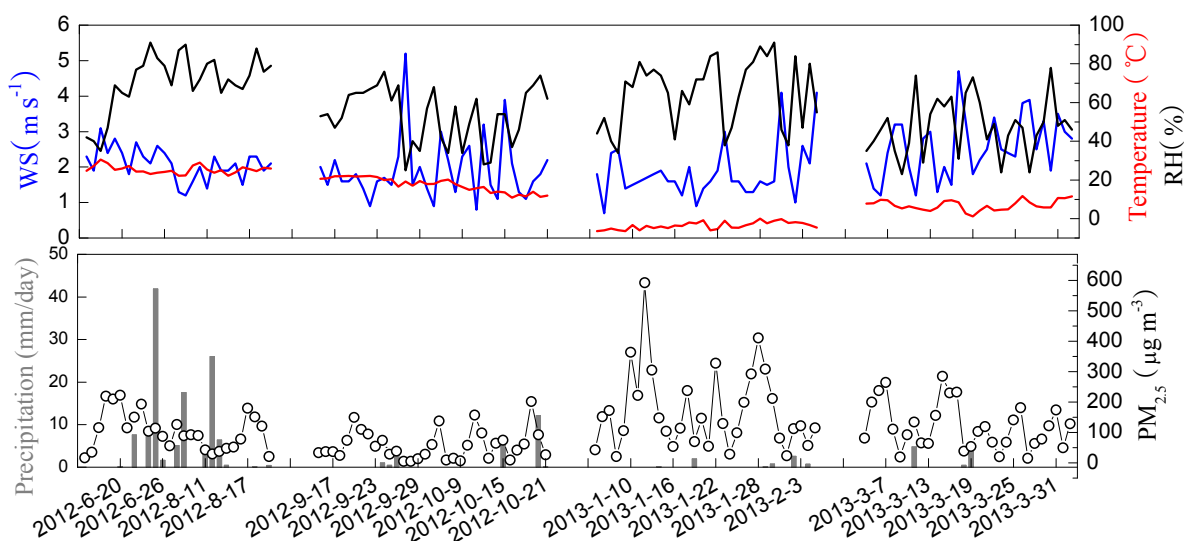
### Temporal Variations of PM<sub>2.5</sub> Mass Concentration

The time series of daily PM<sub>2.5</sub> mass concentration in

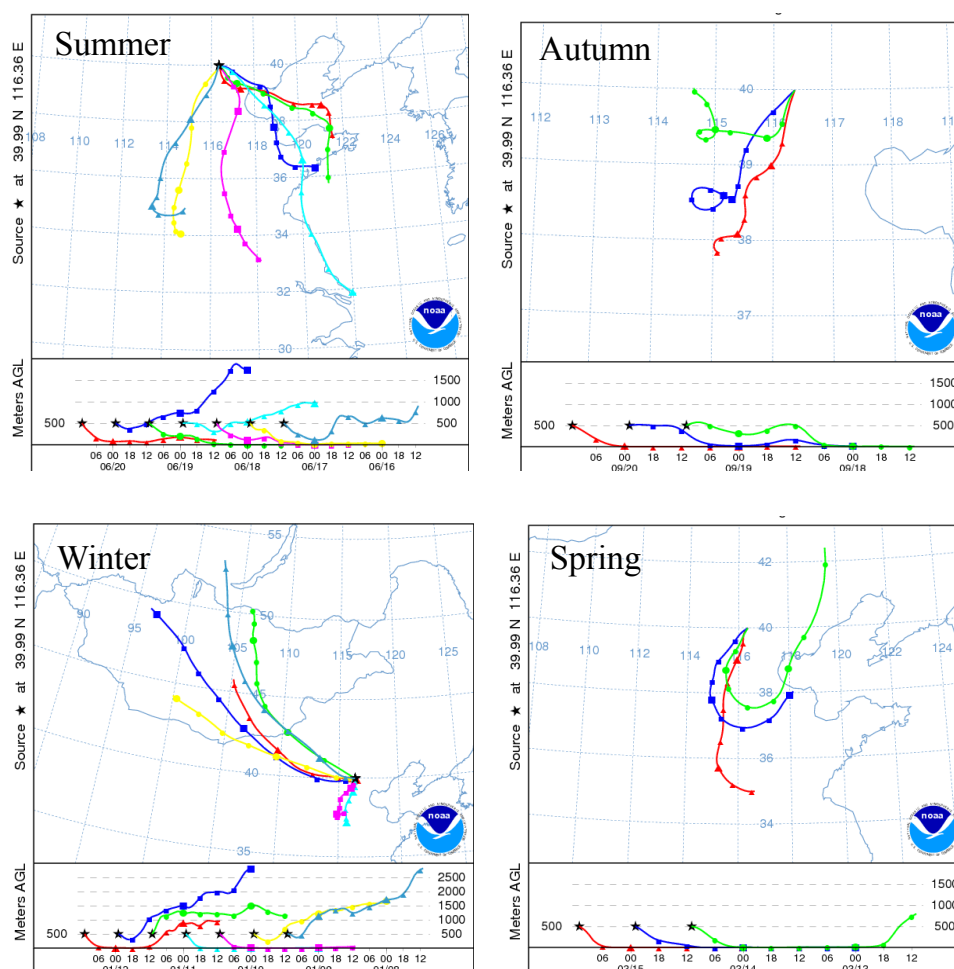
Beijing are illustrated in Fig. 1. Daily PM<sub>2.5</sub> concentrations ranged from 4.3 to 592.4 μg m<sup>-3</sup> with an annual average of  $112.4 \pm 94.4$  μg m<sup>-3</sup> during the study period. The annual average was however lower than the  $135 \pm 63$  μg m<sup>-3</sup> measured on the Peking University campus in 2009 (Zhang *et al.*, 2013), whereas it was comparable with the value observed in the TsingHua University campus during 2005–2006 (Yang *et al.*, 2011a).

