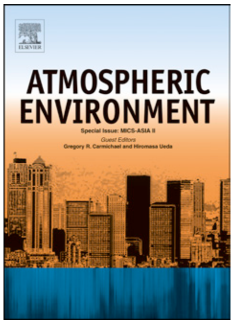

Airborne fine particulate pollution in Jinan, China: concentrations, chemical compositions and influence on visibility impairment

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Airborne fine particulate pollution in Jinan, China: concentrations, chemical compositions and influence on visibility impairment

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Abstract

Daily $PM_{2.5}$ samples were collected simultaneously at an urban site (SD) and a rural (MP) site in Jinan, China from March 2006 to February 2007. The resulting data were analyzed for major inorganic and organic water-soluble ions, 24 elements and carbonaceous species to determine the spatial and temporal variations of $PM_{2.5}$ mass concentrations and chemical compositions and evaluate their contributions to visibility impairment. The annual average concentrations of $PM_{2.5}$ were 148.71 μg m^{-3} and 97.59 μg m^{-3} at SD and MP, respectively. The predominant component of $PM_{2.5}$ was $(NH_4)_2SO_4$ at SD and organic mass at MP, which accounted for 28.71% and 37.25% of the total mass, respectively. The higher SOR (sulfur oxidation ratio) and ratios of OC/EC at SD indicated that the formation of secondary inorganic ions and secondary organic aerosols (SOA) could be accelerated in the urban area. Large size $(NH_4)_2SO_4$ and large size organic mass were the most important contributors to visibility impairment at SD and MP, accounting for 43.80% and 41.02% of the light extinction coefficient, respectively.

Keywords: $PM_{2.5}$, chemical composition, mass closure, visibility impairment.

1. Introduction

China is a world leader as both a producer and consumer of coal, steel and cement. Furthermore, due to its rapid economic development, the number of vehicles in China has increased by 15% annually (China Statistical Yearbook 2009). As a result of these and other factors, China faces serious atmospheric pollution. Fine particulate matter is the principal pollutant in most urban areas (Zhang et al., 2009), drawing worldwide attention for its adverse impact on visibility (Ghim et al., 2005) and public health (Hong et al., 2002).

Shandong Province (15.36 × D_Dd__________ÿáƧƧ________________ D_Dd__________ÿáƧƧ________________2222222222222222222222222222222222222 222222222222222222222222222222222222222222222222222222222222222222 222222222222222222222222222222222222222222222222222222222222222222

333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333333(Zhang et al., 2009). The high intensities of air pollutant emissions in Shandong Province have caused deterioration in the air quality and decreased visibility. Shandong Province has become a highly recognized hazy region near the Bohai Sea, which is one of the four major hazy areas in China (Cheng et al., 2011a). In addition to local air quality problems, there are regional concerns. Using the CMAQ modeling system, Streets et al. (2007) found that Shandong Province might exert a significant influence on the concentration of $PM_{2.5}$ in Beijing during the Olympic Games. Trajectory clustering has shown that Shandong Province is the most important contributor to particulate matter pollution in Tianjin (Kong et al., 2010), and Kim et al. (2009) reported that the Korean Peninsula may be heavily influenced by air masses originating in Shandong.

Jinan, the capital of Shandong Province, is a semi-enclosed area surrounded by the 1000 m peaks of the Taishan and Lushan Mountain and the Yellow River. This region is characterized by poor atmospheric diffusion, which is most notable in winter when the predominant wind direction is NE. It ranked 6 out of the 10 most heavily air-polluted cities in the world in 1999 (Sheng et al., 2000). Despite intensifying atmospheric pollution control measures in recent decades, the air quality in Jinan has not substantially improved. The annual average concentration of $PM_{2.5}$ at the urban site in Jinan was as high as 148.71 $\mu g\ m^{-3}$ in this study, which is among the highest levels reported in the world (Cheng et al., 2011a). Obviously, such a high concentration of airborne fine particles severely reduces visibility; predictably, over the past four decades, visibility has been decreasing in Jinan. In recent years, Jinan has suffered from a heavy haze, and the percentage of seriously hazy days (with visibility below 5 km) reached 8.5% in 2006 (Yang et al., 2007).

Significant progress has been made in our understanding of water-soluble ions in $PM_{2.5}$ (Cheng et al., 2011a; Cheng et al., 2011b; Gao et al., 2011) and size-distribution of particles in Jinan (Xu et al., 2011). However, our understanding of the systematic, long-term variations of fine particle concentration levels and their chemical constituents and impact on visibility impairment, remains incomplete. In this paper, samples of $PM_{2.5}$ collected on a continuous basis from March 2006 to February 2007 simultaneously at an urban site and at a rural site in Jinan were analyzed to obtain detailed information about the chemical characteristics of $PM_{2.5}$ in Jinan, which included 24 inorganic elements and major organic and inorganic water-soluble ions together with organic carbon and elemental carbon. Using these observation data, we analyzed the seasonal and spatial variations of $PM_{2.5}$ mass concentrations, their chemical constituents and the influence exerted on them by meteorological conditions. The revised IMPROVE formula was then applied to estimate the contributions of $PM_{2.5}$ chemical components to the aerosol light extinction coefficient.

2. Methodology

2.1 Site description

The city of Jinan (36°40′04"N,117°02′01"E), with a population of approximately 6,000,000, is located in north central Shandong Province, between Mount Tai in the south and the Yellow River in the north. $PM_{2.5}$ samples were simultaneously collected at an urban site and a rural site (Fig.1). The urban sampling site is 20 m above ground, on the rooftop of the Information Science and Engineering Building at Shandong University. Because the site is in a prosperous business district with convenient traffic and high population density, it provides information about the exposure of the population to $PM_{2.5}$ in Jinan. The rural sampling site, on the other hand, is located at the Miao Pu National Forest Park Monitoring Station of the Jinan Environmental Protection Bureau, a part of the Jinan Air Quality Monitoring Network, which lies approximately 10 km from the urban area. There are few large factories or main communication lines near the site; therefore, it could be considered a clean monitoring station in Jinan. The sampling site is on the roof of a two-story building in Miao Pu National Forest Park Monitoring Station, approximately 6 m above ground.

2.2 Instrumentation and sampling

The Thermo Anderson Chemical Speciation Monitor (Thermo Electron Corporation, Model RAAS2.5-400) was used to collect $PM_{2.5}$ samples at the urban site at Shandong University every 6 days from March 2006 through February 2007. Two airstreams flying at the rate of 16.7 L min^{-1} were connected to a Teflon filter (1 μm pore size and 47 mm diameter, Pall Gelman Inc.) for the $PM_{2.5}$ mass, while water-soluble ions and element analysis and a quartz filter (1 μm pore size and 47 mm diameter, Pall Gelman Inc.) were used to determine the organic and elemental carbon, respectively. A dichotomous sampler (Graseby Anderson G241) was used to collect samples of $PM_{2.5}$ and $PM_{2.5\text{-}10}$ at the MP site. The main flow at the rate of 15.03 L min^{-1} was connected to a Teflon filter (1 μm pore size and 37 mm diameter, Pall Gelman Inc.) for the $PM_{2.5}$ mass, while water soluble ions and element analysis or a quartz filter (1 μm pore size and 37 mm diameter, Pall Gelman Inc.) for the determination of OC and EC every 6 days, alternately. A minor flow at the rate of 1.67 L min^{-1} was connected to glass fiber filters (Ø37 mm) to measure the mass concentrations of $PM_{2.5\text{-}10}$. The mass concentration of PM_{10} at MP could subsequently be obtained ($PM_{2.5}$+$PM_{2.5\text{-}10}$).

