



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 also 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 the 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 inorganic ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, and SO₄²⁻), 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 the five sites, with more than 90 % of sampling days exceeding 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 inorganic ions, OC, EC, and most crustal elements were all highest. Due to stronger photochemical oxidation, the sum of concentrations of secondary inorganic ions (NH₄⁺, NO₃⁻, and SO₄²⁻) was highest in the summer at SDZ, BJ, TJ, and CD. Analysis of electric charges of water-soluble inorganic 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. SOC had more percentages of increase than primary organic carbon (POC) during the winter. 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 roles in Tianjin PM_{2.5} pollution. However, motor vehicle exhausts had played a more important role in Beijing owing to the reduction of coal consumption and sharp increase of cars in recent 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 constantly 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 went 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 resulting from reactive gas and fine particle have appeared and become increasingly conspicuous. In many urban areas of BTH, more than 100 days per year have been in haze, and the annual average visibility has been lower than 15 km in recent years (Zhao et al., 2011, 2012). The average number concentration of particles less than 1000 nm could reach up to 30 000 cm⁻³ in the urban area of Beijing, which is much higher than that in some foreign studies (Wu et al., 2008). The 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 surrounding 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).

The new national ambient air quality standard was issued in February 2012. The standard for PM_{2.5} was first implemented in some key regions and cities in 2012, and will not be implemented nationwide 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 (Cao et al., 2004; Hagler et al., 2006; Duan et al., 2007; Liu et al., 2008), the Yangtze River Delta (Ye et al., 2003; Yang et al., 2005; Wang et al., 2008; Li et al., 2011), 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 have given 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 have focused on the concentrations, correlations, sources or formation of some specific species (such as inorganic ions, carbonaceous components, or organic matters) of PM_{2.5} in Beijing (Yao et al., 2002; Dan et al., 2004; Huang et al., 2006; Wang et al., 2009; Pathak 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; Zhang 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., 2012) have also been discussed for Beijing and the 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, it is quite necessary to obtain the information of regional PM_{2.5} concentrations and their chemical compositions, and also to know their spatial and temporal variations.

In this study, 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, NO₂, SO₂, O₃, 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 and 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 the North China Plain, which is 100 km northeast of the urban area of Beijing and located in the boundary of the 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 areas 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 the 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,

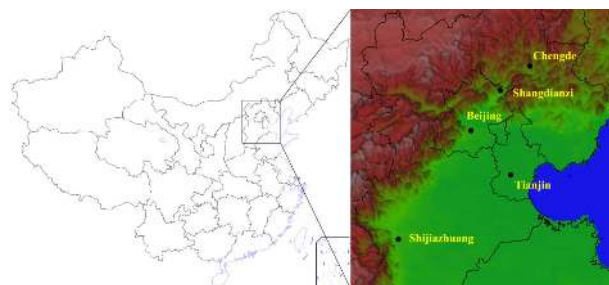
Table 1. Seasonal meteorological conditions at five sampling sites.

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 %

wind speed, and observed visibility for four sampling periods at the five sites were also listed in Table 1 (the dates of four sampling periods, see Sect. 2.2). The meteorological conditions were 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

Aerosol sampling was 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 each day from 09:00 to 08:00 the next 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 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 inorganic ion components.

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

Each polypropylene filter was cut into fragments and put into a conical flask. Then 16 mL of HNO₃ and 4 mL of HClO₄ 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 of de-ionized water was added. After a 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 Autosampler and

