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Characteristics of concentrations and chemical compositions for $PM_{2.5}$ in the region of Beijing, Tianjin, and Hebei, China

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Abstract

In order to study the temporal and spatial variations of $PM_{2.5}$ and its chemical compositions in the region of Beijing, Tianjin, and Hebei (BTH), $PM_{2.5}$ samples were collected at four urban sites in Beijing (BJ), Tianjin (TJ), Shijiazhuang (SJZ), and Chengde (CD) and one site at Shangdianzi (SDZ) regional background station over four seasons from 2009 to 2010. The samples were weighted for mass concentrations and analyzed in laboratory for chemical profiles of 19 elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, Sr, Ti, V, and Zn), eight water-soluble ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}), and carbon fractions (OC and EC). The concentrations of $PM_{2.5}$ and its major chemical species were season-dependent and showed spatially similar characteristics in the plain area of BTH. The average annual concentrations of $PM_{2.5}$ were 71.8–191.2 µg m^{-3} at five sites, with more than 90 % sampling days exceeded 50 µg m^{-3} at BJ, TJ, and SJZ. $PM_{2.5}$ pollution was most serious at SJZ, and the annual concentrations of $PM_{2.5}$, secondary ions, OC, EC, and most of crustal elements were all highest. Due to stronger photochemical oxidation, the sum of concentrations of secondary ions (NH_4^+, NO_3^-, and SO_4^{2-}) was highest in the summer at SDZ, BJ, TJ, and CD. Analysis of electric charges of water-soluble ions indicated the existence of nitric acid or hydrochloric acid in $PM_{2.5}$. For all five sites, the concentrations of OC, EC and also secondary organic carbon (SOC) in the spring and summer were lower than those in the autumn and winter. Stable atmosphere and low temperatures appearing more frequently during autumn and winter facilitated the formation of SOC. The sums of crustal elements (Al, Ca, Fe, Mg, Ti, Ba, and Sr) were higher in the spring and autumn owing to more days with blowing or floating dust. The concentrations of heavy metals were at higher levels in the BTH area by comparison with other studies. In Shijiazhuang and Chengde, the $PM_{2.5}$ pollution was dominated by coal combustion. Motor vehicle exhausts and coal combustion emissions both played important role in Tianjin $PM_{2.5}$ pollution. However, motor vehicle exhausts had played more important role in Beijing owing to the reduction of coal consumption and sharply increase of cars in re-

cent years. At SDZ, regional transportation of air pollutants from southern urban areas was significant.

1 Introduction

The region of Beijing, Tianjin, and Hebei (BTH) is one of the important city agglomerations in China, accounting for 10.9 % of national GDP and 7.8 % of national population in 2010. As result of economic development, the structures of air pollution sources and fuel consumption have always been changing. At present, coal is still the primary fuel in most areas of BTH and widely used for industrial processes and daily life, and more coal is combusted for heating in the winter. However, coal has been gradually being replaced by natural gas and electricity in urban areas of Beijing since 1999 (Beijing Environmental Protection Bureau, 2011). The total amount of motor vehicles for BTH was from 2.56 million in 2000 to 11.01 million in 2010. Owing to direct emissions from motor vehicles and secondary formation by photochemical reaction, more polluted and hazy days resulted from reactive gas and fine particle have appeared and become increasingly conspicuous. In many urban areas of BTH, more than 100 days per year were in haze and the annual average visibility was lower than 15 km in recent years (Zhao et al., 2011, 2012). The average number concentration of particles less than 1000 nm could reach to 30 000 cm^{-3} in urban area of Beijing, which were much higher than that in some foreign studies (Wu et al., 2008). Scattering effect of fine particles is the most important influence factor for visibility, and the scattering coefficients of aerosols accounted for more than 85 % of extinction coefficients in Beijing and around areas (Yan et al., 2008; Garland et al., 2009; Ma et al., 2011). Several studies of aerosol health effects carried out in Beijing have also revealed the relationships between fine particle pollution and morbidity and mortality (Zhang et al., 2000; Guo et al., 2009; Kipen et al., 2010; Wu et al., 2010).

New National Ambient Air Quality Standard was issued on February 2012, and the standard for $PM_{2.5}$ will not be implemented until 2016. So data for $PM_{2.5}$ concentration and composition could not be systematically acquired in most parts of China by now. In China, studies for $PM_{2.5}$ have been gradually carried out since 2000, and mainly focused on the urban areas of the Pearl River Delta, the Yangtze River Delta, and the BTH region. In BTH, most of the related studies about $PM_{2.5}$ chemical compositions have been carried out in Beijing. Some studies gave the general characteristics of $PM_{2.5}$ chemical compositions and discussed their seasonal variations, correlations, or sources (He et al., 2001; Sun et al., 2004; Song et al., 2006). Some studies focused on the concentrations, correlations, sources or formation of some specific species (such as inorganic ions, carbonaceous components, or organic matters) in $PM_{2.5}$ of Beijing (Yao et al., 2002; Dan et al., 2004; Huang et al., 2006; Wang et al., 2009; Ianniello et al., 2011). In addition, the size distributions of aerosol chemical species (Yao et al., 2003; Cheng et al., 2009; Guo et al., 2010; Li et al., 2012), aerosol number concentrations or new particle formation processes (Wu et al., 2007, 2008; Yue et al., 2009, 2011; Shen et al., 2011; Gao et al., 2012) and aerosol optical characteristics or mixing state (Cheng et al., 2009; Deng et al., 2011; Ma et al., 2011, 2012; Chen et al., 2011) were also discussed for Beijing and surrounding region.

$PM_{2.5}$ or fine particles have been systematically analyzed in many studies in Beijing. But $PM_{2.5}$ has seldom been spontaneously sampled and chemically analyzed at several sites in different regions of BTH. Related published data for $PM_{2.5}$ in urban areas of Tianjin and Hebei are lacking. There are no overall analyses for $PM_{2.5}$ chemical compositions for the region of BTH yet. To better control the regional aerosol pollution and carry out some further related studies in BTH, obtaining the information of regional $PM_{2.5}$ concentrations and their chemical compositions and knowing their spatial and temporal variations are quite necessary. So $PM_{2.5}$ was sampled at five sites in BTH over four seasons. The main objectives of this paper are to: (1) characterize spatial and seasonal concentration variations for $PM_{2.5}$ and its chemical compositions, (2) study the interrelations between different compositions, (3) evaluate primary and secondary sources of $PM_{2.5}$, and (4) analyze variations of $PM_{2.5}$ chemical compositions in Beijing in recent years.

The reactive gases (NO, NO_2, SO_2, O_3, CO), light scattering and absorption, and meteorological parameters were also measured at some sites. The further analysis about sources, chemical composition variations, formation processes, optical characteristics or transportations for $PM_{2.5}$ in different pollution episodes will be discussed in other papers.