Each sample was collected for 23.5 hours, beginning at 8:00 am. The glass fiber filters and quartz filters were heated to 600℃ to eliminate all organic species prior to sampling. The Teflon filters were heated at 60℃ and equilibrated in a clean chamber with temperature and humidity automatically controlled at 20± 1℃ and 50± 5%, respectively, for at least 24 h, then weighed on an analytical balance (Sartorius, detection limit 0.001 mg) before and after sampling to arrive at the $PM_{2.5}$ mass. After collection, the samples were sealed in clean plastic bags, transported to the laboratory and stored in a freezer at -4℃ before analysis.

The data of the SO_2 at the MP site was provided by the Miao Pu National Forest Park Monitoring Station of the Jinan Environmental Protection Bureau and was co-located with the $PM_{2.5}$ monitor. The data of the SO_2 at the SD site was provided by the Jinan Shi Zhan Monitoring Station of the Jinan Environmental Protection Bureau, which was about 1000m from the $PM_{2.5}$ monitor.

2.3 Aerosol chemical analyses

Three inorganic ions (NO_3^-, SO_4^{2-} and NH_4^+) and three organic acids (formic, oxalic and acetic acids) were analyzed using ion chromatography (IC; Dionex 2500, USA). A separation column (Dionex Ionpac AS11), a guard column (Dionex Ionpac AG 11) and a self-regenerating suppressor (ASRS-ULTR AΠ4-mm) were used for anion analysis; a separation column (Dionex Ionpac CS14), a guard column (Dionex Ionpac CG 14) and a self-regenerating suppressor (CSRS ULTRA Π 4-mm) were used for cation analysis. The details of this procedure were described by Yang et al. (2007). The Teflon filters were analyzed for 24 elements (Al, Na, Cl, Mg, Si, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sr, Cd, Ba and Pb) using X-ray fluorescence (XRF). The carbon contents were determined using a CNH elemental analyzer (MT-5 Yanaco New Science Corporation, Japan) in a thermal procedure. The OC content was obtained at 450℃, and the same sample was then measured at 950℃ to obtain the EC content. The standard deviation of the direct measurement of EC was 0.30%, much lower than that found using the subtraction method (0.60%), where the content of OC and TC were determined directly at different temperatures in the combustion oven (450 °C for OC and 950 °C for TC), before the content of element carbon (EC) was calculated (EC=TC-OC) (Dong et al., 2004). A direct measurement of EC should improve the EC measurement accuracy because error propagation and the appearance of the negative value of EC are avoided. The number of filters for the analysis of water-soluble ions, OC/EC and elements is 52, 53, 54 and 51, 53, 51 at SD and MP respectively.

3. Results and discussion

3.1 Ambient concentrations of $PM_{2.5}$

The variations in $PM_{2.5}$ concentration during the sampling period are shown in Table 1 and Fig. 2; these range from 30.16-392.55 μg m^{-3} at SD and 15.05-294.83 μg m^{-3} at MP, with an average of 148.71 μg m^{-3} at SD and 97.59 μg m^{-3} at MP. These measurements are 9.91 and 6.51 times the annual US NAAQS standards of $PM_{2.5}$ (15 μg m^{-3}), respectively. The results clearly show that fine particulate pollution is particularly bad in Jinan, especially in the urban area.

The concentrations of $PM_{2.5}$ at MP and SD showed a high correlation (r=0.75), implying that $PM_{2.5}$ may have similar sources in MP and SD. Jinan is surrounded by mountains on 3 sides, and the anticyclone system under the height of 600 m in Shandong Province could hinder the diffusion of pollutants (Cheng et al., 2011a). The prevailing wind direction is northeast in winter and southwest in the other seasons. Because SD is located northeast of MP, these factors are likely to influence the concentrations of $PM_{2.5}$ at MP and SD.

As illustrated in Fig. 2, the $PM_{2.5}$ mass concentration showed an apparent seasonal variation, in which high values were common in winter and autumn and lower values predominated in spring and summer. Wind speed multiplies the mixing height, which is defined as atmospheric dilution rate per unit length; this can be used to evaluate the diffusion capability of the atmosphere (Chua et al., 2004). The meteorological parameters of the four seasons are shown in Table 2. The dilution rate of the atmosphere in winter was noticeably lower, at 54.47% of the dilution rate in spring. A combination of low atmospheric diffusion capacity and an increase of particulate matter emission related to heating in winter led to serious fine particle pollution. During the dust storm period, the concentration of $PM_{2.5}$ was 0.84-1.35 times the annual average, while the concentration of PM_{10} was 1.35-2.19 times the annual average, indicating that dust storms have a greater impact on PM_{10} than $PM_{2.5}$. After a sandstorm, the concentration of PM_{10} decreased rapidly, demonstrating that the impact is short-term and does not result in an accumulation of particulate matter in the air. The averages of $PM_{2.5}/PM_{10}$ at SD and MP were 0.52 and 0.43, respectively, implying that fine particulate pollution at the urban site is more serious than at the rural site.

3.2 Chemical compositions

3.2.1 Water-soluble ions

The concentrations of major chemical components in $PM_{2.5}$ are provided in Table 1. The sum of SO_4^{2-}, NO_3^- and NH_4^+ contributed 38.1% and 37.5% to $PM_{2.5}$ mass concentrations at SD and MP, respectively, indicating that SO_4^{2-}, NO_3^- and $NH_4^+$are the dominant ions in $PM_{2.5}$ in Jinan.

SO_4^{2-} and NH_4^+ exhibit a similar seasonal trend, which is high in the summer and winter and lower in the spring. However, the maximum and minimum concentrations of NO_3^- appeared in the winter and summer, respectively. The SOR may be used to indicate the reaction process and the extent of transformation from SO_2 to SO_4^{2-}. At SD, the SOR was as follows: summer (0.62) > autumn (0.41) > spring (0.38) > winter (0.18). At MP, on the other hand, the SOR was as follows: summer (0.49) > autumn (0.24) > spring (0.23) > winter (0.10). The formation of SO_4^{2-} from SO_2 mainly includes the gas-phase reaction of SO_2 and OH radical and heterogeneous reaction (metal catalyzed oxidation or H_2O_2/O_3 oxidation) (Ziegler et al., 1979). The gas-phase oxidation of SO_2 to SO_4^{2-} by an OH radical is positively related to the temperature (Seinfeld et al., 1986). The average RH in the winter is lower than the average for the entire year, which also does not favor an aqueous heterogeneous reaction. The lowest SOR was observed in the winter, as expected. The high concentration of SO_4^{2-} in the winter may be due to the high concentration of SO_2, but the strong solar radiation (high temperature) and high RH and O_3 concentrations in summer may accelerate the secondary conversion in the atmosphere and lead to the high SOR and SO_4^{2-} concentrations. The SOR at SD is higher than at MP, which implies that the highly polluted atmosphere is favorable for the transformation of SO_2.