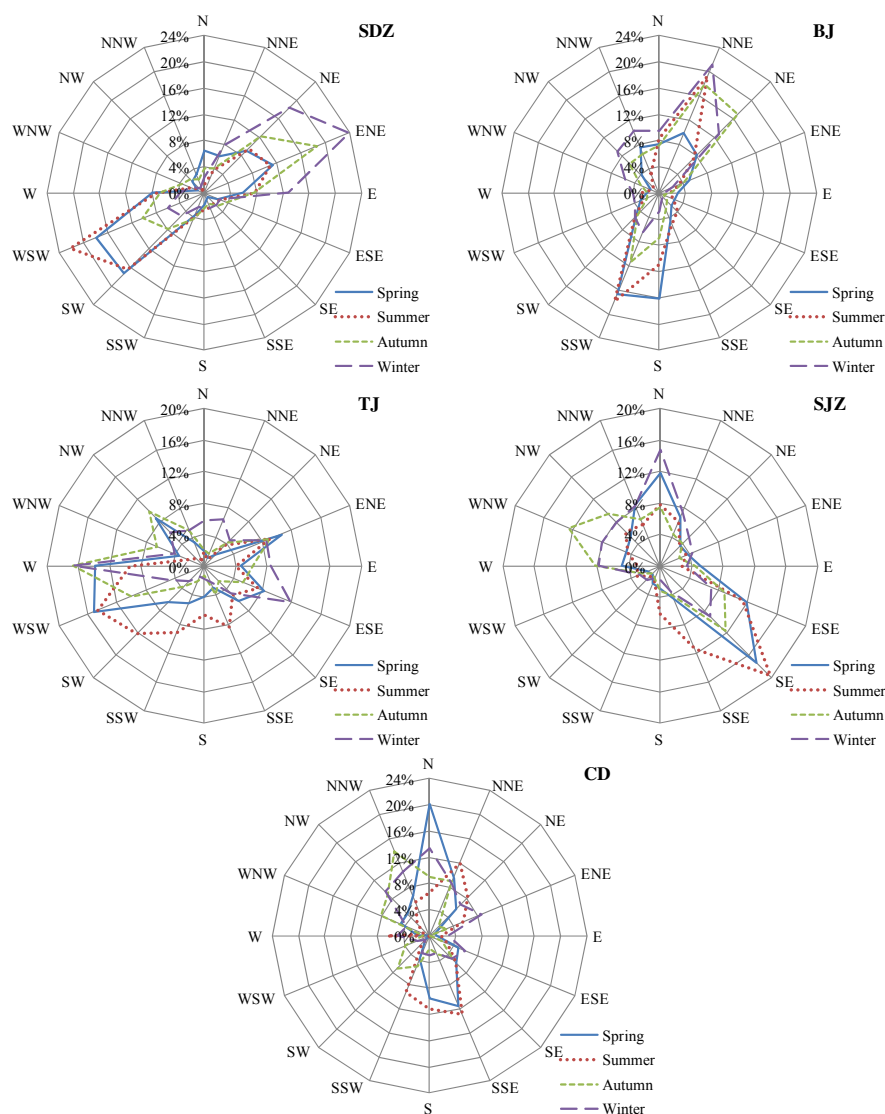


Fig. 2. Wind roses of all four sampling periods at each site.

analyzed by ion chromatography (ICS-1000, DIONEX) for water-soluble inorganic ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}).

A 0.5 cm² 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 being equilibrated for 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 filters, 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

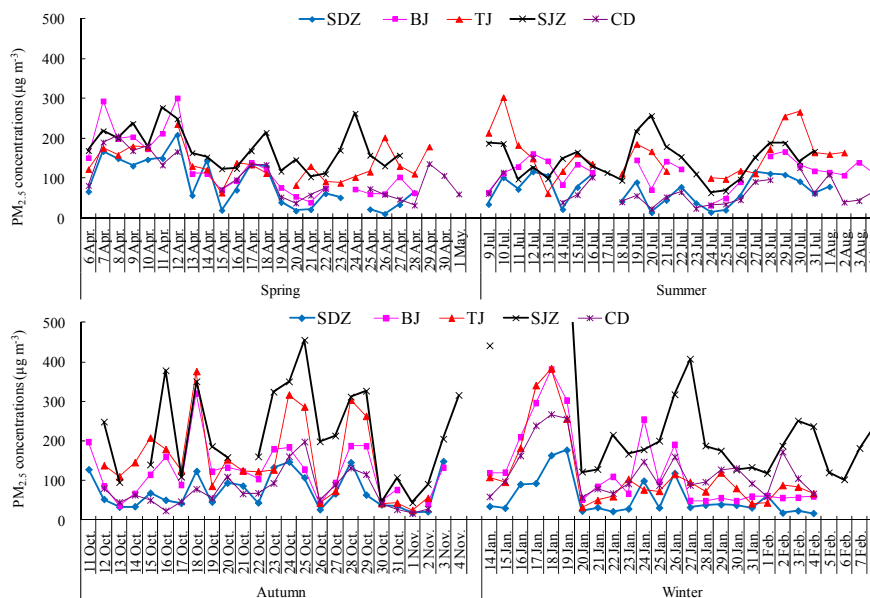


Fig. 3. PM_{2.5} concentration time series at the five sites. * 19 January for SJZ was 759.6 $\mu\text{g m}^{-3}$.