2 Sampling and analysis

2.1 Sampling sites and meteorological conditions

As shown in Fig. 1, five sites were selected in the BTH area. Beijing and Tianjin are two municipalities that are directly administrated by the central government and are surrounded by Hebei province. Shijiazhuang is the capital of Hebei. Beijing, Tianjin, and Hebei are located in the North China Plain. Shangdianzi is a regional background station of atmospheric compositions used as the representative site of North China Plain, which is 100 km northeast to the urban area of Beijing and located in the boundary of plain area. It is also one of the Global Atmosphere Watch (GAW) stations, and the detailed instructions for Shangdianzi had been previously reported (Zhao et al., 2009). Chengde is one city located in the northern mountainous area of Hebei. Four sites were separately located in the urban area of Beijing, Tianjin, Shijiazhuang, and Chengde, and all placed on the roofs of local meteorological bureaus. Another sampling site was set at Shangdianzi. In this paper, the sampling sites for Shangdianzi, Beijing, Tianjin, Shijiazhuang, and Chengde are abbreviated as SDZ, BJ, TJ, SJZ, and CD.

The seasonal wind roses of five sites during all four sampling periods are depicted in Fig. 2, and the corresponding calm wind frequencies are listed in Table 1. The prevailing wind directions at SDZ, BJ, and SJZ were all dominated by the nearby topography, and wind directions at CD were closely related to the direction of urban valley area surrounded by mountains. The wind directions in TJ were influenced by land and sea breeze (Fig. 1). In the BTH area, wind is mainly from the south in the summer and from the north in the winter. The topography not only governs the wind directions, but also decides the regional transportation of air pollutants. The average values of temperature, relative humidity, wind speed, and observed visibility for four sampling periods at five sites were also listed in Table 1 (the dates of four sampling periods, see Sect. 2.2). The meteorological conditions was similar in the BTH area; for all four seasons, temperature ranked in the order of CD < SDZ < BJ < TJ < SJZ, wind speed was lowest at SJZ, and visibility was lowest at TJ; for all five sites, temperature ranked in the order of winter < autumn < spring < summer, relative humidity was highest and visibility was lowest in the summer, wind speed was highest in the spring, and calm wind was most frequent in the autumn.

2.2 Sample collection and chemical analysis

Aerosols sampling were performed in spring (6 April to 1 May 2009), summer (9 July to 4 August 2009), autumn (11 October to 4 November 2009) and winter (14 January to 8 February 2010). $PM_{2.5}$ was sampled from 09:00 a.m. to next 08:00 a.m. each day. Owing to precipitation or occasional sampler instability, more than 25 days were taken to assure at least 20 valid samples for each period at each site. Two parallel medium-volume samplers (TH-150A, $100\,\mathrm{L\,min^{-1}}$) were used at each site for collecting $PM_{2.5}$ on 90 mm polypropylene filters and quartz fiber filters. Polypropylene filters were used for analysis of inorganic elements. Quartz fiber filters were used for carbon and water-soluble ions components,

Each polypropylene filter was cut into fragments and put into a conical flask. Then 16 mL HNO_3 and 4 mL $HClO_4$ were added into the flask and heated by an electric stove until there was ∼ 3 mL residual left. After cooling, the solution was filtered and decanted into a test tube and diluted to 15 mL with ultrapure water. Then an ICP-AES (ULTIMA, JY) was used for analysis of 19 elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, Sr, Ti, V, and Zn).

A 1/4 piece of each quartz fiber filter was put into a glass tube and 10 mL de-ionized water was added. After 15 min ultrasonic bath at room temperature, the solution was drawn into a 5 mL syringe, filtered by a syringe filter, and injected into a polymeric vial with filter cap. The polymeric vials were put into a Dionex AS-DV Autosamplers and analyzed by an ion chromatography (ICS-1000, DIONEX) for water-soluble ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}).

A 0.5 cm^2 punch from each quartz fiber filter was analyzed by a thermal optical carbon analyzer (DRI-2001A) for eight carbon fractions, following the IMPROVE_A protocol (Chow et al., 1993, 2001, 2007).

2.3 Quality control

Quartz-fiber filters were all baked at 800 °C for 3 h prior to sampling to remove adsorbed organic vapors; and polypropylene filters were also heated at 80 °C for 2 h to remove volatile materials. Before and after sampling, the filters were weighed after equilibrated for at least 24 h in a desiccator. All the samples were stored in a refrigerator under 3 °C and analyzed for chemical species in less than a month. Compared with quartz fiber filter, polypropylene filters have higher moisture sensitivity and lower collection efficiency (over 90 % of $PM_{2.5}$ mass by quartz fiber filters for most polypropylene filters). So the $PM_{2.5}$ concentrations were from gravimetric analysis of quartz fiber filters. The concentrations of all species were calculated by mass divided by sampling air flows.

Adsorption of gases and vapors from the airstream will lead to positive artifacts for measurements of sulfates, nitrates, and organic compounds; evaporation of sulfates, nitrates, and organic compounds into the passing airstream will lead to negative artifacts. The artifacts were often estimated by a field blank filter or a collocated filter placed behind the sampling filter. For quartz fiber filters, positive and negative biases of organic gases had been found to approximately cancel each other under some circumstances (Watson and Chow, 2002; Eatough et al., 2003). Different batches of quartz-fiber filters may also have different equilibrium properties for organic gases (Kirchstetter et al.,

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2001). So the artifacts of organic matter were not taken into account when calculating the concentrations of carbon fractions. The quartz fiber filters used in this study had lower alkalinity (less than 25 µeq g^{-1}), so the adsorption artifacts of oxides of nitrogen and nitric acid could be essentially eliminated. The volatilization lost of NH_4NO_3 from filter has been found during sampling, especially during the warm mouths and during the warmest periods of the day (Zhang and McMurry, 1992; Ashbaugh and Eldred, 2004; Chow et al., 2005). Because of the limitation of sampler, the volatilized nitrate and volatilized ammonium were difficult to predict and estimate. The NO_3^- concentrations in this paper all represented non-volatilized parts of nitrate.

Some materials can be dissolved into the solution during pre-treatment of laboratory analysis, such as extraction, digestion, filtration, or injection. For example, we found that the glass tube for extraction dissolved out small amounts of Na^+ and the syringe filters for solution filtration also had Na^+ and SO_4^{2-} leaching. Thus, over two blank filters were also analyzed when analyzing each set of samples (samples for one season at one site) following the same procedures for both of inorganic elements and water-soluble ions analysis. And the blank concentrations of inorganic elements and water-soluble ions were subtracted to get actual concentrations. The detection limits for inorganic elements and water-soluble ions were determined by the three times of standard deviation of over 20 analyses of pure solvent used for extraction. The actual concentrations of each inorganic element or water-soluble ion in valid samples were all much higher than the detection limit and the standard variation of blank concentrations. After baked at 800 °C, the residual carbon on the quartz fiber filters was negligible, and the detection limits for OC and EC were three times of standard deviation of over 20 pre-baked blank filter analyses.

3 Results and discussions

3.1 $PM_{2.5}$ concentrations

The $PM_{2.5}$ concentrations for all the samples at five sites (Fig. 3) show similar fluctuations. The annual average concentrations were 71.8–191.2 µg m^{-3}, ranked in order as SDZ < CD < BJ < TJ < SJZ. The annual concentrations exceeded 100 µg m^{-3} at BJ, TJ, and SJZ. SDZ is a background station without significant pollution sources within 30 km of the site. However, the $PM_{2.5}$ concentration at SDZ was still high, mainly owing to the regional transportation from southern urban area. According to our $PM_{2.5}$ continuous monitoring data, the $PM_{2.5}$ concentrations were quite higher when blowing southwest wind than the moment when blowing wind from other directions at SDZ and also at BJ (Zhao et al., 2009). The distributions of $PM_{2.5}$ concentrations at five sites (Fig. 4) also show that the $PM_{2.5}$ pollution was quite severe in the BTH area. The $PM_{2.5}$ concentrations exceeded 50 µg m^{-3} in more than 90 % sampling days at BJ, TJ, and SJZ, and even exceeded 100 µg m^{-3} in more than 88 % sampling days at SJZ.