The total formic, acetic and oxalic acids accounted for 0.39% and 0.45% of the mass of $PM_{2.5}$ at SD and MP, respectively. The concentrations of these organic acids in Jinan were comparable with those in Beijing (Wang et al., 2007) and New York City (Khwaja et al., 1995), indicating that the pollution condition of these organic acid among the big cities was similar. Acetic acid is mainly produced from primary emissions, while formic acid comes mainly from secondary transformations. The ratio of acetic to formic acid (A/F) is used to evaluate the relative importance of primary emissions and secondary emissions. The A/F ratios were relatively low at SD (<1), implying that secondary formation is important. In comparison, the higher annual A/F ratio at MP (>1) indicates that primary emissions are the dominant source of carboxylic acids. The much higher A/F ratios in the spring and summer at MP (>2) are likely due to rapid leaf expansion (Wang et al., 2007).

Oxalic acid showed apparent correlations with formic acid at SD r=0.45) and at MP (r=0.67) and was principally observed in droplet form (Yao et al., 2002). Therefore, we may infer that secondary formation is the main source of oxalic acid and that an in-cloud or heterogeneous formation process was expected.

3.2.2 Carbonaceous species

Variations of the concentrations of OC and EC at SD and MP are presented in Fig. 3. There was no apparent spatial difference between the observed concentrations of OC and EC at SD and MP. Furthermore, similar seasonal variations of the concentrations of OC and EC at SD and MP were observed, with the lowest appearing in spring and summer; the concentrations continued to increase steadily, reaching their maximum concentrations in the winter. The concentrations of OC and EC often reached their peak value at the same time, implying the inner correlation of OC and EC and their common sources.

The correlation of OC and EC may reflect the common sources of carbonaceous aerosol; in other words, the positive correlation between OC and EC may indicate that they have a common source (Turpin et al., 1991). The regressive relationship between OC and EC is shown in Fig. 4. The correlations between OC and EC at SD and MP were both higher in autumn and winter, suggesting that OC and EC may have common sources in autumn and winter, possibly biomass burning and coal combustion (Zhang et al., 2009). The lower correlation between OC and EC that appears in summer at SD and spring at MP implies that OC and EC may have different sources in the spring and summer, which might be related to the influence of dust storms coming from the northwest of China in the spring and the high temperatures in summer that favor the formation of SOA (Turpin et al., 1995). It has been suggested that if the ratio of OC/EC>2.0, SOC will be formed (Turpin et al., 1990). The ratios of OC/EC at SD and MP were in the range of 2.34-15.41 and 2.14-11.30, with averages of 5.4 and 4.7, respectively, indicating that SOC may be formed both in SD and MP and that the SOC pollution at SD was more serious than that at MP. The concentration of SOC was estimated through the following equation: OC_{sec}= $(OC)_{tot}$-(EC)*$(OC/EC)_{pri}$. The least square method was used to estimate the value of $(OC/EC)_{pri}$ (2.4); the detail of this method is described in the references (Strader et al., 1999). SOC accounted for 48.3% and 47.5% of the OC at SD and MP, respectively, suggesting that SOC is an important organic component of $PM_{2.5}$. The extremely high values of OC_{sec} /OC in winter may be related to the combination of the increasing emissions of the precursors of SOC, including VOC and SVOC, the poor conditions for diffusion and the scant amount of rainfall in winter, which may favor the active photochemical reaction of VOC and SVOC to form SOC (Lin et al., 2002).

3.2.3 Inorganic elements

In this study, the elements were divided into two groups, one related to anthropogenic activity and the other to typical crustal elements. The crustal elements (Ca, Al, Si, Fe, Mg and Ti) showed a similar seasonal variation, with high values appearing in spring and lower values appearing in summer. The concentrations of the indicator elements of coal burning (Cl, Br and Se) in winter are much higher than in other seasons, and no apparent seasonal variations were observed in the elements that come primarily from industrial sources (Sc, V, Zn, Cr, Mn, Co, Ni, Cu, Ba, Pb, Cd, As and Sr). This indicates that the contribution of burning coal to elemental pollution increased in winter, while the contributions of industrial sources were consistent.

The enrichment factor, defined as $EF=(C_i/C_n)_{environment}/(C_i/C_n)_{background}$ is useful in judging the contributions of natural and anthropogenic sources (Gao et al., 2001). In this study, Al is chosen as the reference element. The seasonal variations of EF at SD and MP are shown in Fig. 5. The EF of Al, Mg, Fe, Na and Ca are all lower than 10, indicating that these elements are mostly from the local and adjacent soil. The EF values of Cl, K, Mn, Ni, Cu, Zn, Br and Pb are much higher than 10, demonstrating that these elements had close relationships with anthropogenic activity and are less influenced by soil dust (Duan et al., 2006). Except for Cl at MP, the EF of all the elements reached their minimum levels in spring, implying an increase of the contribution of soil sources, which may be related to frequent dust storms. The EF of Cl and Br was higher in winter, which may be related to the rapidly increase in burning coal for heat in the winter. Apparent variations of the EF of Mn, Ni, Zn, Cu and Pb were not observed, except that they are lower in the spring, indicating that contribution from industrial sources is stable throughout the four seasons.

3.2.4 Mass closure

The mass closure of $PM_{2.5}$ was made under three assumptions. First, in addition to carbon, organic mass contains other elements, such as hydrogen, oxygen and nitrogen. The concentration of organic mass is calculated as 1.8 times the concentration of OC, according to the revised IMPROVE formula. Second, we assume that crustal elements exist as oxides and the soil dust concentration is the sum of the oxides of the main crustal elements (Al_2O_3, SiO_2, CaO, FeO, Fe_2O_3, TiO_2). The formula as follows was used: [Soil]=2.20[Al]+2.49[Si]+1.63[Ca]+2.42[Fe]+1.94[Ti] (Kim et al., 2001). Third, the concentration of trace elements is also assumed to be the sum of oxides of the corresponding elements, except the Al, Si, Ca, Fe and Ti.

The mass closures of $PM_{2.5}$ at SD and MP in all four seasons are presented in Fig. 6. The chemical component percentages in $PM_{2.5}$ at SD and MP are different than those of $(NH_4)_2SO_4$, which accounts for 28.71% of the mass of $PM_{2.5}$ and is the primary component of $PM_{2.5}$ at SD; organic mass ranked second, accounting for 26.98% of the $PM_{2.5}$ mass. However, the contribution of organic mass ranked first in the $PM_{2.5}$ at MP and $(NH_4)_2SO_4$ ranked second, accounting for 37.25% and 25.96% of the $PM_{2.5}$ mass, respectively. The higher percentage of organic mass at MP may be related to the higher vegetation coverage and requires further study. The contributions of the other components followed the same order of NH_4NO_3, soil, EC and trace elements at SD and MP. The unidentified components are comparable between SD and MP, accounting for 22.81% and 18.82%, respectively, which may be related to the decomposition of semi-volatile compounds such as ammonium nitrate and ammonium chloride; a backup nylon filter should be used to avoid sampling artifacts (Ye et al., 2003; Duan et al., 2006). The largest amount of unidentified components is expected to appear in the summer, when the high temperature can promote the decomposition of semi-volatile compounds. However, the largest unidentified fraction appeared in the spring at both SD and MP, which indicates that the temperature did not have a substantial impact on the unidentified percentage; the unexplained category might result from the contributions of some nonanalyzed crustal and trace elements species coming primarily from the soil. Similar results were observed in the study of $PM_{2.5}$ in Taiwan (Lin et al., 2002) and South Korea (Lee et al., 2001). The contributions of the chemical components showed similar seasonal variations in SD and MP. The contribution of $(NH_4)_2SO_4$ reached its maximum in summer, reflecting the rapid oxidation rate of SO_2 in summer. The level of organic mass was highest in autumn and winter; this may be due to the rapid increase of primary organic mass emissions and secondary organic mass formation through gas-aerosol reactions and low temperatures, which may inhibit the VOC and SVOC into the gas phase. The percentage of soil apparently increased in spring, which may be due to frequent dust storms.