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., 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 $25 \mu\text{eq g}^{-1}$), so the adsorption artifacts of oxides of nitrogen and nitric acid could be essentially eliminated. Volatilization loss of NH_4NO_3 from the filter has been found during sampling, especially during the warm months 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 the 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 that 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 inorganic elements and water-soluble inorganic ions analysis. And the blank concentrations of inorganic elements and water-soluble inorganic ions were subtracted to get actual concentrations. The detection limits for inorganic elements and water-soluble inorganic ions were determined by three times the 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 being 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 the 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 samples at the five sites (Fig. 3) show similar fluctuations. The annual average concentrations were $71.8\text{--}191.2 \mu\text{g m}^{-3}$, ranked in order as $\text{SDZ} < \text{CD} < \text{BJ} < \text{TJ} < \text{SJZ}$. The annual concentrations exceeded $100 \mu\text{g m}^{-3}$ 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 the southern urban area. According to our PM_{2.5} continuous monitoring data, the PM_{2.5} concentrations were quite higher when southwest wind was blowing than the moment when wind was blowing from other directions at SDZ and also at BJ (Zhao et al., 2009). The distributions of PM_{2.5} concentrations at the 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 $50 \mu\text{g m}^{-3}$ on more than 90 % of sampling days at BJ, TJ, and SJZ, and even exceeded $100 \mu\text{g m}^{-3}$ on more than 88 % of sampling days at SJZ.

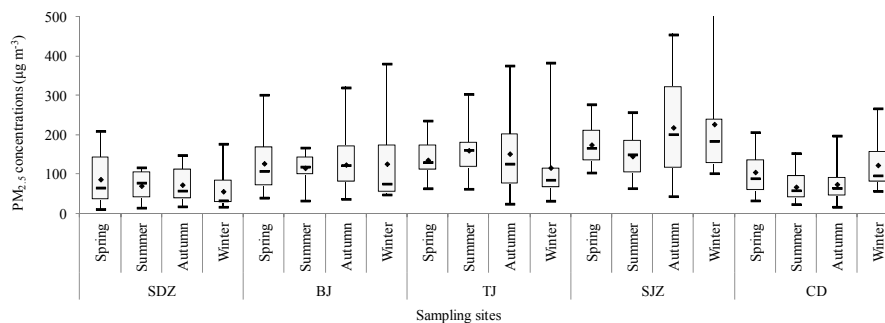


Fig. 4. Seasonal PM_{2.5} concentrations at the five sites. The boxes and whiskers denote the minimums, 25 percentiles, medians, 75 percentiles, and maximums; the dots denote the mean values. * Max. for winter at SJZ was 759.6 $\mu\text{g m}^{-3}$.

There was a four-day 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 $\mu\text{g m}^{-3}$ 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 $\mu\text{g m}^{-3}$ at SJZ if all samples were obtained during that 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 was 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 inorganic 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 Table 2 and Table 3, respectively. We calculated the correlation coefficients among all chemi-

cal 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 the 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 inorganic 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 inorganic ions, OC, EC, and most 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 O₃, 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 O₃ level could also facilitate the formation of secondary inorganic 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 $\mu\text{g m}^{-3}$ at the five sites, only accounting for 4.0–5.1 % of PM_{2.5} mass.

Crustal elements were mainly from fugitive dust influenced by the overall level of urban sanitation, greening cover, human earthmoving activities, and dust control.