There was a four days heavy pollution episode from 16 to 19 January 2010, with a higher degree of atmospheric stability, a high level of $PM_{2.5}$, and lower visibility. However, $PM_{2.5}$ was only sampled at SJZ on 19 January because of problems with the sampler. At four urban sites, the maximum concentrations during four seasons all appeared in this pollution episode. The $PM_{2.5}$ concentration on 19 January reached 759.6 µg m^{-3} at SJZ. According to the winter concentration trends in Fig. 3, the maximum concentration would be higher and the winter average concentration could reach about 300 µg m^{-3} at SJZ if all samples were obtained during this episode.

At SDZ, new particle formation events occurred most frequently in the spring and the number concentrations were also highest for nucleation mode, Aitken mode, and accumulation mode (Shen et al., 2011). In addition, more windy days and large tracts of bare land caused more contribution of fugitive dust in the spring. So the maximum concentration appeared and the seasonal concentration was also highest in the spring.

In the winter, more particles were emitted from coal combustion for heating, thus the seasonal $PM_{2.5}$ concentrations at SJZ and CD were highest in the winter. $PM_{2.5}$ was relatively stable for BJ in all four seasons, because the energy used for heating and industrial processes were mainly electricity and natural gas except for limited residential coal consumption in the urban areas of Beijing. The finding that $PM_{2.5}$ at TJ was highest in the summer is unexpected and was attributed to the summer having more days with a stable atmosphere and higher concentrations of secondary ions (see Sect. 3.2.2).

3.2 Chemical compositions

3.2.1 Spatial concentration variations

The annual average concentrations of $PM_{2.5}$ species and seasonal average concentrations of major components therein at all five sites are listed in Tables 2 and 3, respectively. We calculated the correlation coefficients among all chemical species of samples from all four seasons at each site. Inorganic elements of Al, Ca, Fe, Mg, Ti, Ba, and Sr had strong correlations (mostly more than 0.80) with each other at each site, reflecting the common crustal sources. The NH_4^+, NO_3^-, and SO_4^{2-} in atmosphere were basically formed by a gas-to-particle process as a result of chemical reactions of precursor gases (Seinfeld and Pandis, 2006; Guo et al., 2010; Ianniello et al., 2011), so we call them "secondary ions" in this paper.

In Shijiazhuang, a great deal of coal was combusted every year for industrial processes and daily life, the amount of cars had increased rapidly year by year, and a lot of buildings were under construction or demolition during sampling periods. The average wind speed was also lowest at SJZ. All of these conditions above made the aerosol pollution in Shijiazhuang become worrying, and the annual concentrations of secondary ions, OC, EC, and most of crustal elements at SJZ were highest for all five sites.

At SDZ, the annual concentrations of $PM_{2.5}$, crustal elements, OC, and EC were lowest, but the annual concentrations of NH_4^+, NO_3^-, and SO_4^{2-} were higher than at CD. According to the prevailing wind directions of BJ and SDZ, the regional transportation of aerosol from southern urban areas to SDZ should not be discounted. The level of O_3, which is the most important photochemical oxidant, was higher at SDZ than at BJ (Liu et al., 2008). Except for the regional transportation, the higher O_3 level could also facilitate the formation of secondary ions at SDZ by photochemical oxidation of reactive gases.

The annual average OC and EC concentrations were both in the order of SDZ < BJ < TJ < CD < SJZ at all five sites. The levels of OC and EC at CD were even slightly higher than at BJ and TJ mainly owing to the simpler energy and pollution structure dominated by coal combustion. The annual OC/EC in $PM_{2.5}$ was relatively consistent in BTH, 2.56–2.87 at each site.

The annual average concentrations of crustal elements (Al, Ca, Fe, Mg, Ti, Ba, and Sr) were 2.87–8.27 $\mu g\,m^{-3}$ at five sites, only accounting for 4.0–5.1 % of $PM_{2.5}$ mass. Crustal elements were mainly from fugitive dust influenced by overall level of urban sanitation, greening cover, human earthmoving activities, and dust control.

3.2.2 Secondary ions

For environments with an abundant of NH_3, NH_4HSO_4 and $(NH_4)_2SO_4$ are sequentially generated. And the fine particulate SO_4^{2-} is not volatile. Ammonium nitrate is often formed in areas with high ammonia and nitric acid concentrations and low sulfate concentrations (Seinfeld and Pandis, 2006). Secondary ions (NH_4^+, NO_3^-, and SO_4^{2-}) were major components of $PM_{2.5}$ in BTH, which comprise 24–43 % of annual average $PM_{2.5}$ mass at five sites. The mass ratios of secondary ions to $PM_{2.5}$ were all highest in the summer (42–61 % of summer $PM_{2.5}$) (Fig. 5). At each site, the NH_4^+ and SO_4^{2-} had similar seasonal trends and highest concentrations in the summer (Table 3). In the BTH area, the correlation coefficients (CCs) between NH_4^+ and SO_4^{2-} were obviously

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higher than CCs between NH_4^+ and NO_3^- and CCs between NO_3^- and SO_4^{2-} (Table 4). It means sulfate had been better neutralized by NH_4^+ on the filters. The SO_4^{2-} in the summer was evidently higher than NO_3^- and also much higher than SO_4^{2-} in other seasons at each site. However, SO_2 was usually lowest in the summer; not only because of less fuel combustion but also owing to the highest conversion rate of SO_2 to SO_4^{2-} resulted from the strongest photochemical oxidation in the summer (Table 5). Besides, the mean concentration of NH_3 in summer period of Beijing was several times higher than in the other period (Ianniello et al., 2010), and the better thermal stability of sulfate also facilitated the accumulation of SO_4^{2-}. The NO_3^- concentrations had not evidently fluctuated as SO_4^{2-}. Nitrate is more sensitive to temperature, and higher temperature does not favor the formation of nitrate. According to previous studies in Beijing, a large portion of nitrate, chloride, and ammonium could evaporate from the filters, especially in the summer (Ianniello et al., 2011).

The annual averages of NO_3^-/SO_4^{2-} were 0.89, 1.07, 0.75, 0.85, and 0.45 for SDZ, BJ, TJ, SJZ, and CD, respectively. The lowest NO_3^-/SO_4^{2-} at CD could also reflect the dominated coal combustion sources for particles. Higher NO_3^-/SO_4^{2-} at BJ and SDZ depicted that more fractions of particles resulted from motor vehicle exhaust.

In some studies, all NO_3^- and SO_4^{2-} were assumed to be in the form of NH_4NO_3 and $(NH_4)_2SO_4$ (or NH_4HSO_4) and the calculated and measured NH_4^+ agreed well (DeBell et al., 2006; Louie et al., 2005). We also calculated the molar concentrations of positive electric charges of NH_4^+ ($PEC = NH_4^+/18$) and negative electric charges of NO_3^- and SO_4^{2-} ($NEC = NO_3^-/62 + SO_4^{2-}/96 \times 2$). If all SO_4^{2-} was assumed to be in the form of HSO_4^-, then $NEC = (NO_3^-/62 + SO_4^{2-}/96)$. At five sites, the correlations between PEC and NEC were significant. The seasonal average PEC and NEC at five sites were depicted in Fig. 6. Except for autumn and winter season at CD, NH_4^+ was far from enough to match NO_3^- and SO_4^{2-} in all four seasons at each site. However, the sum of positive electric charges of all analyzed cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) well balanced the negative charges of SO_4^{2-} in most cases. It indicated the existence of acid. As mentioned above, the dissociation of NH_4NO_3 and NH_4Cl probably resulted in some residue of HNO_3 and HCl on the filters.