As illustrated in Fig. 1, daily PM<sub>2.5</sub> mass concentrations varied significantly during all four seasons. The PM<sub>2.5</sub> mass concentration, during the most polluted period (592.4 μg m<sup>-3</sup>), was almost 150 times higher than that during the cleanest period (4.3 μg m<sup>-3</sup>). There were seven heavily polluted periods with mass concentration of PM<sub>2.5</sub> exceeded 200 μg m<sup>-3</sup>. What is worse, five severely polluted days, exceeding 300 μg m<sup>-3</sup>, were observed in January of 2013. As shown in Fig. 2, during the pollution episodes in summer, autumn and winter, air masses were mainly from the south or southeast of Beijing, indicating that regional transport was important for the high level of PM<sub>2.5</sub> in Beijing. The mechanism for the formation of the severe haze episode in January 2013 was discussed by Wang *et al.* (2014), who showed that it was related to both the external factor of unfavorable meteorological conditions and the internal factors including rapid secondary transformation of primary gaseous pollutants to secondary aerosols.

The seasonal variations of PM<sub>2.5</sub> were evident. The average mass concentration of PM<sub>2.5</sub> was highest in winter, decreased in spring and summer, and was lowest in autumn. Daily PM<sub>2.5</sub> concentration exceeded the China National Ambient Air Quality Standards (75 μg m<sup>-3</sup>) on 56.6% of days during all study periods, whereas it was 66.6% in summer, 24.2% in autumn, 75% in winter and 63.3% in spring, indicating that pollution in Beijing were serious and control measures should be undertaken to alleviate the PM<sub>2.5</sub> loading. Influenced by the increased emissions from residential heating and biomass burning, as well as the adverse dispersion and deposition conditions such as low wind speed and rare precipitation (Xu *et al.*, 2012b), the mass concentration of PM<sub>2.5</sub> in winter was higher than any other seasons. The second highest seasonal PM<sub>2.5</sub> was observed in spring. The local crustal materials re-suspended into the atmosphere due to the stronger winds in spring might increase the PM<sub>2.5</sub> concentration (Zhang *et al.*, 2012). The mass concentrations of PM<sub>2.5</sub> in summer were higher than the value in autumn, which were contradictory to the trends reported in the literature (Wang *et al.*, 2011; Zhou *et al.*, 2012; Zhao *et al.*, 2013c). This may be explained by two reasons. One is that part of the sampling days in summer were in poor condition while the days of autumn were in good conditions. As shown in Fig. 1, the wind speeds were lower and the relative humidity was higher in summer than autumn, which is favorable for the accumulation of pollutants and the formation of second aerosols. Another one maybe the differences of photochemical reactions during the two seasons. Furthermore, it should be noticed that summer had more precipitation than any other seasons, yet not the lowest PM<sub>2.5</sub> level. This was likely because more secondary aerosols formed due to the high temperatures, and photochemical reactions may overwhelm the precipitation scavenging effect.



**Fig. 1.** Time series of measured  $PM_{2.5}$  mass concentrations and meteorological parameters.

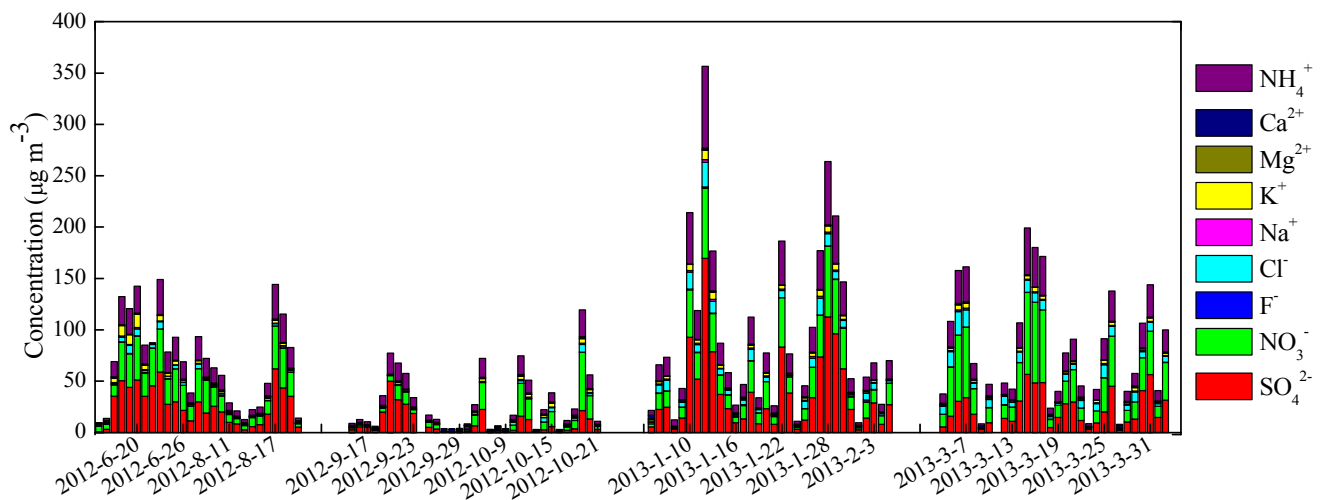


**Fig. 2.** 48-h back trajectories of air mass arriving in Beijing for typical pollution episode in different seasons.

#### **Annual Average and Seasonal Variations of Water-Soluble Inorganic Ions**

The daily mass concentrations of water-soluble inorganic ions (WSIIs) in  $PM_{2.5}$  are illustrated in Fig. 3, and the