3.2.2 Secondary inorganic ions

For environments with an abundance of NH₃, the NH₄HSO₄ and (NH₄)₂SO₄ are sequentially generated; the fine particulate SO₄²⁻ 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 inorganic ions (NH₄⁺, NO₃⁻, and SO₄²⁻) were major components of PM_{2.5} in BTH, which comprise 24–43% of annual average PM_{2.5} mass at the five sites. The mass ratios of secondary inorganic ions to PM_{2.5} were all highest in the summer (42–61% of summer PM_{2.5}) (Fig. 5). At each site, the NH₄⁺ and SO₄²⁻ had similar seasonal trends and highest concentrations in the summer (Table 3). In the BTH area, the correlation coefficients (CCs) between NH₄⁺ and SO₄²⁻ were obviously higher than CCs between NH₄⁺ and NO₃⁻ and CCs between NO₃⁻ and SO₄²⁻ (Table 4). This means sulfate had been better neutralized by NH₄⁺ on the filters. The SO₄²⁻ in the summer was evidently higher than NO₃⁻ and also much higher than SO₄²⁻ in other seasons at each site. However, SO₂ was usually lowest in the summer, not only because of less fuel combustion but also owing to the highest conversion rate of SO₂ to SO₄²⁻ resulting from the strongest photochemical oxidation in the summer (Table 5). Furthermore, the mean concentration of NH₃ in the 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 SO₄²⁻. The NO₃⁻ concentrations had not evidently fluctuated as SO₄²⁻. 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 NO₃⁻/SO₄²⁻ were 0.89, 1.07, 0.75, 0.85, and 0.45 for SDZ, BJ, TJ, SJZ, and CD, respectively. The lowest NO₃⁻/SO₄²⁻ at CD could also reflect the dominating coal combustion sources for particles. Higher NO₃⁻/SO₄²⁻ at BJ and SDZ showed that a greater fraction of particles resulted from motor vehicle exhaust.

In some studies, all NO₃⁻ and SO₄²⁻ were assumed to be in the form of NH₄NO₃ and (NH₄)₂SO₄ (or NH₄HSO₄), and the calculated and measured NH₄⁺ agreed well (DeBell et al., 2006; Louie et al., 2005). We also calculated the molar concentrations of positive electric charges of NH₄⁺ (PEC=NH₄⁺/18) and negative electric charges of NO₃⁻ and SO₄²⁻ (NEC=NO₃⁻/62+SO₄²⁻/96×2). If all SO₄²⁻ was assumed to be in the form of HSO₄⁻, then NEC=(NO₃⁻/62+SO₄²⁻/96). At the five sites, the correlations between PEC and

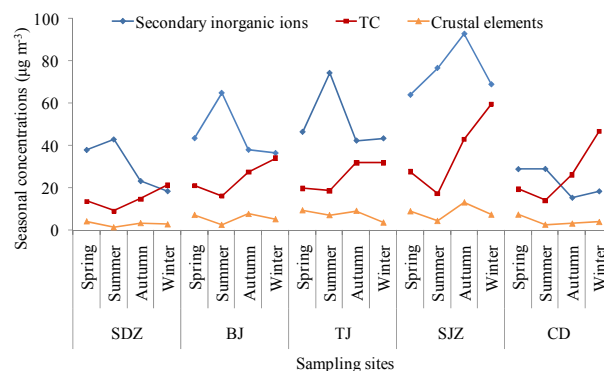


Fig. 5. Seasonal concentrations of secondary inorganic ions, TC, and crustal elements at the five sites.

NEC were significant. The seasonal average PEC and NEC at the five sites were depicted in Fig. 6. Except for autumn and winter seasons at CD, NH₄⁺ was far from enough to match NO₃⁻ and SO₄²⁻ in all four seasons at each site. However, the sum of positive electric charges of all analyzed cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) well balanced the negative charges of SO₄²⁻ in most cases. It indicated the existence of acid.

As mentioned above, ammonium nitrate is often formed in areas with high ammonia and nitric acid concentrations, and low sulfate concentrations. According to thermodynamic results from laboratory experiment, NH₄NO₃ would not be expected to be formed in BTH under summer conditions (Ianniello et al., 2011). But in this study, the highest concentrations of NO₃⁻ had formed in acidic and ammonium-poor aerosol in the summer. In the study of Ianniello et al. (2011), very similar seasonal trends for secondary inorganic ions were reported. In the study of Pathak et al. (2009), high concentrations of NO₃⁻ were also found in the ammonium-poor PM_{2.5} samples at the Beijing site in the summertime. According to the discussions of these above literatures, the nitrate was most probably formed via the heterogeneous hydrolysis of N₂O₅ on the surface of the moist and acidic aerosols. In addition, the internal mixture of nitrate with sulfate made the deliquescent particles able to easily absorb HNO₃ and reduced the thermodynamic dissociation constant *K_n* for NH₄NO₃. Moreover, the dissociation of NH₄NO₃ and NH₄Cl probably resulted in some residue of HNO₃ and HCl on the filters.