3.2.3 Carbonaceous components

The carbonaceous aerosol pollution exhibited obvious seasonal characteristics. For all five sites, the OC and EC concentrations in the spring and summer were lower than those in the autumn and winter (Fig. 7). The seasonal fluctuations in the level of OC and EC reflected more aerosol was emitted from more fuel combustion for heating in the winter. In the winter, SJZ had the highest seasonal OC concentration (47.2 $\mu g\,m^{-3}$) and CD had the highest seasonal EC concentration (13.1 $\mu g\,m^{-3}$) for five sites. As mentioned above, the OC and EC concentrations would be much higher in the winter at SJZ if all samples were obtained during that heavy pollution episode. Similar with seasonal trends of OC and EC, the OC/EC values were also lowest in the summer and higher in the spring and autumn at each site and highest in the winter at every site except CD.

In this study, an EC tracer method was used to calculate the seasonal concentrations of secondary organic carbon (SOC) (Turpin and Huntzicker, 1995; Castro et al., 1999; Cao et al., 2004, 2007). The seasonal SOC concentrations and SOC/OC are listed in Table 6. Similarly to OC and EC, SOC and POC (OC-SOC) concentrations were also higher in the autumn and winter and lowest in the summer. However, SOC increased more times than POC during the winter. In the study of Cao (2007), the SOC concentrations were also higher in the winter for several northern Chinese cities. Compared with secondary ions, the levels of SOC showed opposite seasonal trends. Secondary ions are most important products for nucleation by photochemical reactions, but measurements of freshly nucleated particle composition show that organic compounds are responsible for most growth in new particle formation events (Allan et al., 2006; Stolzenburg et al., 2005; Smith et al., 2008). In addition, there are more days with stable atmosphere and low temperatures during the autumn and winter, which can facilitate the accumulation of air pollutants and accelerate the condensation or adsorption of volatile organic compounds. A more detailed description of SOC calculation will be published in other paper.

3.2.4 Inorganic elements

The sums of crustal elements (Al, Ca, Fe, Mg, Ti, Ba, and Sr) were higher in the spring and autumn at SDZ, BJ, TJ, and SJZ and only higher in the spring at CD (Fig. 5). According to the recorded weather phenomena, there were two or three days with blowing or floating dust during spring and autumn sampling periods. The sampled aerosol was mainly soil particles from local or other place during those days.

Heavy metals can cause seriously bodily damage, especially to children (Fergusson, 1990). At present, there is not a concentration standard for heavy metals in ambient particulate matter. The annual or seasonal concentrations of heavy metal elements in $PM_{2.5}$ in some other studies are summarized in Table 7. By comparison, all analyzed heavy metals were evidently detected in urban areas of mainland China; the concentrations of heavy metals were at higher levels, even at SDZ background station. In the BTH area, BJ, TJ, and SJZ had higher heavy metals concentrations, and Zn, Pb, Mn, Cu, Cr, and As at five sites were all much higher than those in other studies. Except for the lowest concentrations in the summer, there was not common seasonal trend for each element at five sites.

Pb and Zn were most abundant heavy metals in $PM_{2.5}$ in the BTH area. The annual average concentrations of Pb plus Zn were 0.266–0.975 $\mu g\,m^{-3}$ at five sites, and were close to 1.0 $\mu g\,m^{-3}$ at TJ and SJZ. Pb had stronger correlations with Zn, K, and EC at each site (Table 8). Pb and Zn have always been found together from minerals to industrial productions and processes. EC is essentially a primary pollutant, and K is mainly from biomass burning and decomposition. The stronger correlations among Pb, Zn, and K indicate their common sources of metal processing and fuel or biomass combustion.

3.2.5 Temporal variations of Beijing $PM_{2.5}$ chemical compositions

$PM_{2.5}$ has been systematically studied in Beijing in some previous studies. The seasonal average concentrations of $PM_{2.5}$ chemical species of Beijing from two previous studies (He et al., 2001; Sun et al., 2004) were listed in Table 9. He et al. (2001) sampled $PM_{2.5}$ at two urban sites of Beijing (Chegongzhuang and Tsinghua) from 1999 to 2000. The Chegongzhuang site in study by He et al. (2001) and the BJ site in this study were only 2.4 km apart. The BNU site in study by Sun et al. (2004) was 6.4 km away from the BJ site in this study. So the $PM_{2.5}$ data of Chegongzhuang site in He et al. (2001) was more comparable with data of this study. Compared with studies of He (2001) and Sun (2004), the concentration levels of secondary ions and carbon components had significantly varied.

The annual concentration of SO_4^{2-} and NO_3^- increased from 14.47 and 10.3 $\mu g\,m^{-3}$ in study of He (2001) to 19.07 and 20.47 $\mu g\,m^{-3}$ in this study. The NO_3^- in all four seasons had evidently increased, reflecting the influences by NO_x emissions from sharply increased motor vehicles. The SO_4^{2-} in the spring and summer increased from 10.15 and 17.14 $\mu g\,m^{-3}$ to 16.42 and 33.76 $\mu g\,m^{-3}$, respectively. However, the SO_4^{2-} in the autumn and winter decreased from 12.55 and 24.87 $\mu g\,m^{-3}$ to 11.53 and 14.23 $\mu g\,m^{-3}$, respectively. The opposite seasonal trends of SO_4^{2-} show the evidences of the decreased coal consumption in the winter and the raised level of photochemical reaction in the summer over the past ten years. In addition, NH_4^+ and NO_3^- were also varied from lower in the summer and highest in the winter to lower in the winter and highest in the summer.

Compared with study by He (2001), the OC and EC concentrations in all four seasons have decreased. The ratio of winter concentration divided by summer concentration for EC decreased from 1.77 to 1.21. This decrease also indicates that aerosol emissions from coal combustion, especially from winter coal combustion for heating, were remarkably reduced in Beijing.

Compared with previous studies, the concentrations of Ca and Mg were about doubled and Mn, Ni, Pb, and Zn were lowered by one fourth to half as they were 10 yr ago.

4 Conclusions

The $PM_{2.5}$ pollution was severe in the BTH area, with average annual concentrations of 71.8–191.2 $\mu g\,m^{-3}$ at five sites. The $PM_{2.5}$ concentrations in more than 90 % sampling days exceeded 50 $\mu g\,m^{-3}$ at BJ, TJ, and SJZ. The meteorological condition and pollution sources that influenced aerosol pollution were season-dependent. Thus the concentrations of $PM_{2.5}$ and its major chemical species were also season-dependent and showed spatially similar characteristics in the plain area of BTH.