average concentrations of each ion together with annual average values are listed in Table 1. The average concentration of the nine detected ions was  $69.0 \pm 61.8 \mu\text{g m}^{-3}$ , accounting for 57.8% of  $PM_{2.5}$  mass concentration, showing that the



**Fig. 3.** Variations of the daily mass concentration of nine WSIs in PM<sub>2.5</sub>.

**Table 1.** Average concentrations of PM<sub>2.5</sub>, chemical species (µg m<sup>-3</sup>) and meteorological parameters.

Species	Annual	Summer	Autumn	Winter	Spring
PM <sub>2.5</sub>	112.4 ± 94.4	103.3 ± 62.2	58.3 ± 49.2	169.1 ± 130.4	119.6 ± 76.1
SO <sub>4</sub> <sup>2-</sup>	24.2 ± 26.1	26.3 ± 18.3	9.38 ± 11.5	38.9 ± 38.9	22.8 ± 16.7
NO <sub>3</sub> <sup>-</sup>	20.3 ± 19.1	21.6 ± 13.5	9.12 ± 12.5	22.7 ± 18.6	29.5 ± 24.0
F <sup>-</sup>	0.22 ± 0.33	0.28 ± 0.30	0.07 ± 0.08	0.42 ± 0.50	0.10 ± 0.14
Cl <sup>-</sup>	4.33 ± 0.61	2.37 ± 2.08	0.99 ± 1.61	6.45 ± 5.33	7.62 ± 5.02
Na <sup>+</sup>	0.61 ± 0.51	0.46 ± 0.35	0.30 ± 0.43	0.92 ± 0.60	0.77 ± 0.36
K <sup>+</sup>	2.20 ± 2.18	2.71 ± 3.29	1.31 ± 1.12	2.70 ± 2.26	2.20 ± 1.30
Mg <sup>2+</sup>	0.16 ± 0.11	0.16 ± 0.07	0.19 ± 0.08	0.16 ± 0.17	0.10 ± 0.07
Ca <sup>2+</sup>	1.11 ± 0.56	0.90 ± 0.34	1.15 ± 0.51	0.78 ± 0.54	1.61 ± 0.47
NH <sub>4</sub> <sup>+</sup>	15.8 ± 13.7	16.2 ± 9.9	6.91 ± 7.18	22.4 ± 11.3	18.4 ± 11.9
OC	17.1 ± 17.1	9.28 ± 5.85	8.62 ± 6.93	33.2 ± 23.4	16.1 ± 10.2
EC	5.60 ± 5.13	3.57 ± 2.00	3.59 ± 3.06	9.16 ± 6.94	5.80 ± 4.58
TEMP/°C	11.2 ± 11.1	25.3 ± 2.07	17.5 ± 3.70	-3.68 ± 1.81	6.91 ± 2.65
RH/%	58.8 ± 17.6	71.4 ± 15.1	53.4 ± 14.4	65.0 ± 17.4	47.8 ± 14.6
WS/m s <sup>-1</sup>	2.09 ± 0.81	2.09 ± 0.45	1.91 ± 0.89	1.84 ± 0.76	2.57 ± 0.86
PR/mm	1.31 ± 4.98	4.79 ± 9.64	0.71 ± 2.41	0.19 ± 0.58	0.35 ± 1.29

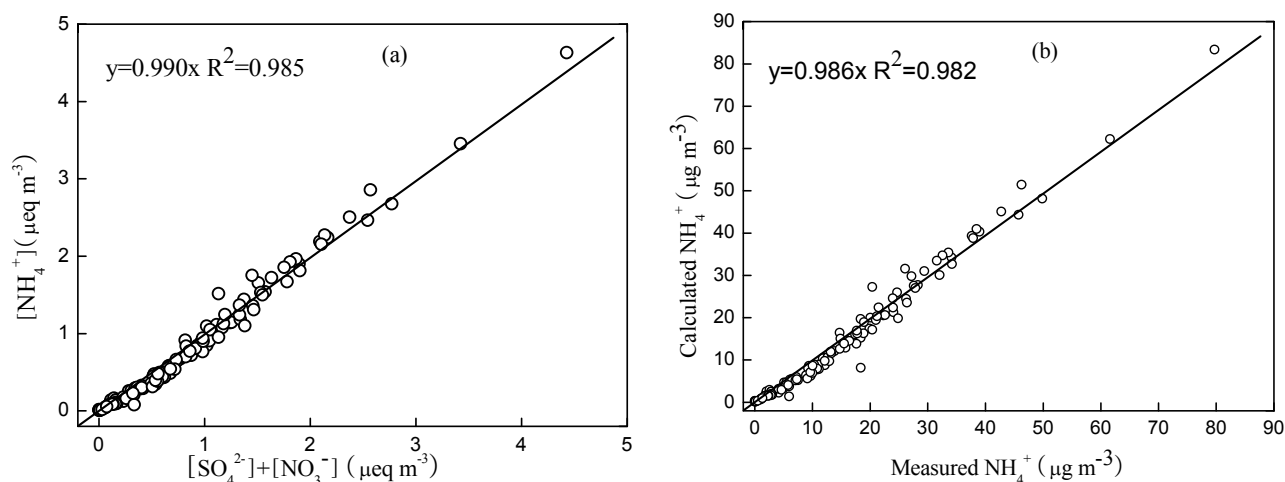
percentages of WSIs in PM<sub>2.5</sub> was higher than those measured in 2009 (Zhang *et al.*, 2013). Secondary inorganic aerosols (SNA, including SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) were major components of WSIs, comprising 80.3% of annual average total WSIs. From a seasonal perspective, SO<sub>4</sub><sup>2-</sup> had the highest concentration in winter and the lowest concentration in autumn. The higher concentrations of SO<sub>4</sub><sup>2-</sup> in winter might be caused by the coal combustion for residential heating.