3.2.3 Carbonaceous components

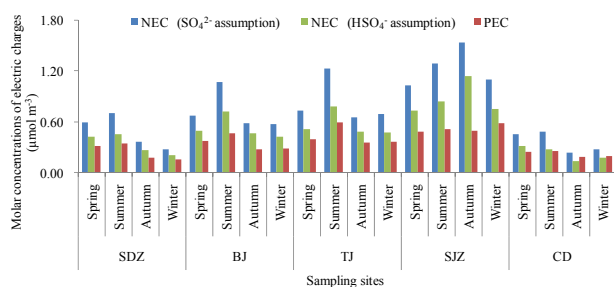
The carbonaceous aerosol pollution exhibited obvious seasonal characteristics. For all five sites, the OC and EC concentrations in the autumn and winter were higher than those in the spring and summer (Fig. 7), and OC had higher rates of increase than EC. According to the study of Chow et al. (2004), PM_{2.5} emissions from coal-burning sources had high OC abundances and high OC/EC values. The seasonal

Table 4. Correlation coefficients among NH₄⁺, NO₃⁻, and SO₄²⁻ 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

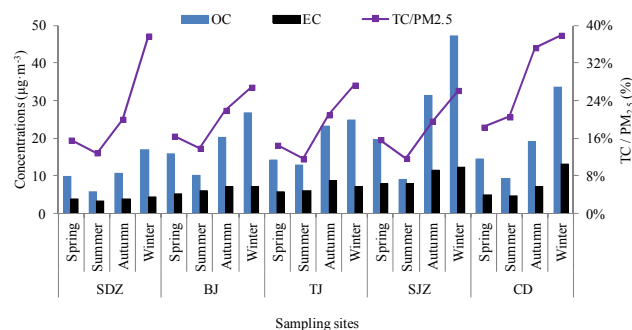
Table 5. Seasonal SO₂ concentrations for sampling periods at SDZ and BJ (μg m⁻³).

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

**Fig. 6.** Molar concentrations of positive electric charges of NH₄⁺ (PEC) and negative electric charges of NO₃⁻ and SO₄²⁻ (NEC).

fluctuations in the level of OC and EC reflected that 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 μg m⁻³), and CD had the highest seasonal EC concentration (13.1 μg m⁻³) for the 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 to 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), and four to five samples with the lowest OC/EC ratios were used to calculate coefficients in the POC (primary organic carbon) expression during a given season at each site. The data from days with blowing dust, floating dust, or precipitation were removed before the analysis. 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 had more percentages

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

of increase than POC during the winter. In the study of Cao et al. (2007), the SOC concentrations were also higher in the winter for several northern Chinese cities. Compared with secondary inorganic ions, the levels of SOC showed opposite seasonal trends. The stable atmosphere and low temperature, which appeared more frequently during the autumn and winter, could facilitate the accumulation of air pollutants and accelerate the condensation or adsorption of volatile organic compounds onto pre-existing aerosol. Because the profiles of particulate organic compounds were not obtained, the actual processes of secondary formation for OC in the winter could not be revealed in this paper and needed to be deeply discussed. A more detailed description of SOC calculation has been published in another paper (Zhao et al., 2013).

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 places during those days.

Heavy metals can cause serious 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

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

	SDZ		BJ		TJ		SJZ		CD	
	SOC ($\mu\text{g m}^{-3}$)	SOC/OC (%)	SOC ($\mu\text{g m}^{-3}$)	SOC/OC (%)	SOC ($\mu\text{g m}^{-3}$)	SOC/OC (%)	SOC ($\mu\text{g m}^{-3}$)	SOC/OC (%)	SOC ($\mu\text{g m}^{-3}$)	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^a ($\mu\text{g m}^{-3}$).

	2009–2010 ^b (This study)					2000–2001 (Ho et al., 2003, 2006)		2000–2001 (Louie et al., 2005)		2000–2002 (Vega et al., 2004)		1998–1999 (Hueglin et al., 2005)		2005 (Lv et al., 2007)		2006 (Feng et al., 2008)
	Annual					Winter	Summer	Annual	Winter and spring	Annual	Spring	Summer	Autumn			
	SDZ ^c	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			

^a The significant figures of concentration values follow respective paper; “–” represent element concentrations that were not analyzed or given.

^b Sampling period.

^c Sampling site.

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 metal concentrations, and Zn, Pb, Mn, Cu, Cr, and As at all five sites were all much higher than those in other studies. Except for the lowest concentrations in the summer, there was no common seasonal trend for each element at five sites.