In Shijiazhuang and Chengde, the $PM_{2.5}$ pollution was dominated by coal combustion. The annual concentrations of secondary ions, OC, EC, and most of crustal elements at SJZ were highest for all five sites. Motor vehicle exhausts and coal combustion emissions both played important role in Tianjin $PM_{2.5}$ pollution. However, motor vehicle exhausts had played more important role in Beijing owing to the reduction of coal consumption and sharply increase of cars. At Shangdianzi background station, regional transportation of air pollutants from southern urban areas was significant.

The sum of concentrations of secondary ions (NH_4^+, NO_3^-, and SO_4^{2-}) was highest in the summer at SDZ, BJ, TJ, and CD, due to stronger photochemical oxidation. Except for autumn and winter season at CD, NH_4^+ was far from enough to match NO_3^- and SO_4^{2-} in all four seasons at each site. So nitric acid or hydrochloric acid probably existed in $PM_{2.5}$ on the filters.

For all five sites, the OC and EC concentrations in the spring and summer were lower than those in the autumn and winter, reflecting more aerosols emitted from fuel combustions for heating. Compared with secondary ions, the levels of SOC showed opposite seasonal variations. Because the stable atmosphere and low temperatures appearing more frequently during the autumn and winter could facilitate the accumulation of air pollutants and accelerate the condensation or adsorption of volatile organic compounds. The sums of crustal elements (Al, Ca, Fe, Mg, Ti, Ba, and Sr) were higher in the spring and autumn at SDZ, BJ, TJ, and SJZ and only higher in the spring at CD owing to more days with blowing or floating dust. The concentrations of heavy metals were at higher levels in the BTH area, even at SDZ background station. Pb and Zn were most abundant heavy metals in $PM_{2.5}$. Pb had stronger correlations with Zn, K, and EC at each site indicating their common sources of metal processing and fuel or biomass combustion.

Compared with results in studies of Beijing carried out ten years before, the concentrations of secondary ions had changed from highest in the winter to highest in the summer, and the levels of OC and EC in all four seasons had decreased. So the characteristics of aerosol pollution in Beijing have changed from simple type of coal combustion to complex type dominated by motor vehicle exhausts.

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Table 1. Seasonal meteorological conditions at five sampling sites.

Sites	Season	Temperature (°C)	Relative humidity (%)	Wind speed (m s^{-1})	Visibility (km)	Calm wind frequency (%)
SDZ	Spring	15.0	49.6	3.28	29.1	1.92 %
	Summer	24.7	77.2	2.44	19.8	3.86 %
	Autumn	9.5	53.0	2.37	30.5	4.83 %
	Winter	−6.3	47.1	2.38	34.9	3.69 %
BJ	Spring	17.0	51.5	2.31	17.8	1.12 %
	Summer	26.6	78.2	1.53	11.7	3.24 %
	Autumn	11.3	62.7	1.65	18.7	4.00 %
	Winter	−2.0	48.5	2.06	21.0	3.21 %
TJ	Spring	17.1	50.2	2.14	12.3	2.08 %
	Summer	27.3	70.4	1.47	8.0	3.55 %
	Autumn	13.4	52.1	1.53	12.1	10.33 %
	Winter	−1.0	49.7	1.52	11.9	4.97 %
SJZ	Spring	17.6	53.7	1.79	13.3	3.21 %
	Summer	27.4	73.1	1.44	10.7	1.54 %
	Autumn	14.1	56.8	1.37	12.8	7.00 %
	Winter	−0.2	47.2	1.25	10.9	4.49 %
CD	Spring	12.9	51.8	2.05	24.3	7.69 %
	Summer	23.6	75.8	1.63	21.6	6.48 %
	Autumn	6.7	60.7	1.76	24.1	17.00 %
	Winter	−9.7	54.5	1.44	24.8	8.65 %

Table 2. Annual averages concentrations of $PM_{2.5}$ species at each site (µg m^{-3}).

	SDZ	BJ	TJ	SJZ	CD
Mass	71.79 ± 47.51	123.45 ± 71.59	141.47 ± 78.03	191.19 ± 104.29	92.41 ± 54.62
NH_4^+	4.49 ± 3.70	6.37 ± 3.91	7.64 ± 4.27	9.33 ± 4.47	4.06 ± 2.70
NO_3^-	12.22 ± 14.29	20.47 ± 18.07	18.83 ± 15.77	30.38 ± 28.30	5.81 ± 7.31
SO_4^{2-}	13.75 ± 14.93	19.07 ± 16.36	24.97 ± 22.59	35.63 ± 23.00	13.00 ± 11.80
OC	10.78 ± 6.80	18.15 ± 13.84	18.81 ± 12.90	26.52 ± 21.68	18.98 ± 16.07
EC	3.87 ± 1.94	6.32 ± 2.93	6.86 ± 3.28	9.77 ± 4.81	7.41 ± 4.31
Al	0.57 ± 0.68	0.97 ± 1.23	1.17 ± 1.32	1.41 ± 1.62	0.75 ± 0.69
Ba	0.01 ± 0.01	0.02 ± 0.02	0.03 ± 0.02	0.04 ± 0.03	0.02 ± 0.02
Ca	1.09 ± 1.15	2.42 ± 3.00	3.28 ± 3.79	4.27 ± 5.60	1.63 ± 1.73
Fe	0.86 ± 0.77	1.49 ± 1.43	2.02 ± 1.70	1.84 ± 1.76	1.28 ± 1.00
Mg	0.32 ± 0.35	0.59 ± 0.70	0.69 ± 0.80	0.64 ± 0.72	0.38 ± 0.34
Sr	0.00 ± 0.00	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.02	0.02 ± 0.02
Ti	0.02 ± 0.02	0.04 ± 0.04	0.04 ± 0.04	0.04 ± 0.05	0.08 ± 0.10
As	0.01 ± 0.01	0.03 ± 0.05	0.02 ± 0.01	0.02 ± 0.02	0.01 ± 0.01
Cd	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.00 ± 0.00
Co	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Cr	0.04 ± 0.21	0.02 ± 0.12	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
Cu	0.02 ± 0.03	0.04 ± 0.03	0.14 ± 0.27	0.04 ± 0.04	0.02 ± 0.01
Mn	0.04 ± 0.03	0.07 ± 0.04	0.10 ± 0.07	0.12 ± 0.08	0.06 ± 0.05
Ni	0.01 ± 0.02	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.00
Pb	0.07 ± 0.07	0.14 ± 0.11	0.22 ± 0.14	0.30 ± 0.22	0.11 ± 0.08
V	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.01
Zn	0.20 ± 0.15	0.32 ± 0.24	0.75 ± 0.43	0.68 ± 0.47	0.28 ± 0.23
K	1.26 ± 1.09	1.73 ± 1.27	2.15 ± 1.35	3.42 ± 2.14	1.15 ± 0.91
P	0.06 ± 0.04	0.09 ± 0.07	0.10 ± 0.07	0.15 ± 0.09	0.11 ± 0.09
Cl^-	0.76 ± 1.06	2.92 ± 3.46	8.14 ± 6.10	8.69 ± 7.88	1.84 ± 1.93
Na^+	0.29 ± 0.14	0.53 ± 0.45	0.63 ± 0.30	0.69 ± 0.30	0.30 ± 0.17
K^+	1.19 ± 1.10	1.68 ± 1.29	2.08 ± 1.36	3.40 ± 2.14	1.10 ± 0.93
Mg^+	0.14 ± 0.11	0.18 ± 0.11	0.23 ± 0.13	0.25 ± 0.15	0.12 ± 0.10
Ca^{2+}	0.74 ± 0.68	1.55 ± 1.38	1.79 ± 1.44	2.62 ± 2.27	0.91 ± 0.71

Table 3. Seasonal average concentrations of major components at five sites ($\mu g\, m^{-3}$).