3.3 Contributions of the species in $PM_{2.5}$ to the bext

The visual range can be calculated as follows:

V=3.91/bext (Koschmieder, 1925)

where bext is the light extinction coefficient. Visibility is inversely proportional to the bext, so the higher the bext, the lower the visibility.

The revised algorithm proposed by the IMPROVE program for use in estimating light extinction from aerosol chemical compositions was applied in this study.

$b_{ext} \approx 2.2\times f_s(RH)\times[\text{Small Sulfate}] + 4.8\times f_L(RH)\times[\text{Large Sulfate}] + 2.4\times f_s(RH) \times [\text{Small Nitrate}] + 5.1\times f_L(RH)\times[\text{Large Nitrate}] + 2.8\times[\text{Small Organic Mass}] + 6.1\times[\text{Large Organic Mass}] + 10\times[\text{Elemental Carbon}] + 1\times[\text{Fine Soil}] + 1.7\times f_{ss}(RH) \times[\text{Sea Salt}] + 0.6\times[\text{Coarse Mass}] + \text{Rayleigh Scattering} + 0.33\times[NO_2(ppb)]$

The major novelties of using the revised IMPROVE algorithm from the equation in our study (Yang et al., 2007) include the following: splitting the total sulfate, nitrate and organic carbon into two fractions, large and small sizes; changing the coefficient (from 1.4 to 1.8) to calculate the organic mass from organic carbon; and the new addition of sea salt and NO_2.The computational process of the revised algorithm was obtained from http://vista.cira.colostate.edu/improve/Publications/GrayLit/019_RevisedIMPROVE eq. Because the soil and coarse mass contribute only small fractions to the bext (Cheung et al., 2005), soil and coarse mass were excluded from this study. Given that the size of the hygroscopic species may increase with relative humidity and result in the variation of the bext, the hygroscopic species growth function f(RH) was introduced to the formula to indicate the influence of the relative humidity. Three water growth adjustment terms (f_S(RH), f_L(RH) and f_{SS}(RH), respectively) were used for the small-size and large-size distribution sulfate and nitrate compounds and for sea salt, respectively. The value of the Rayleigh scattering is approximately 12 Mm^{-1} for sites near sea level.

The result of the bext calculated from the data set from March 2006 through February 2007 was 778.16 Mm^{-1}at SD and 528.48 Mm^{-1} at MP, higher than in our previous study (Yang et al., 2007), indicating that the visibility in Jinan has continued to deteriorate. The bext similarly showed clear seasonal variations at both SD and MP. The highest measurements were obtained in winter, which may be due to the high concentration of fine particles caused by the combination of increasing pollutant emissions and inverse atmospheric diffusion conditions. The contributions of chemical components in $PM_{2.5}$ to bext at SD and MP across the four seasons are detailed in Fig. 7. The relative average contributions of the species in $PM_{2.5}$ at SD and MP are different in that large size ammonium sulfate is the largest contributor at SD (43.80%), similar to our previous study at SD and studies at Hongkong (Cheung et al., 2005) and Brisban (Chan et al., 1999). The contribution of large size organic mass (41.02%) at MP indicates that the rural area of Jinan experiences more serious organic pollution. The contribution of large size ammonium sulfate reached its maximum in the summer, possibly due to the large fraction of sulfate in $PM_{2.5}$ and its ability to absorb water vapor, which can enhance light scattering under the high relative humidity of summer. Large size organic mass is the largest contributor to bext in the autumn and winter, which is closely related to the relatively high concentration of organic mass in the autumn and winter.

4. Conclusion

The daily $PM_{2.5}$ mass concentrations ranged from 30.16-392.55 μg m^{-3} and 15.05-294.83 μg m^{-3} at SD and MP, respectively, with an average of 148.71 μg m^{-3} and 97.59 μg m^{-3} and are 9.91 and 6.51 times the U.S.EPA's NAAQS. This indicates that fine particulate pollution was very serious in Jinan and worst in the urban area. The most abundant species contributing to the $PM_{2.5}$ were ammonium sulfates and organic mass, accounting for a total of 55.69% and 63.21% at SD and MP, respectively. $(NH_4)_2SO_4$ was the primary component of $PM_{2.5}$ at SD, while the content of organic mass ranked first in the $PM_{2.5}$ at MP. The higher SOR at SD showed that the secondary inorganic ion pollution was more serious in the urban area. The correlation coefficients between OC and EC showed that OC and EC may have common sources in the winter and autumn. The high ratio of OC/EC in Jinan implied that the formation of secondary organic aerosol was active in Jinan and stronger at the urban location. The results of the revised IMPROVE formula showed that the contributions of large size sulfate and large size organic mass in fine particle form to light extinction were significant at SD and MP, respectively.

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1. Chemical components and impact on visibility of $PM_{2.5}$ were studied in a highly polluted area.
2. Formation of secondary inorganic ions and secondary organic aerosol was active at urban area.
3. $(NH_4)_2SO_4$ and OM were the most abundant species and the main contributors to b_{ext}.

Table 1 Seasonal average concentrations of chemical species in $PM_{2.5}$ in Jinan (unit: μg m^{-3})