Pb and Zn were the 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 $\mu\text{g m}^{-3}$ at all five sites, and were close to 1.0 $\mu\text{g m}^{-3}$ 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 the study by He et al. (2001) and the BJ site in this study were only 2.4 km apart. The BNU site in the 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 the Chegongzhuang site in He et al. (2001) was more comparable with data of this study. Compared with studies of He et al. (2001) and Sun et al. (2004), the concentration levels of secondary inorganic ions and carbon components had significantly varied.

The annual concentration of SO₄²⁻ and NO₃⁻ increased from 14.47 and 10.3 $\mu\text{g m}^{-3}$ in study of He et al. (2001) to 19.07 and 20.47 $\mu\text{g m}^{-3}$ in this study. The NO₃⁻ in all four seasons had evidently increased, reflecting the influences by NO_x emissions from the sharp increase in motor vehicles. The SO₄²⁻ in the spring and summer increased from 10.15 and 17.14 $\mu\text{g m}^{-3}$ to 16.42 and 33.76 $\mu\text{g m}^{-3}$, respectively. However, the SO₄²⁻ in the autumn and winter decreased from 12.55 and 24.87 $\mu\text{g m}^{-3}$ to 11.53 and 14.23 $\mu\text{g m}^{-3}$, respectively. The opposite seasonal trends of SO₄²⁻ show the evidence 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, NH₄⁺ and NO₃⁻ were also varied from lower in the summer and highest in the winter to lower in the winter and highest in the summer.

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 ($\mu\text{g m}^{-3}$).

	Chengongzhuang (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.

Compared with the study by He et al. (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 of what 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 $\mu\text{g m}^{-3}$ at the five sites. The PM_{2.5} concentrations on more than 90 % of sam-

pling days exceeded 50 $\mu\text{g m}^{-3}$ 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 inorganic ions, OC, EC, and most crustal elements at SJZ were highest for all five sites. Motor vehicle exhausts and coal combustion emissions both played important roles in Tianjin PM_{2.5} pollution. However, motor vehicle exhausts had played a 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 inorganic 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 seasons 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 inorganic ions, the levels of SOC showed opposite seasonal variations. 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 the 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 inorganic 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 a simple type of coal combustion to a complex type dominated by motor vehicle exhausts.