The seasonal variations of NO<sub>3</sub><sup>-</sup> were different from SO<sub>4</sub><sup>2-</sup>. Vehicular exhaust was the main source of NO<sub>x</sub>, while coal combustion may also contribute to NO<sub>x</sub> (Zhang, 2014). The maximum concentrations of NO<sub>3</sub><sup>-</sup> were observed in spring. The coal burning for residential heating in early spring may release NO<sub>x</sub>, resulting in relatively higher NO<sub>3</sub><sup>-</sup> concentration. Although high temperature may promote photochemical processes, NO<sub>3</sub><sup>-</sup> was observed slightly lower in summer than spring due to the evaporation from filter at high temperature. Meanwhile, the variation of NH<sub>4</sub><sup>+</sup> was consistent with that of PM<sub>2.5</sub>. The lowest concentration of NH<sub>4</sub><sup>+</sup> was observed

in summer, which may also be caused by evaporating from the filters at high temperature.

First, we assumed that the presence of NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> was in the form of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> rather than NH<sub>4</sub>HSO<sub>4</sub>. The charge balance between [NH<sub>4</sub><sup>+</sup>] and [SO<sub>4</sub><sup>2-</sup>+NO<sub>3</sub><sup>-</sup>] was analyzed in the present study (Fig. 4). The slope of the linear regression was 0.990 with a correlation coefficient R<sup>2</sup> = 0.985, indicating that the SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were fully neutralized by NH<sub>3</sub> in the form of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub>. According to the charge balance, the calculated concentrations of NH<sub>4</sub><sup>+</sup> were well correlated to the measured one, with a relationship of  $y = 0.986x$  and a correlation coefficient R<sup>2</sup> = 0.982. Thus, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> can be estimated by the SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> mass concentration multiplied by a factor of 1.38 and 1.29, respectively.

Previous study has shown that Cl<sup>-</sup> might be derived from coal combustion when the Cl<sup>-</sup>/Na<sup>+</sup> equivalent concentration ratios were larger than the mean ratio (1.17) for sea water (Wang *et al.*, 2006). The ratios of [Cl<sup>-</sup>]/[Na<sup>+</sup>] were 3.35, 2.14, 4.55, and 6.41 in summer, autumn, winter, and spring,



**Fig. 4.** Linear relationships of  $[\text{NH}_4^+]$  versus  $[\text{NO}_3^- + \text{SO}_4^{2-}]$  (a) and correlation between calculated and measured concentration of  $\text{NH}_4^+$  (b).

respectively, indicating that the higher concentrations of  $\text{Cl}^-$ , especially in winter, were caused by the increased amount of coal combustion for heating.  $\text{Ca}^{2+}$  would be more likely originated from the re-suspended road dust and long-range transported dust (Gao *et al.*, 2014). Concentrations of  $\text{Ca}^{2+}$  were highest in the spring, which might be ascribed to the high loading of crustal dust due to strong wind in spring.  $\text{K}^+$  had a higher concentration in both summer and winter than in spring and autumn. Wheat straw burning during the summer harvest may cause the elevated concentration of  $\text{K}^+$ , while the high concentrations of  $\text{K}^+$  in winter may be related to the biomass burning for residential heating.

#### Annual Average and Seasonal Variations of Carbonaceous Compounds

Carbonaceous aerosols accounted for 20.6%, 31.8%, 39.4%, and 23.9% of  $\text{PM}_{2.5}$  in summer, autumn, winter, and spring, respectively, with an annual average of 29.6%. Temporal variations of OC, EC and OC/EC in  $\text{PM}_{2.5}$  are shown in Fig. 5, and summary statistics of OC and EC among four seasons are listed in Table 1. The annual average mass concentration of OC and EC in  $\text{PM}_{2.5}$  was  $17.1 \pm 17.1 \mu\text{g m}^{-3}$  and  $5.6 \pm 5.1 \mu\text{g m}^{-3}$ , respectively, which were lower than those observed in previous years (Duan *et al.*, 2006; Wang *et al.*, 2011; Yang *et al.*, 2011b; Zhou *et al.*, 2012), but close to those observed most recently (Zhang *et al.*, 2013; Zhao *et al.*, 2013c). These lower OC and EC levels were mainly due to energy restructuring. Beijing has largely switched from residential and industrial coal to natural gas or central steam since 2006.