	SD					MP				
	spring	Summer	autumn	winter	average	spring	summer	autumn	winter	average
Mass (ug/m^3)	143.25	129.04	134.89	204.89	148.71	93.46	69.56	93.21	146.80	97.59
Acetic	0.05	0.08	0.08	0.10	0.08	0.12	0.11	0.08	0.09	0.10
Formic	0.07	0.11	0.09	0.11	0.09	0.05	0.05	0.08	0.09	0.07
Oxalic	0.32	0.50	0.46	0.28	0.40	0.25	0.27	0.20	0.16	0.22
Nitrate	9.06	6.71	9.15	20.12	10.58	7.27	1.83	4.32	9.73	5.49
Sulfate	21.91	37.36	27.80	37.70	30.92	15.40	24.63	14.73	18.34	18.43
Ammonium	9.69	14.67	12.57	20.47	13.99	6.66	8.17	6.11	11.15	7.97
OC	15.76	14.99	23.96	35.75	22.19	13.44	9.30	22.50	35.24	20.20
OC_{sec}	8.20	7.80	13.50	22.30	12.10	7.50	3.00	11.20	23.10	10.90
EC	3.25	3.08	4.49	5.74	4.10	2.80	3.19	5.27	5.67	4.33
Al	1.64	0.41	0.69	0.78	0.86	0.63	0.3	0.24	0.27	0.34
Na	0.48	0.42	0.57	0.63	0.52	0.23	0.21	0.26	0.28	0.24
Cl	1.66	0.63	2.96	6.77	2.7	1.46	0.09	1.68	3.81	1.7
Mg	0.37	0.1	0.19	0.18	0.21	0.15	0.06	0.06	0.07	0.08
Si	4.00	0.91	1.57	1.81	2.02	1.49	0.68	0.6	0.68	0.81
K	3.47	4.32	4.73	4.58	4.3	2.55	2.22	2.53	2.74	2.51
Ca	1.59	0.61	1.25	1.09	1.13	0.73	0.63	0.45	0.62	0.59
Sc	0.01	0.01	0.01	0.02	0.01	--	--	--	--	--
Ti	0.15	0.04	0.06	0.09	0.08	0.05	0.03	0.03	0.03	0.03
V	0.01	0.01	--	--	--	--	--	--	0.01	--
Cr	0.02	0.02	0.02	0.03	0.02	0.01	0.02	0.01	0.01	0.01
Mn	0.09	0.05	0.12	0.16	0.1	0.06	0.03	0.06	0.07	0.06
Fe	1.94	0.99	1.61	2.02	1.59	0.83	0.5	0.62	0.61	0.63
Co	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01
Ni	0.01	0.01	0.01	0.01	0.01	0.01	--	0.01	--	0.01
Cu	0.02	0.02	0.03	0.05	0.03	0.01	0.02	0.02	0.02	0.02
Zn	0.38	0.56	0.55	0.99	0.59	0.29	0.22	0.29	0.51	0.32
As	0.02	0.03	0.02	0.03	0.02	0.01	0.01	0.01	0.01	0.01
Se	0.01	0.01	0.02	0.04	0.02	0.01	0.01	0.01	0.02	0.01
Br	0.06	0.04	0.08	0.15	0.08	0.03	0.02	0.05	0.09	0.05
Sr	0.02	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01
Cd	0.01	0.01	--	--	0.01	0.01	0.01	0.01	0.01	0.01
Ba	0.07	0.04	0.07	0.07	0.06	0.04	0.04	0.03	0.03	0.03
Pb	0.20	0.28	0.31	0.43	0.3	0.24	0.29	0.19	0.26	0.25

Table 2 Seasonal average meteorological conditions during the sampling period in Jinan

	Concentration of $PM_{2.5}$ ($\mu g\ m^{-3}$)	Temperature (℃)	Mixing height (m)	Wind speed ($m\ s^{-1}$)	Relative humidity (%)	Atmospheric dilution rate
spring	143.3	15.4	975.8	3.8	45.0	4423.9
summer	129.0	26.9	722.1	2.8	66.2	2599.4
autumn	134.9	17.2	680.0	2.9	62.8	2508.9
winter	204.9	2.7	586.3	3.1	52.6	2409.5

Figure Captions

Fig. 1 Aerosol sampling at an urban site and a rural site in Jinan

Fig. 2 Temporal variations of $PM_{2.5}$ mass, PM_{10} mass and gaseous pollutant concentrations in Jinan from March 2006 to February 2007

Fig. 3 OC and EC concentrations and OC/EC ratio in Jinan during the sampling period

Fig. 4 Regression relationship between OC and EC in four seasons in Jinan

Fig. 5 Seasonal variations of enrichment factors of the elements in $PM_{2.5}$ in Jinan

Fig. 6 Annual and seasonal contributions of chemical species to $PM_{2.5}$ mass concentrations in Jinan

Fig. 7 Annual and seasonal contributions of chemical components in $PM_{2.5}$ to the light extinction coefficient in Jinan