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References

- Ashbaugh, L. L. and Eldred, R. A.: Loss of Particle Nitrate From Teflon Sampling Filters: Effects on Measured Gravimetric Mass in California and in the IMPROVE Network, *J. Air Waste Manage. Assoc.*, 54, 93–104, 2004.
- Beijing Environmental Protection Bureau (BEPB): Report on the state of the environment in Beijing (1994–2011), <http://www.bjepb.gov.cn/portal0/tab181/>, last access: 22 December 2012.
- Cao, J. J., Lee, S. C., Chow, J. C., Watson, J. G., Ho, K. F., Zhang, R. J., Jin, Z. D., Shen, Z. X., Chen, G. C., Kang, Y. M., Zou, S. C., Zhang, L. Z., Qi, S. H., Dai, M. H., Cheng, Y., and Hu, K.: Spatial and seasonal distributions of carbonaceous aerosols over China, *J. Geophys. Res.*, 112, D22S11, doi:10.1029/2006JD008205, 2007.
- Cao, J. J., Lee, S. C., Ho, K. F., Zou, S. C., Fung, K., Li, Y., Watson, J. G., and Chow, J. C.: Spatial and seasonal variations of atmospheric organic carbon and elemental carbon in Pearl River Delta Region, China, *Atmos. Environ.*, 38, 4447–4456, 2004.
- Castro, L. M., Pio, C. A., Harrison, R. M., and Smith, D. J. T.: Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations, *Atmos. Environ.*, 33, 2771–2781, 1999.
- Chen, J., Zhao, C. S., Ma, N., Liu, P. F., Göbel, T., Hallbauer, E., Deng, Z. Z., Ran, L., Xu, W. Y., Liang, Z., Liu, H. J., Yan, P., Zhou, X. J., and Wiedensohler, A.: A parameterization of low visibilities for hazy days in the North China Plain, *Atmos. Chem. Phys.*, 12, 4935–4950, doi:10.5194/acp-12-4935-2012, 2012.
- Cheng, Y. F., Berghof, M., Garland, R. M., Wiedensohler, A., Wehner, B., Müllner, T., Su, H., Zhang, Y. H., Achtert, P., Nowak, A., Pöschl, U., Zhu, T., Hu, M., and Zeng, L. M.: Influence of soot mixing state on aerosol light absorption and single scattering albedo during air mass aging at a polluted regional site in northeastern China, *J. Geophys. Res.*, 114, D00G10, doi:10.1029/2008JD010883, 2009.
- Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G.: The DRI thermal/optical reflectance carbon analysis system: Description, evaluation and application in U.S. air quality studies, *Atmos. Environ.*, 27A, 1185–1201, 1993.
- Chow, J. C., Watson, J. G., Crow, D., Lowenthal, D. H., and Merrifield, T.: Comparison of IMPROVE and NIOSH carbon measurements, *Aerosol Sci. Tech.*, 34, 23–34, 2001.
- Chow, J. C., Watson, J. G., Kuhns, H., Etyemezian, V., Lowenthal, D. H., Crow, D., Kohl, S. D., Engelbrecht, J. P., and Green, M. C.: Source profiles for industrial, mobile, and area sources in the Big Bend Regional Aerosol Visibility and Observational study, *Chemosphere*, 54, 185–208, 2004.
- Chow, J. C., Watson, J. G., Lowenthal, D. H., and Magliano, K. L.: Loss of PM_{2.5} Nitrate from Filter Samples in Central California, *J. Air Waste Manage. Assoc.*, 55, 1158–1168, 2005.
- Chow, J. C., Watson, J. G., Antony Chen, L.-W., Oliver Chang, M. C., Robinson, N. F., Trimble, D., and Kohl, S.: The IMPROVE-A temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long-term database, *J. Air Waste Manage.*, 57, 1014–1023, 2007.
- Dan, M., Zhuang, G. S., Li, X. X., Tao, H. R., and Zhuang, Y. H.: The characteristics of carbonaceous species and their sources in PM_{2.5} in Beijing, *Atmos. Environ.*, 38, 3443–3452, 2004.
- DeBell, L. J., Gebhart, K. A., Hand, J. L., Malm, W. C., Pitchford, M. L., Schichtel, B. A., and White, W. H.: IMPROVE Report IV-Spatial and Seasonal Patterns and Temporal Variability of Haze and its Constituents in the United States, Cooperative Institute for Research in the Atmosphere, Colorado State University, 2006.
- Deng, Z. Z., Zhao, C. S., Ma, N., Liu, P. F., Ran, L., Xu, W. Y., Chen, J., Liang, Z., Liang, S., Huang, M. Y., Ma, X. C., Zhang, Q., Quan, J. N., Yan, P., Henning, S., Mildenberger, K., Sommerhage, E., Schäfer, M., Stratmann, F., and Wiedensohler, A.: Size-resolved and bulk activation properties of aerosols in the North China Plain, *Atmos. Chem. Phys.*, 11, 3835–3846, doi:10.5194/acp-11-3835-2011, 2011.