The seasonal variations of OC and EC showed similar patterns to that of  $\text{PM}_{2.5}$  mass, with higher concentrations in winter and spring, and lower concentrations in summer and autumn. The higher concentrations in winter and spring can be explained by a combination of emission source and meteorological conditions. There was a “heating season” from November to the following March in Beijing. Coal combustion and biomass burning for local heating were likely a cause of high OC and EC levels. On the other hand, low wind speed and low precipitation during winter were

conductive to the accumulation of pollutants, contributing to the high carbon loading.

OC concentrations were all higher than those of EC during all sampling periods. The SOC concentrations could be estimated roughly using the minimum OC/EC ratio method, which suggested that samples having the lowest OC/EC ratio contained almost exclusively primary organic aerosols (POC) (Castro *et al.*, 1999). Then, the concentrations of SOC can be estimated by the following equations:

$$\text{POC} = \text{EC} \times (\text{OC/EC})_{\min} \quad (4)$$

$$\text{SOC} = \text{OC} - \text{POC} \quad (5)$$

where  $(\text{OC/EC})_{\min}$  was the value of the lowest OC/EC ratio. Since the validity of the  $(\text{OC/EC})_{\min}$  was crucial to calculate the POC, three samples with the lowest OC/EC ratios were used during a given season (Lim and Turpin, 2002; Yuan *et al.*, 2006). Based on the  $(\text{OC/EC})_{\min}$  of 1.63, 1.46, 2.17 and 2.26 in summer, autumn, winter and spring, the average concentrations of SOC were 3.53, 3.53, 13.4, and 2.99  $\mu\text{g m}^{-3}$ , which accounted for 35.3%, 40.7%, 42.6%, and 13.1% of OC, respectively. Similar to SNA, SOC were highest in winter. The stable atmosphere and cool temperature in winter could facilitate accumulation of air pollutants and accelerate the condensation of volatile organic compounds onto particles. The concentrations of SNA were higher in spring, and the lowest in autumn. While the concentrations of SOC were equal in summer and autumn, and the lowest concentration appeared in spring. In the spring, the wind was strong, and the pollutants have been dispersed, which was unfavorable for the OC aging and thereby caused lower SOC formation. Thus, the higher concentrations of OC in spring might almost be fresh particles.

#### Chemical Mass Balance

As shown in Fig. 6, the reconstructed  $\text{PM}_{2.5}$  mass was significantly correlated with the measured value ( $R^2 > 0.98$ ) during the four seasons. This implied that the reconstruction of eight major components in  $\text{PM}_{2.5}$  adopted in this study



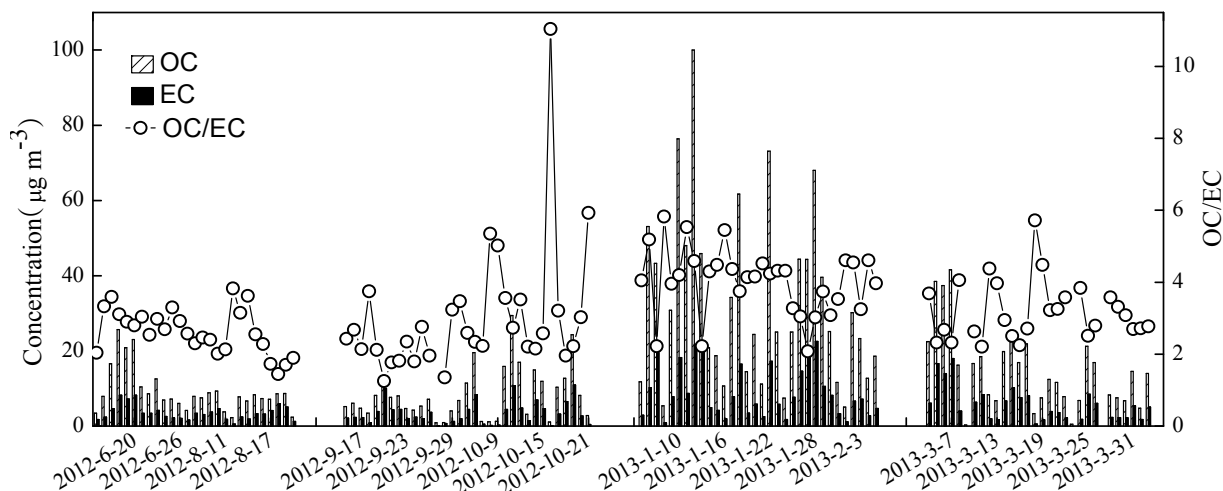


Fig. 5. Temporal variations of OC, EC and OC/EC in PM<sub>2.5</sub>.