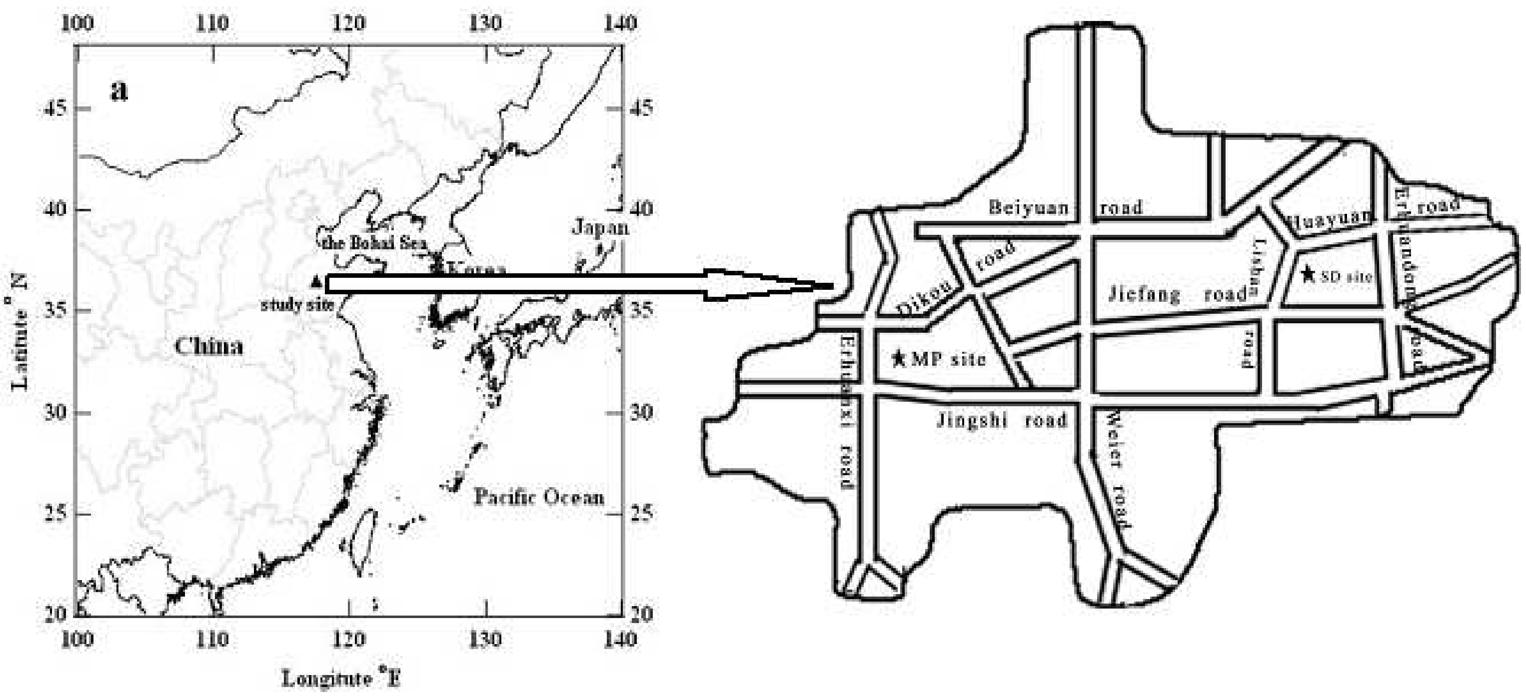

Fig. 1 Aerosol sampling at an urban site and a rural site in Jinan

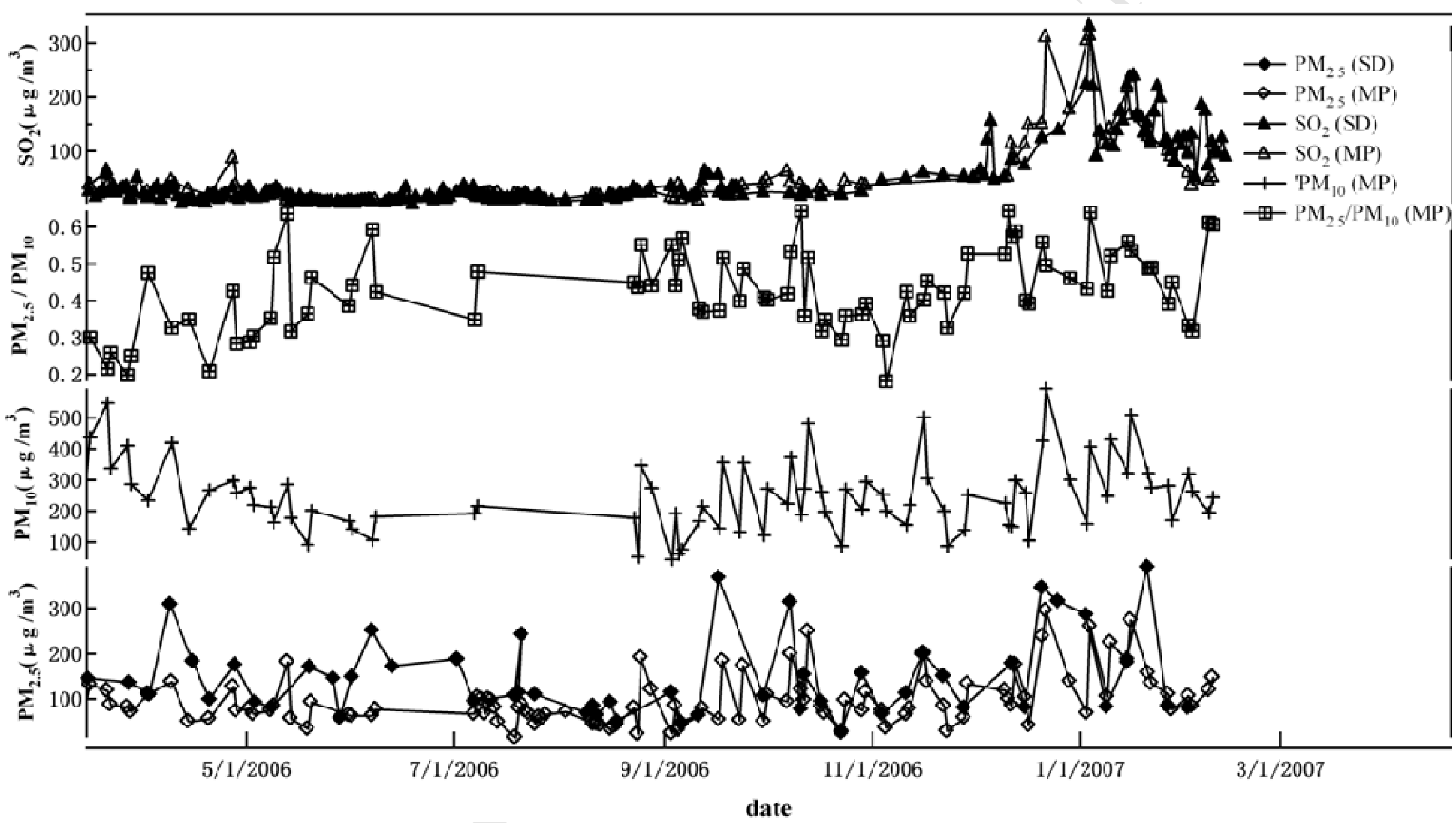

Fig.2 Temporal variations of $PM_{2.5}$ mass, PM_{10} mass and gaseous pollutants concentrations in Jinan from March 2006 to February 2007

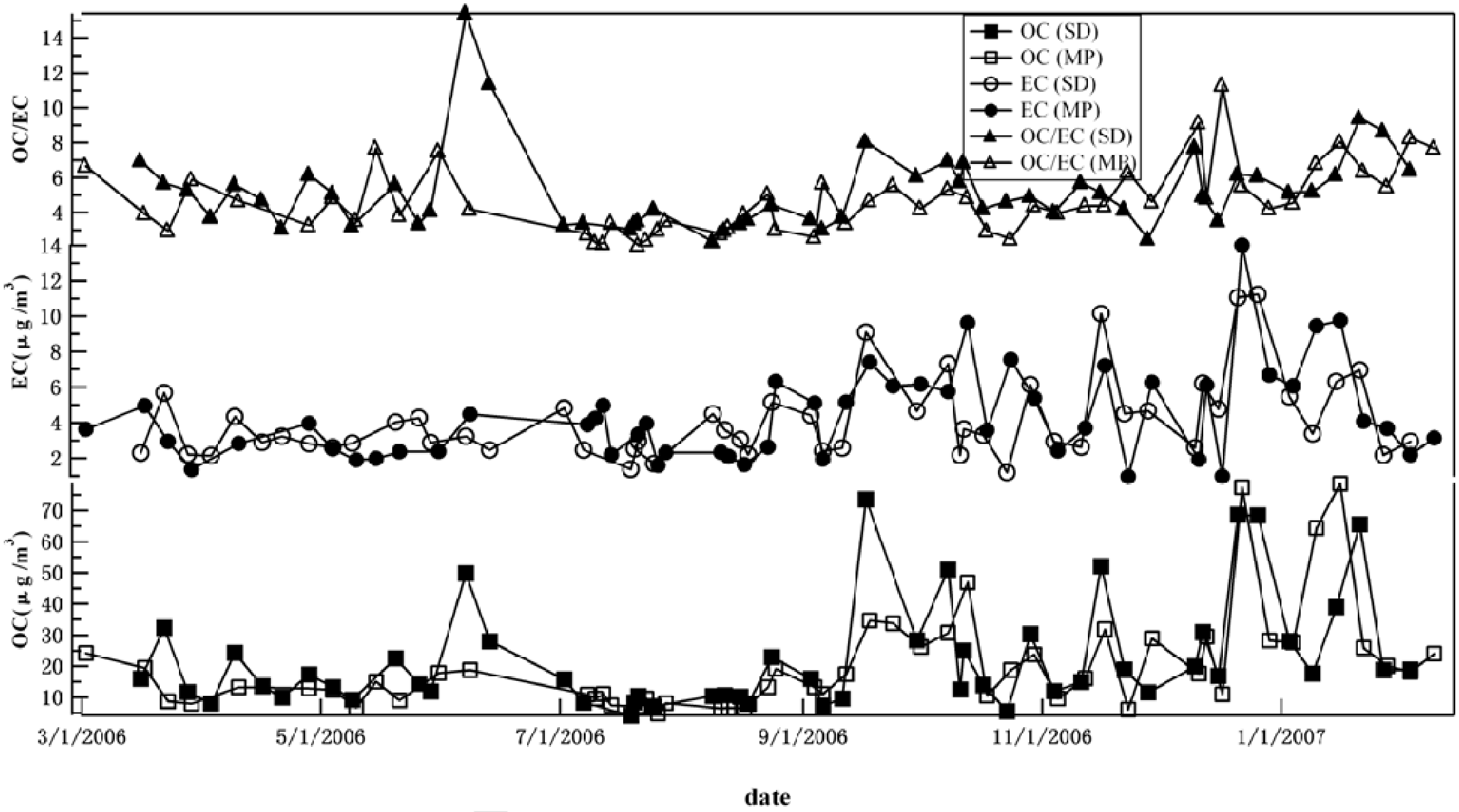

Fig. 3 OC and EC concentrations and the OC/EC ratio in Jinan during the sampling period