Species	SDZ				BJ				TJ				SJZ				CD			
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
NH_4^+	5.67	6.28	3.23	2.83	6.77	8.43	5.01	5.21	7.09	10.63	6.40	6.58	8.68	9.27	8.90	10.47	4.46	4.66	3.44	3.63
NO_3^-	16.48	12.41	11.20	8.84	20.35	22.76	21.54	17.09	18.75	21.09	20.11	15.48	26.46	24.93	46.01	25.30	11.02	4.62	2.55	5.20
SO_4^{2-}	15.73	24.17	8.68	6.64	16.42	33.76	11.53	14.23	20.64	42.71	15.82	21.33	28.89	42.53	37.96	33.24	13.29	19.60	9.21	9.42
OC	9.71	5.74	10.74	16.84	15.79	10.13	20.16	26.80	14.10	12.70	23.08	24.85	19.63	9.10	31.50	47.24	14.47	9.27	19.05	33.59
EC	3.85	3.34	3.89	4.41	5.17	5.90	7.06	7.14	5.65	5.90	8.81	6.99	7.83	7.94	11.41	12.17	4.86	4.63	7.18	13.09
Al	0.85	0.21	0.51	0.71	1.25	0.34	1.26	1.03	1.57	0.95	1.42	0.72	1.62	0.60	1.99	1.48	1.32	0.36	0.51	0.82
Ba	0.02	0.01	0.01	0.01	0.03	0.01	0.02	0.03	0.04	0.02	0.04	0.02	0.03	0.01	0.04	0.05	0.03	0.01	0.01	0.03
Ca	1.53	0.54	1.30	0.91	3.37	1.16	3.29	1.85	4.63	3.49	3.89	1.12	4.29	2.51	7.11	3.22	3.34	1.02	1.13	1.06
Fe	1.25	0.43	0.99	0.74	1.65	0.73	2.05	1.55	2.24	1.90	2.64	1.31	2.07	0.87	2.65	1.84	1.89	0.86	1.06	1.34
Mg	0.44	0.09	0.44	0.30	0.72	0.21	0.84	0.57	0.77	0.64	1.03	0.33	0.69	0.29	1.03	0.58	0.63	0.26	0.31	0.33
Sr	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.02	0.01	0.01	0.03
Ti	0.04	0.01	0.02	0.02	0.05	0.02	0.06	0.05	0.05	0.04	0.06	0.02	0.05	0.02	0.06	0.05	0.07	0.04	0.03	0.19
As	0.01	0.01	0.01	0.00	0.03	0.05	0.02	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.03	0.03	0.01	0.01	0.01	0.01
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.18	0.00	0.01	0.00	0.06	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cu	0.04	0.02	0.02	0.02	0.05	0.04	0.04	0.04	0.24	0.06	0.12	0.12	0.03	0.02	0.06	0.06	0.02	0.01	0.01	0.03
Mn	0.04	0.02	0.05	0.05	0.07	0.04	0.09	0.09	0.09	0.07	0.14	0.10	0.10	0.08	0.14	0.16	0.06	0.04	0.05	0.10
Ni	0.03	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00
Pb	0.07	0.06	0.08	0.06	0.14	0.13	0.15	0.15	0.23	0.19	0.23	0.23	0.22	0.22	0.32	0.43	0.09	0.07	0.11	0.17
V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01
Zn	0.19	0.18	0.25	0.19	0.34	0.38	0.27	0.30	0.85	0.70	0.71	0.73	0.50	0.63	0.77	0.81	0.27	0.11	0.33	0.39

Table 4. Correlation coefficients among NH_4^+, NO_3^-, and SO_4^{2-} at each site.

	SDZ		BJ		TJ		SJZ		CD	
	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}
SO_4^{2-}	0.754	–	0.730	–	0.787	–	0.799	–	0.635	–
NH_4^+	0.898	0.935	0.895	0.894	0.863	0.950	0.823	0.905	0.832	0.902

Table 5. Seasonal SO_2 concentrations for sampling periods at SDZ and BJ ($\mu g\,m^{-3}$).

	Spring	Summer	Autumn	Winter
SDZ	14.6	4.3	16.0	26.9
BJ	25.6	13.4	19.4	45.3

Table 6. Seasonal SOC concentrations and SOC/OC ratios by site.

	SDZ		BJ		TJ		SJZ		CD	
	SOC ($\mu g\,m^{-3}$)	SOC/OC (%)	SOC ($\mu g\,m^{-3}$)	SOC/OC (%)	SOC ($\mu g\,m^{-3}$)	SOC/OC (%)	SOC ($\mu g\,m^{-3}$)	SOC/OC (%)	SOC ($\mu g\,m^{-3}$)	SOC/OC (%)
Spring	1.80	18.5	2.55	16.2	3.74	26.5	5.81	29.6	2.31	16.0
Summer	0.69	12.0	2.15	21.2	2.75	21.7	1.56	17.2	1.17	12.7
Autumn	1.54	14.4	4.54	22.5	7.45	32.3	8.74	27.8	6.65	34.9
Winter	3.14	18.7	8.66	32.3	7.28	29.3	13.19	27.9	19.38	57.7

Table 7. Comparisons of heavy metal element concentrations in different studies* (µg m^{-3}).

			2009–2010^a			2000–2001		2000–2001	2000–2002	1998–1999	2005		2006
			(This study)			(Ho et al., 2003, 2006)		(Louie et al., 2005)	(Vega et al., 2004)	(Hueglin et al., 2005)	(Lv et al., 2007)		(Feng et al., 2008)
			Annual			Winter	Summer	Annual	Winter and spring	Annual	Spring	Summer	Autumn
	SDZ^b	BJ	TJ	SJZ	CD	HK-PolyU		HK-TW	Mexico	Zurich-Kaserne	Shanghai		Guangzhou
As	0.0111	0.0282	0.0181	0.0215	0.0107	0.00393	0.00153	0.006	0.01	0.00047	0.0058	0.0072	–
Cd	0.0015	0.0033	0.0039	0.0060	0.0039	–	–	0.0023	0.01	0.00031	–	–	0.0046
Co	0.0005	0.0009	0.0010	0.0009	0.0007	–	–	0.000	0	–	–	–	–
Cr	0.0423	0.0199	0.0134	0.0116	0.0075	0.00243	0.00083	0.001	0	–	0.0023	0.0019	–
Cu	0.0219	0.0443	0.1380	0.0412	0.0186	0.01732	0.01680	0.0089	0.05	0.0061	0.0172	0.0285	0.0554
Mn	0.0398	0.0726	0.1023	0.1171	0.0604	0.00996	–	0.012	0.02	0.0035	0.0104	0.0099	0.0673
Ni	0.0082	0.0075	0.0073	0.0065	0.0036	0.00534	–	0.0054	0.01	0.0031	0.0073	0.0063	0.0064
Pb	0.0694	0.1421	0.2205	0.2978	0.1107	0.07686	–	0.0718	0	0.021	0.0057	0.0120	0.2070
V	0.0020	0.0033	0.0049	0.0038	0.0092	0.00446	0.00977	0.014	0.03	0.0011	–	–	–
Zn	0.1966	0.3243	0.7462	0.6775	0.2783	0.28656	0.06229	0.1739	0.36	–	0.1566	0.1283	0.5376

* The significant figures of concentration values follow respective paper.