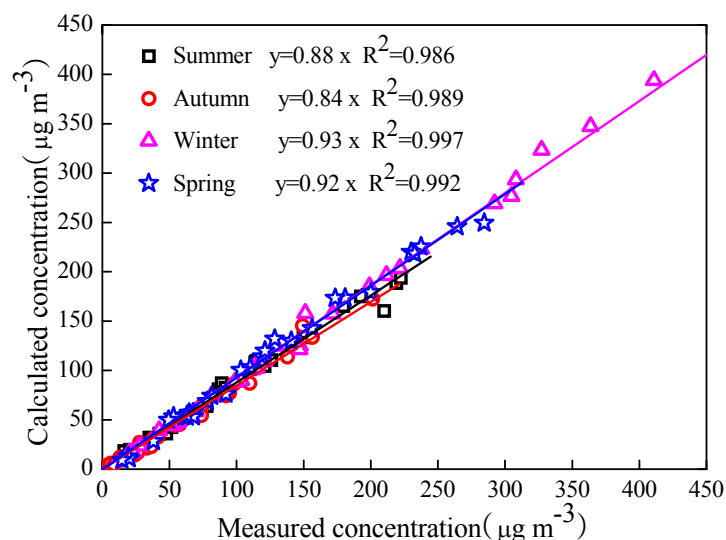


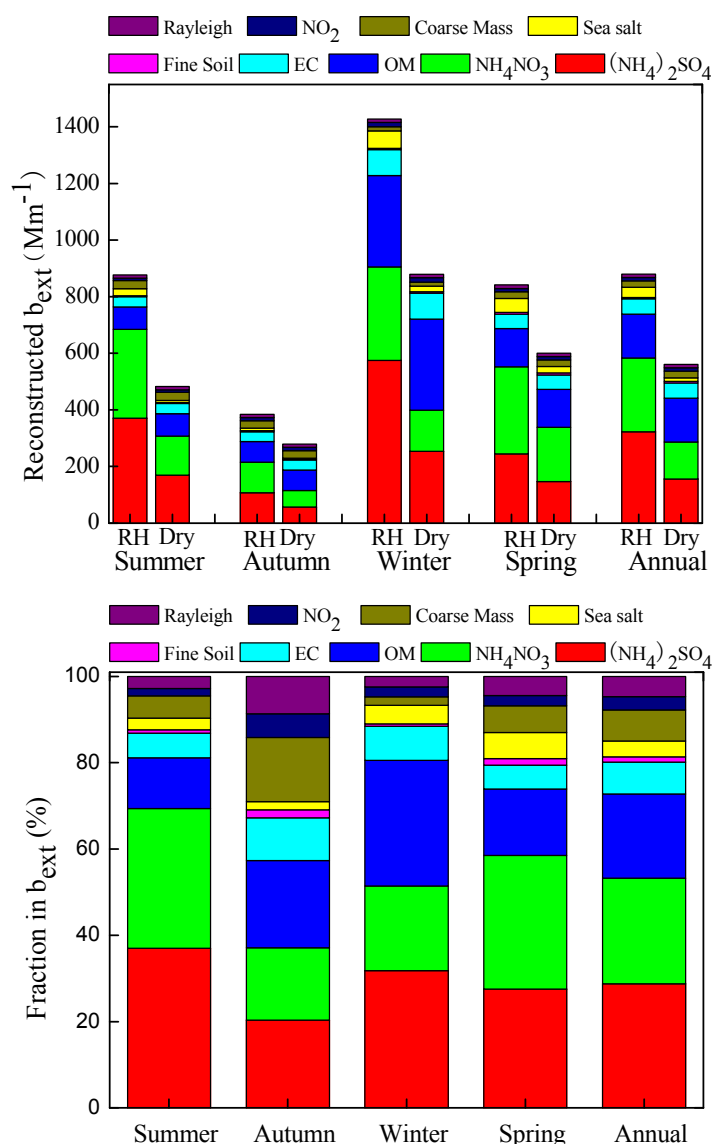
Fig. 6. Scatter plots of measured and calculated PM<sub>2.5</sub> mass concentrations by season.

was reasonable. Compared with measured PM<sub>2.5</sub> mass, the reconstructed values were found to be underestimated by 13% on average, but about 20% in autumn. The underestimation of the reconstructed PM<sub>2.5</sub> mass was mainly associated with two factors. The water-soluble components such as NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> are likely to be absorbed by water during weighting, which may lead to positive biases in measured PM<sub>2.5</sub> mass concentration (Tsai and Kuo, 2005). Additionally, the factor used in converting a given analyzed species to a certain component was critical for PM<sub>2.5</sub> mass reconstruction. The factor of 1.8 has been used for the conversion of OM from OC in previous studies (Yang *et al.*, 2012; Tao *et al.*, 2013), which was related to the quantities of aging organic matter. If we adopted the factor of 1.8 to estimate the OM mass in autumn and winter, the underestimation will be reduced by 3%.

#### Contributions of Each Chemical Component to Light Extinction

The seasonal variations of  $b_{\text{ext}}$  as well as the contribution

of each species to  $b_{\text{ext}}$  are shown in Fig. 7. The value of  $b_{\text{ext}}$  was highest in winter ( $1427.4 \pm 1274.3 \text{ Mm}^{-1}$ ), followed by summer and spring ( $877.3 \pm 586.5$  and  $841.3 \pm 589.3 \text{ Mm}^{-1}$ , respectively), and lowest in autumn ( $384.9 \pm 381.7 \text{ Mm}^{-1}$ ), with an annual  $b_{\text{ext}}$  value of  $879.9 \pm 872.7 \text{ Mm}^{-1}$ . Compared with other cities in China, the annual value of  $b_{\text{ext}}$  observed in Beijing was much higher than that observed in Xiamen and Guangzhou (Zhang *et al.*, 2012; Tao *et al.*, 2014), comparable with that observed in Jinan and Chengdu (Yang *et al.*, 2012; Song *et al.*, 2013), but was lower than that obtained in Xi'an (Cao *et al.*, 2012). Compared with other  $b_{\text{ext}}$  values obtained in Beijing, the value of  $b_{\text{ext}}$  in this study was higher than that observed in 2008 (Li *et al.*, 2013a) and 2012 (Tian *et al.*, 2014), and comparable with that obtained in 2006 (Jung *et al.*, 2009). The highest  $b_{\text{ext}}$  in winter may be associated with the high concentrations of PM<sub>2.5</sub>. Furthermore, PM<sub>2.5</sub> mass concentration was found to be higher in spring than summer, while the  $b_{\text{ext}}$  value had a distinctly contrasting pattern with slightly higher values in summer than spring. The phenomenon may be due to the