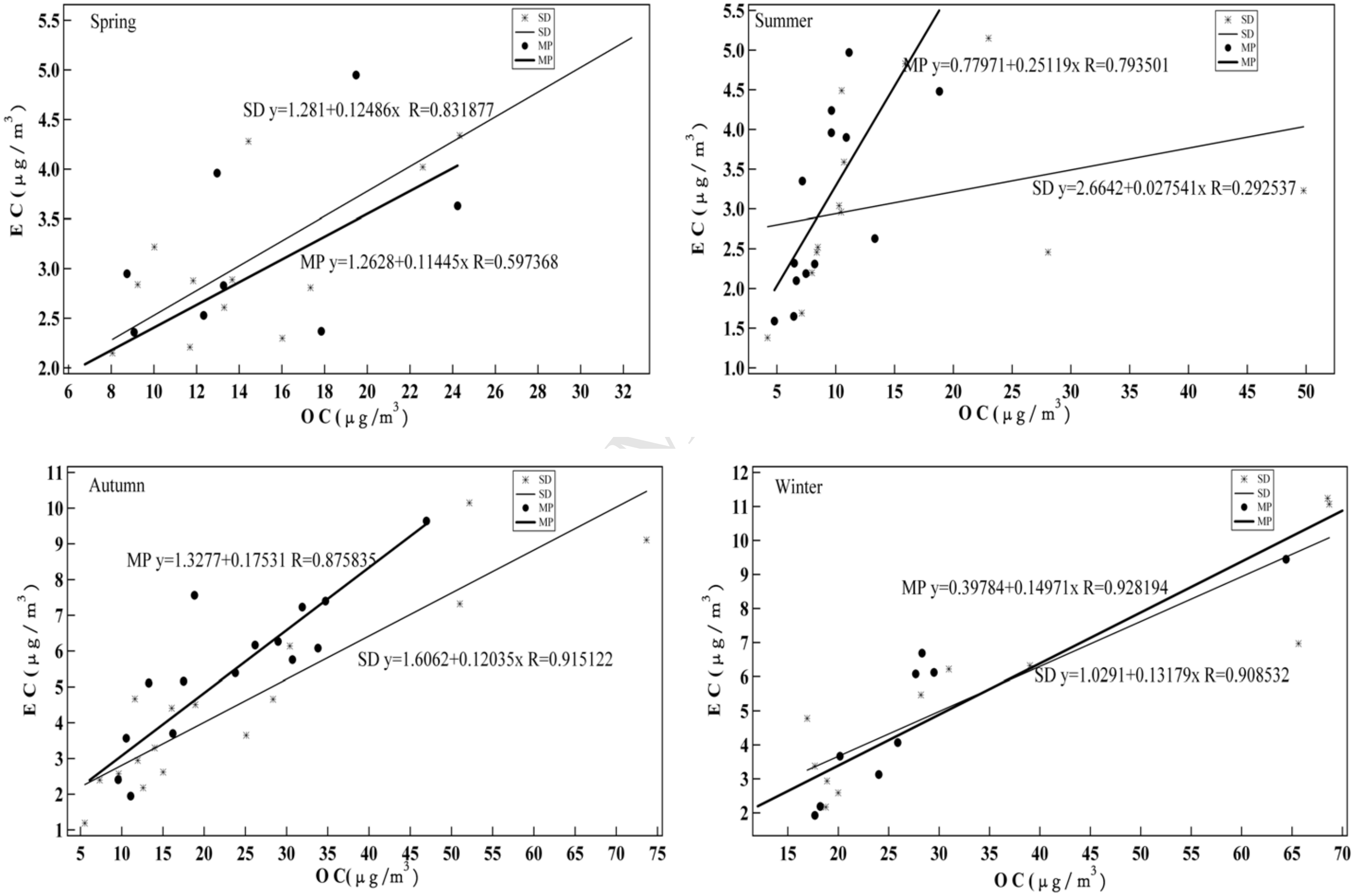

Fig. 4 Regression relationship between OC and EC in four seasons in Jinan

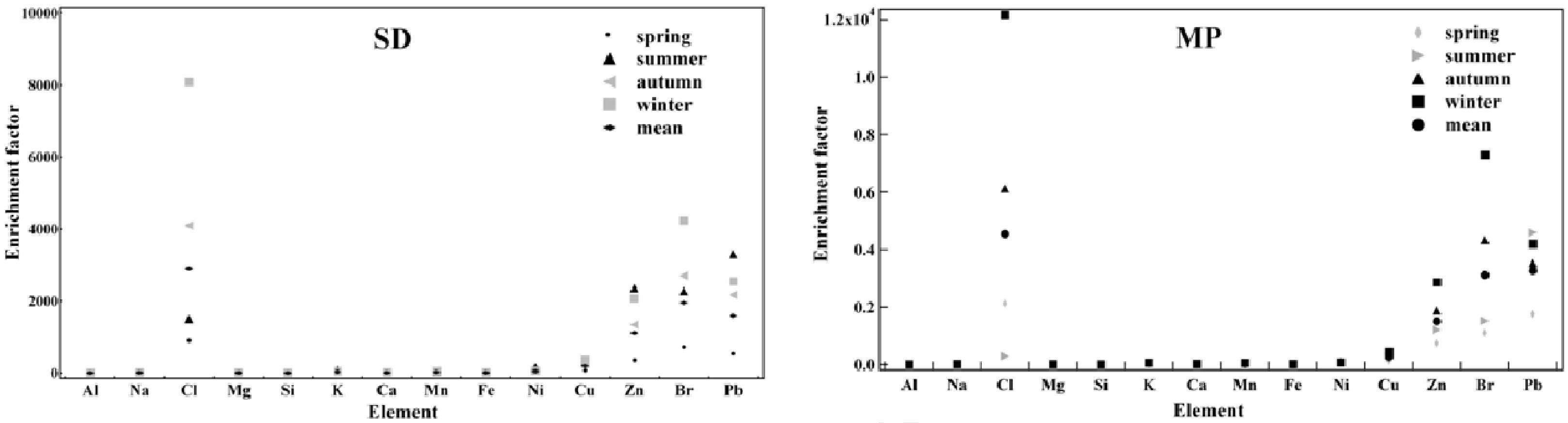

Fig. 5 Seasonal variations of the enrichment factors of elements in $PM_{2.5}$ in Jinan