"–" represent element concentrations that were not analyzed or given.

[a] Sampling period.

[b] Sampling site.

Table 8. Correlation coefficients between Pb and Zn, Pb and K, and Pb and EC.

	SDZ			BJ			TJ			SJZ			CD		
	Zn	K	EC	Zn	K	EC	Zn	K	EC	Zn	K	EC	Zn	K	EC
Pb	0.891	0.901	0.729	0.874	0.798	0.738	0.823	0.866	0.720	0.887	0.793	0.905	0.879	0.773	0.725

Table 9. Seasonal concentrations of $PM_{2.5}$ chemical species for Beijing in previous studies ($\mu g\,m^{-3}$).

	Chegongzhuang (1999–2000)[a] (He et al., 2001)					BNU (2002–2003) (Sun et al., 2004)	
	Spring	Summer	Autumn	Winter	Annual	Summer	Winter
Mass	88.6	76.0	111.6	175.9	115	77.3	135.7
NH_4^+	4.28	5.70	4.91	7.80	6.22	10.4	12.9
NO_3^-	7.26	4.59	11.16	15.35	10.3	12.2	17.0
SO_4^{2-}	10.15	17.14	12.55	24.87	14.47	16.0	30.4
OC	18.21	13.42	28.79	31.49	21.5	11.5[b]	33.2
EC	6.67	6.27	10.23	11.08	8.7	5.2	11.0
Al	1.37	0.44	0.73	0.74	0.8	0.53	1.11
Ba	–	–	–	–		–	–
Ca	1.71	0.924	1.55	1.05	1.23	0.75	1.67
Fe	1.52	0.76	1.32	1.17	1.14	0.65	1.04
Mg	0.31	0.15	0.26	0.19	0.22	0.22	0.32
Sr	–	–	–	–		0.02	0.02
Ti	–	–	–	–		0.03	0.07
As	–	–	–	–		0.01	0.05
Cd	–	–	–	–		0.0037	0.0112
Co	–	–	–	–		0.0039	0.0036
Cr	–	–	–	–		0.02	0.02
Cu	0.028	0.022	0.032	0.051	0.035	0.04	0.08
Mn	0.09	0.075	0.14	0.10	0.097	0.03	0.08
Ni	0.004	0.009	0.001	0.003	0.015	0.06	0.08
Pb	0.26	0.22	0.28	0.40	0.304	0.11	0.31
V	–	–	–	–		0.0190	0.0025
Zn	0.425	0.343	0.511	0.612	0.48	–	–

[a] Sampling site and period.

[b] OC and EC in samples of BNU were analyzed by CHN elemental analyzer.

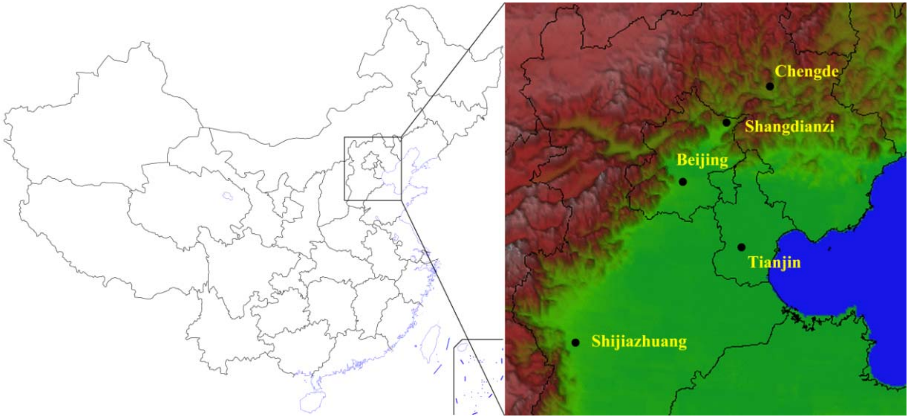

Fig. 1. Sampling sites of $PM_{2.5}$.

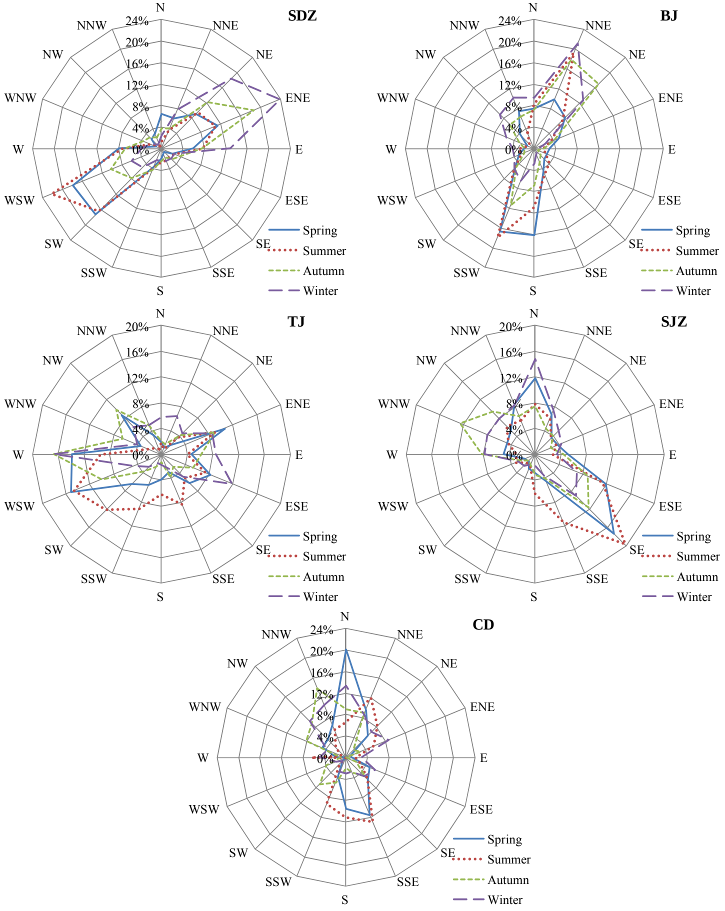

Fig. 2. Wind roses of all four sampling periods at each site.