**Fig. 7.** Seasonal variations of  $b_{ext}$  and relative contributions of each species to the total  $b_{ext}$ .

high relative humidity in summer. Previous studies showed that hygroscopic species such as  $(NH_4)_2SO_4$  and  $NH_4NO_3$  can absorb water vapor, which can significantly influence its particle size as relative humidity increased, thus enhancing the scattering coefficient and proportionately reducing visibility (Malm and Day, 2001; Malm *et al.*, 2003).

Dry extinction coefficients ( $b_{ext,dry}$ ) were estimated by Eq. (3) with  $f(RH) = 1$ , while ambient extinction coefficients ( $b_{ext}$ ) were estimated using Eq. (3) in which the hygroscopic growth of inorganic components was considered. As illustrated in Fig. 7, average reconstructed  $b_{ext,dry}$  was  $560.3 \pm 492.2 Mm^{-1}$ , while  $b_{ext}$  dependent on the magnitude of RH, reached to  $879.9 \pm 872.7 Mm^{-1}$ . The difference between average  $b_{ext,dry}$  and  $b_{ext}$  was 26.6% during the entire four seasons. It is worth noting that the difference between  $b_{ext,dry}$  and  $b_{ext}$  was as high as 37.9% in summer, whereas it was only 23.6% in spring. As discussed above, it was mainly attributed to SNA water absorption at higher relative humidity that the  $b_{ext}$  was larger in summer than spring despite higher

concentrations being observed in spring rather than summer.

As shown in Fig. 7, during the entire study period,  $(NH_4)_2SO_4$ ,  $NH_4NO_3$  and OM, the three dominant chemical species, accounted for 72.7% of the total  $b_{ext}$ .  $(NH_4)_2SO_4$  was the largest contributor to  $b_{ext}$ , accounting for 28.8%, followed by  $NH_4NO_3$  (24.4%), OM (19.5%), EC (7.39%), and coarse mass (7.23%), while fine soil, sea salt,  $NO_2$  and Rayleigh made a minor contribution, together accounting for 12.7%. It should be noted that there was an evident seasonal variations in contributions to  $b_{ext}$  from each species. The sum contributions of  $(NH_4)_2SO_4$  and  $NH_4NO_3$  to  $b_{ext}$  were the largest in summer, accounting for 69.4% of  $b_{ext}$ , while it decreased to 37.1% in autumn. It implied that gas-particle conversion was a likely key path for the accumulation of fine particles in summer. Another reason for the higher percentage of  $(NH_4)_2SO_4$  and  $NH_4NO_3$  in summer was their ability to absorb water vapor, which can enhance  $b_{ext}$  under high relative humidity. In contrast, the contribution of OM was the lowest in summer, accounting only for 11.7%, while it



approximated 2.5 times higher in winter than that in summer, which is closely related to the relatively high concentrations of OM in winter. Furthermore, the contributions of coarse mass, EC, and Rayleigh to  $b_{\text{ext}}$  could not be ignored during autumn.

The air quality index (AQI) is an index for reporting daily air quality (<http://www.airnow.gov/index.cfm?action=aqbasics.aqi>). In Beijing,  $\text{PM}_{2.5}$  was the primary pollutant, thus, the AQI in this study was calculated according to the concentration of  $\text{PM}_{2.5}$ . In addition, the value of AQI was published on line every day by Beijing Municipal Environmental Protection Bureau, thus, it is interesting to discuss the extinction under different AQI. The air quality conditions were classified into six categories from the best to the worse according to AQI: stage I ( $\text{AQI} \leq 50$ ), stage II ( $51 \leq \text{AQI} \leq 100$ ), stage III ( $101 \leq \text{AQI} \leq 150$ ), stage IV ( $151 \leq \text{AQI} \leq 200$ ), stage V ( $201 \leq \text{AQI} \leq 300$ ), and stage VI ( $\text{AQI} > 300$ ). Since the chemical components did not change significantly during the polluted periods, only stage I (clean period) and VI (polluted period) were compared during the entire sampling periods in Fig. 8. The fractions of the extinction coefficients caused by particles increased from 81.2% during stage I to 98.9% in stage VI. The dominant contributors to  $b_{\text{ext}}$  were coarse mass, Rayleigh, OM and  $(\text{NH}_4)_2\text{SO}_4$  under stage I, accounting for 21.2%, 15.9%, 18.3%, and 14.2%, respectively. In contrast, it is noted that  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  were the main contributor to  $b_{\text{ext}}$  during stage VI, accounting for nearly 67.1%, but fine soil, coarse mass,  $\text{NO}_2$  and Rayleigh had a minor contribution, together accounting for less than 3% of  $b_{\text{ext}}$ . It is apparent that the contribution of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  to  $b_{\text{ext}}$  was much higher during the polluted air conditions than the clean air conditions, implying that  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  played a crucial role in the atmospheric visibility impairment in Beijing. OM and EC was fairly constant during the study period accounting for 18.8% and 7.04%, respectively, while the contribution of  $\text{NO}_2$  and Rayleigh decreased sharply from stage I to VI, from 7.71% and 15.9% to 0.76% and 0.43%, respectively. As discussed above, it is worth noting

that  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$  and OM were responsible for the reduced visibility in Beijing, thus, the reduction of their precursors like  $\text{SO}_2$ ,  $\text{NO}_x$  and VOCs could effectively improve visibility in Beijing.