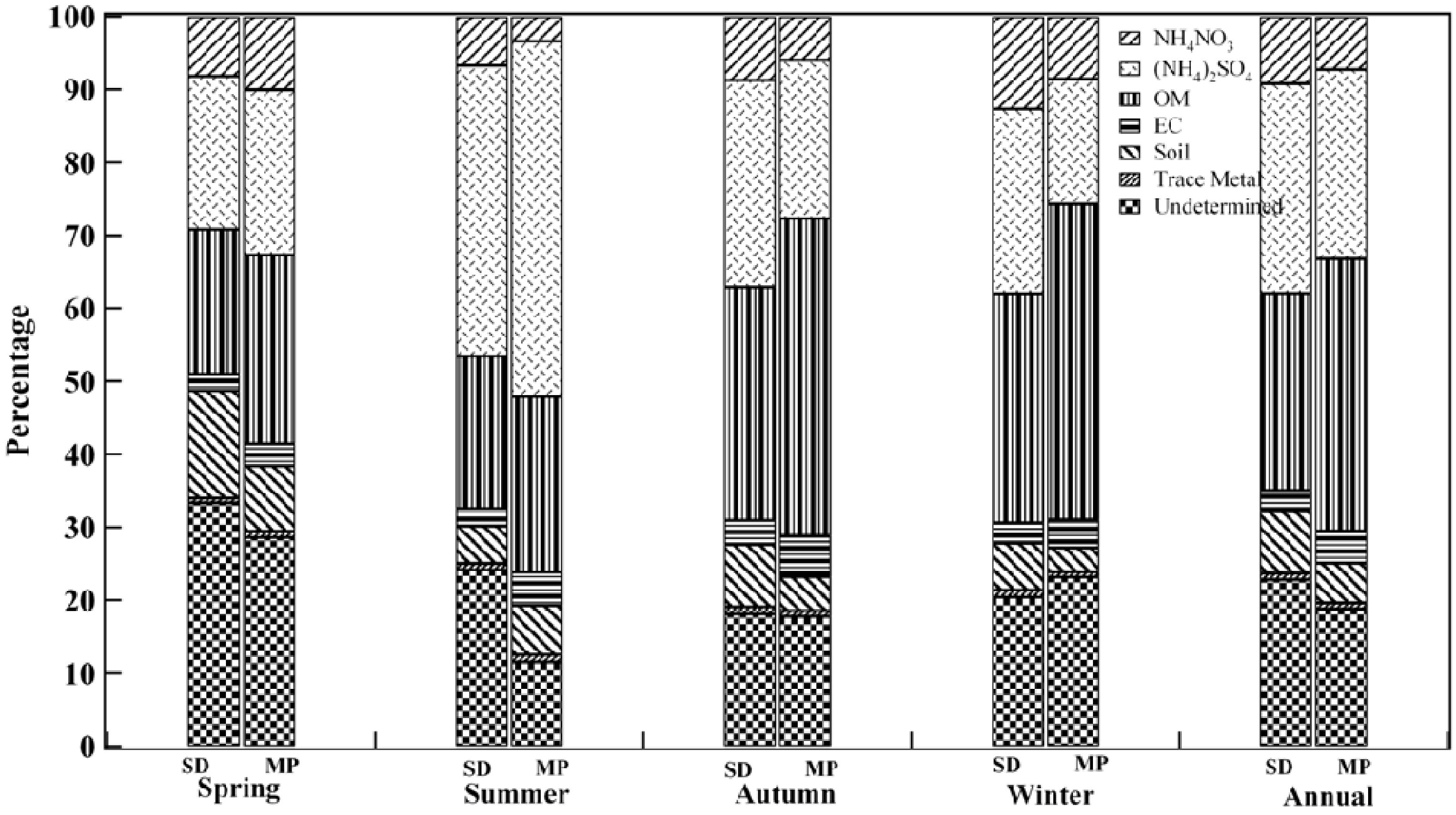

Fig. 6 Annual and seasonal contributions of chemical species to $PM_{2.5}$ mass concentrations in Jinan

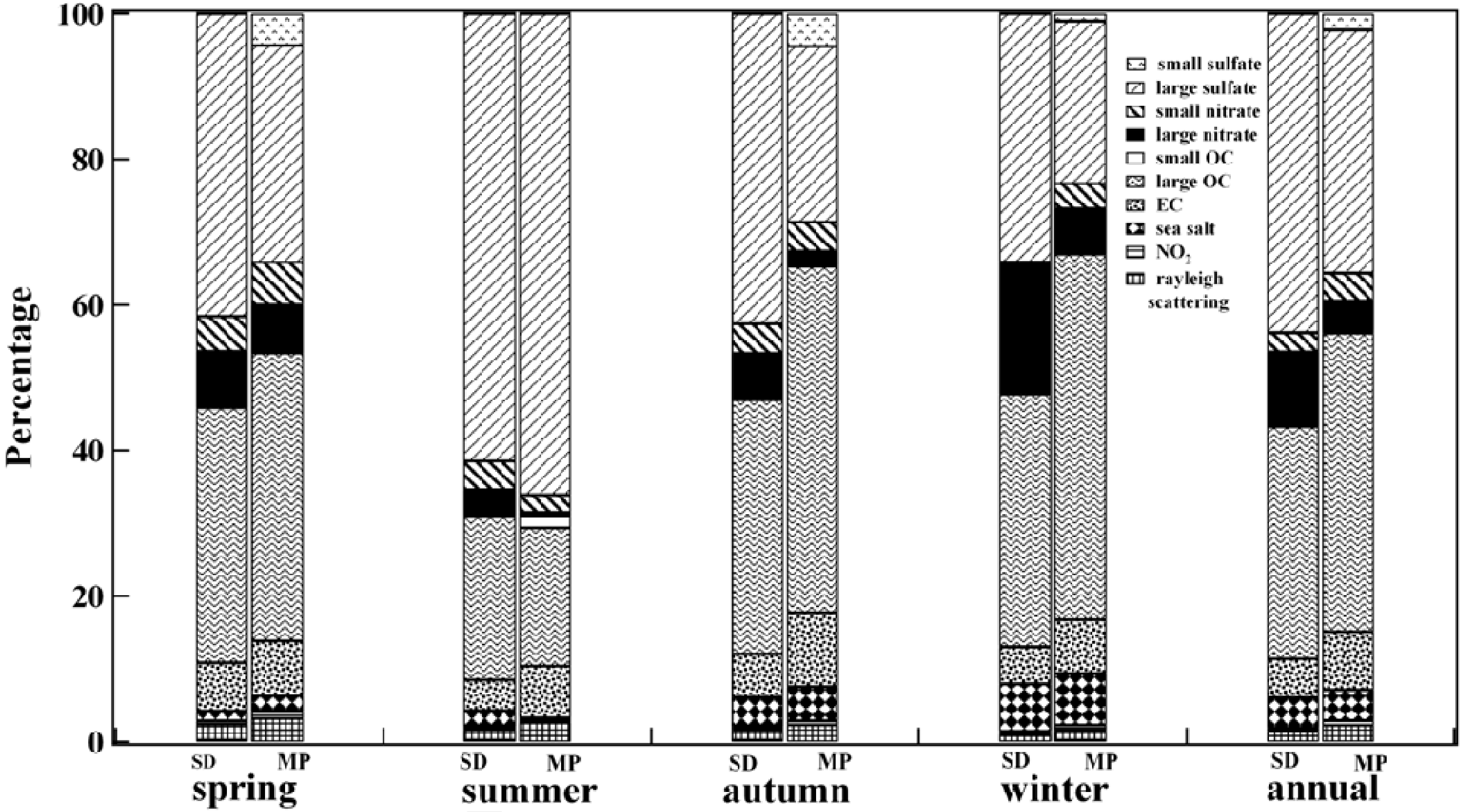

Fig. 7 Annual and seasonal contributions of chemical components in $PM_{2.5}$ to the light extinction coefficient in Jinan