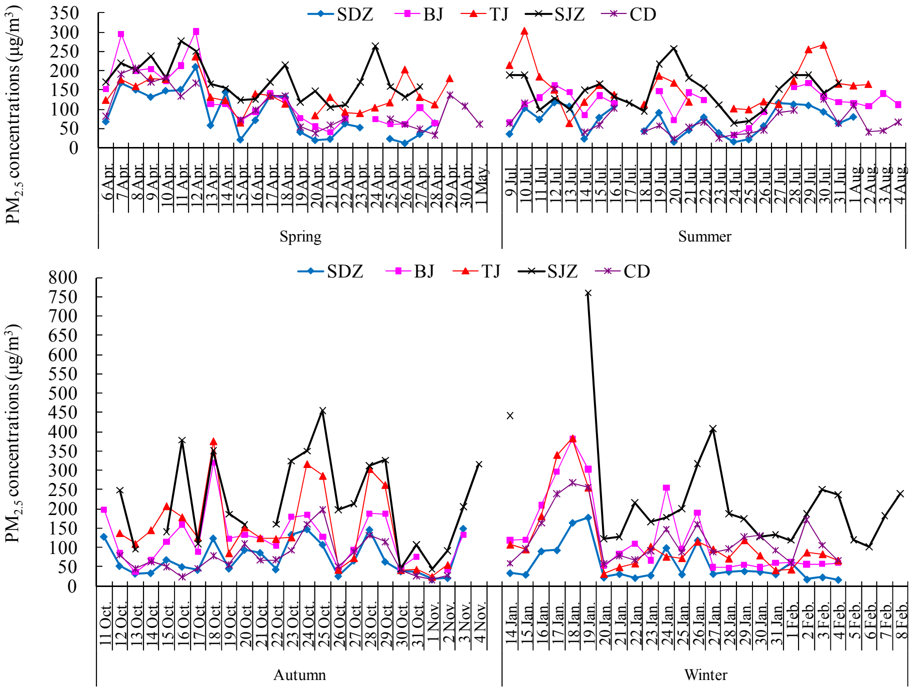

Fig. 3. PM$_{2.5}$ concentration time series at five sites.

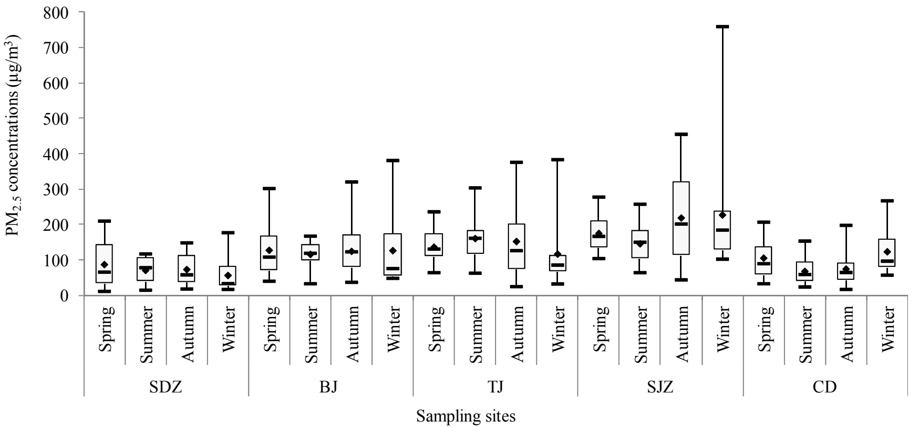

Fig. 4. Seasonal PM$_{2.5}$ concentrations at five sites. The boxes and whiskers denote the minimums, 25 percentiles, medians, 75 percentiles, and maximums, the dots denote the mean values.

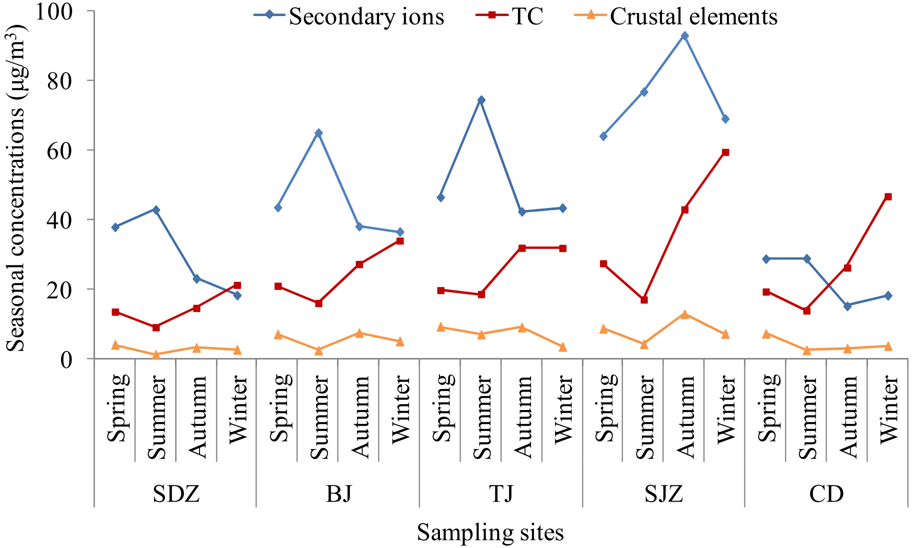

Fig. 5. Seasonal concentrations of secondary ions, TC, and crustal elements at five sites.

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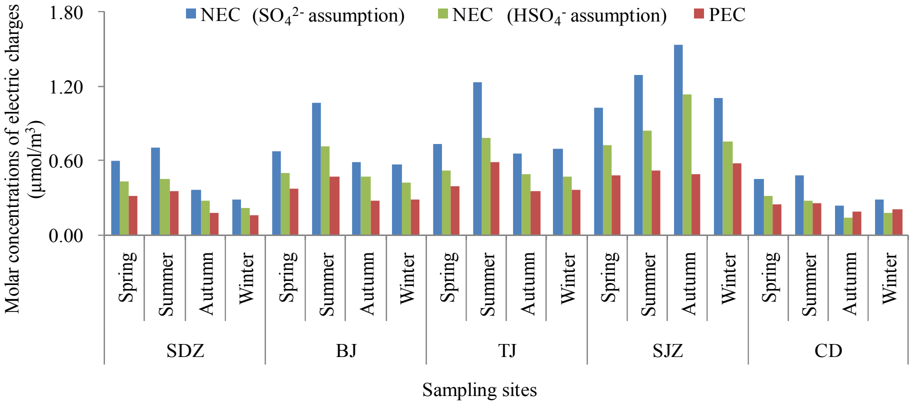

Fig. 6. Molar concentrations of positive electric charges of NH_4^+ (PEC) and negative electric charges of NO_3^- and SO_4^{2-} (NEC).

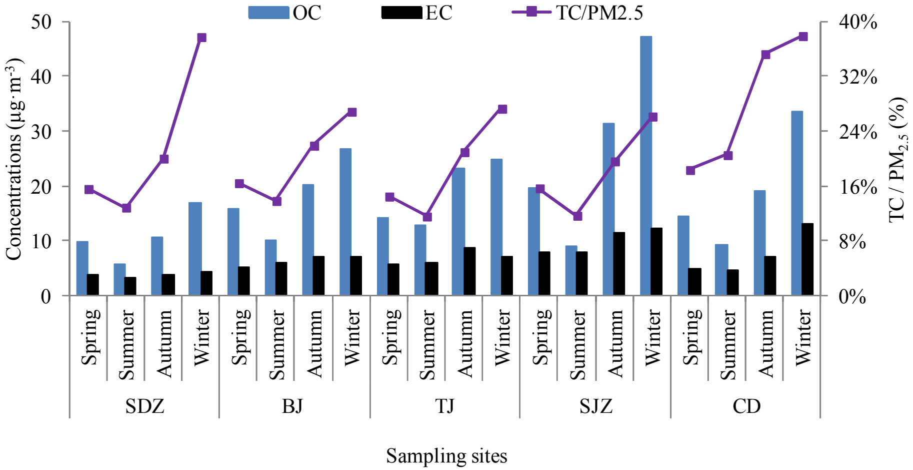

Fig. 7. Average seasonal concentrations of carbonaceous components and TC/$PM_{2.5}$ by study site.