## CONCLUSIONS

During the entire study, daily  $\text{PM}_{2.5}$  mass concentrations ranged from 4.3 to 592.4  $\mu\text{g m}^{-3}$  with an annual average of  $112.4 \pm 94.4 \mu\text{g m}^{-3}$ . The seasonal mass concentrations of  $\text{PM}_{2.5}$  ranked in order of winter > spring > summer > autumn. WSIs and carbonaceous compounds were the major contributors to  $\text{PM}_{2.5}$  mass, accounting for 45.9% and 28.9% of the total, respectively. Overall,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were major components of WSIs, which comprised 80.7% of total WSIs. The annual average mass concentrations of OC and EC in  $\text{PM}_{2.5}$  were  $17.1 \pm 17.1 \mu\text{g m}^{-3}$  and  $5.60 \pm 5.13 \mu\text{g m}^{-3}$ , respectively. The seasonal variations of OC and EC had a similar trend to  $\text{PM}_{2.5}$  mass. The OC/EC ratios varied from 2.64 to 4.02 with an annual average of 3.14, suggesting SOC might be present in Beijing.

Light extinction was reconstructed based on the chemical species using the revised IMPROVE formula over different seasons. The highest  $b_{\text{ext}}$  occurred in winter, followed by summer and spring, and the lowest in autumn, with an annual average value of  $879.9 \pm 872.7 \text{ Mm}^{-1}$ .  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$  and OM were the three dominant chemical species, together accounting for 72.7% of the total  $b_{\text{ext}}$ . On average,  $(\text{NH}_4)_2\text{SO}_4$  was the largest contributor of  $b_{\text{ext}}$ , accounting for 28.8%, followed by  $\text{NH}_4\text{NO}_3$  (24.4%), OM (19.5%), EC (7.39%), and coarse mass (7.23%). Fine soil, sea salt,  $\text{NO}_2$  and Rayleigh had a minor contribution, together accounting for 12.7%. The chemical species experienced different variations in their concentrations and contributions to the total  $b_{\text{ext}}$  under different pollution conditions. During the clean periods (stage I), the contributions of coarse mass and Rayleigh to  $b_{\text{ext}}$  were as high as 21.2% and 15.9%, respectively, while  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  contributed only

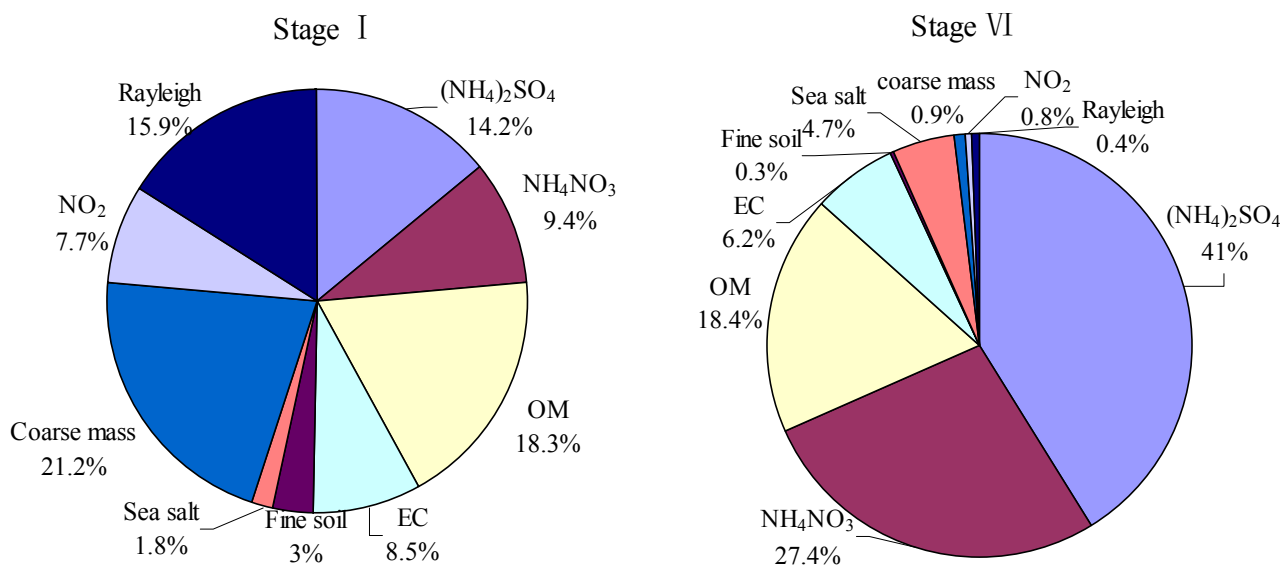


Fig. 8. Relative contributions of each species to  $b_{\text{ext}}$  under different AQI stages.

14.1% and 9.42%. During the polluted periods,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  together accounted for 67.1% of  $b_{\text{ext}}$ , while coarse mass and Rayleigh had a minor contribution with a share of only 3.1%. Therefore, in addition to control primary particulate emissions, the reduction of secondary inorganic aerosols in  $\text{PM}_{2.5}$  could be more effective in improving both air quality and visibility.

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