- Duan, J. C., Tan, J. H., Cheng, D. X., Bi, X. H., Deng, W. J., Sheng, G. Y., Fu, J. M., and Wong, M. H.: Sources and characteristics of carbonaceous aerosol in two largest cities in Pearl River Delta Region, China, *Atmos. Environ.*, 41, 2895–2903, 2007.
- Eatough, D. J., Long, R. W., Modey, W. K., and Eatough, N. L.: Semi-volatile secondary organic aerosol in urban atmospheres: Meeting a measurement challenge, *Atmos. Environ.*, 37, 1277–1292, 2003.
- Feng, X. D., Dang, Z., and Huang, W. L.: Pollution Level and Chemical Speciation of Heavy Metals in PM_{2.5} During Autumn in Guangzhou City, *Environ. Sci.*, 29, 569–575, 2008 (in Chinese).
- Fergusson, J. E.: The heavy elements: Chemistry, environmental impact and health effects, Pergamon Press, Oxford (UK), 1990.
- Gao, J., Chai, F. H., Wang, T., Wang, S. L., and Wang, W. X.: Particle number size distribution and new particle formation: New characteristics during the special pollution control period in Beijing, *J. Environ. Sci.*, 24, 14–21, 2012.
- Garland, R. M., Schmid, O., Nowak, A., Achtert, P., Wiedensohler, A., Gunthe, S. S., Takegawa, N., Kita, K., Kondo, Y., Hu, M., Shao, M., Zeng, L. M., Zhu, T., Andreae, M. O., and Pöschl, U.: Aerosol optical properties observed during Campaign of Air Quality Research in Beijing 2006 (CAREBeijing-2006): Characteristic differences between the inflow and outflow of Beijing city air, *J. Geophys. Res.*, 114, D00G04, doi:10.1029/2008JD010780, 2009.
- Guo, S., Hu, M., Wang, Z. B., Slanina, J., and Zhao, Y. L.: Size-resolved aerosol water-soluble ionic compositions in the summer of Beijing: implication of regional secondary formation, *Atmos. Chem. Phys.*, 10, 947–959, doi:10.5194/acp-10-947-2010, 2010.
- Guo, Y. M., Jia, Y. P., Pan, X. C., Liu, L. Q., and Wichmann, H.-E.: The association between fine particulate air pollution and hospital emergency room visits for cardiovascular diseases in Beijing, China, *Sci. Total Environ.*, 407, 4826–4830, 2009.
- Hagler, G. S. W., Bergin, M. H., Salmon, L. G., Yu, J. Z., Wan, E. C. H., Zheng, M., Zeng, L. M., Kiang, C. S., Zhang, Y. H., Lau, A. K. H., and Schauer, J. J.: Source areas and chemical composition of fine particulate matter in the Pearl River Delta region of China, *Atmos. Environ.*, 40, 3802–3815, 2006.
- He, K. B., Yang, F. M., Ma, Y. L., Zhang, Q., Yao, X. H., Chan, C. K., Cadle, S., Chan, T., and Mulawa, P.: The characteristics of PM_{2.5} in Beijing, China, *Atmos. Environ.*, 35, 4959–4970, 2001.
- Ho, K. F., Lee, S. C., Chan, C. K., Yu, J. C., Chow, J. C., and Yao, X. H.: Characterization of chemical species in PM_{2.5} and PM₁₀ aerosols in Hong Kong, *Atmos. Environ.*, 37, 31–39, 2003.
- Ho, K. F., Lee, S. C., Cao, J. J., Chow, J. C., Watson, J. G., and Chan, C. K.: Seasonal variations and mass closure analysis of particulate matter in Hong Kong, *Sci. Total Environ.*, 355, 276–287, 2006.
- Huang, X. F., He, L. Y., Hu, M., and Zhang, Y. H.: Annual variation of particulate organic compounds in PM_{2.5} in the urban atmosphere of Beijing, *Atmos. Environ.*, 40, 2449–2458, 2006.
- Hueglin, C., Gehrig, R., Baltensperger, U., Gysel, M., Monn, C., and Vonmont, H.: Chemical characterization of PM_{2.5}, PM₁₀ and coarse particles at urban, near-city and rural sites in Switzerland, *Atmos. Environ.*, 39, 637–651, 2005.
- Ianniello, A., Spataro, F., Esposito, G., Allegrini, I., Rantica, E., Ancora, M. P., Hu, M., and Zhu, T.: Occurrence of gas phase ammonia in the area of Beijing (China), *Atmos. Chem. Phys.*, 10, 9487–9503, doi:10.5194/acp-10-9487-2010, 2010.
- Ianniello, A., Spataro, F., Esposito, G., Allegrini, I., Hu, M., and Zhu, T.: Chemical characteristics of inorganic ammonium salts in PM_{2.5} in the atmosphere of Beijing (China), *Atmos. Chem. Phys.*, 11, 10803–10822, doi:10.5194/acp-11-10803-2011, 2011.
- Kipen, H., Rich, D., Huang, W., Zhu, T., Wang, G., Hu, M., Lu, S., Ohman-Strickland, P., Zhu, P., Wang, Y., and Zhang, J.: Measurement of inflammation and oxidative stress following drastic changes in air pollution during the Beijing Olympics: a panel study approach, *Ann. N. Y. Acad. Sci.*, 1203, 160–167, 2010.
- Kirchstetter, T. W., Corrigan, C. E., and Novakov, T.: Laboratory and Field Investigation of the Adsorption of Gaseous Organic Compounds onto Quartz Filters, *Atmos. Environ.*, 35, 1663–1671, 2001.
- Li, L., Chen, C. H., Fu, J. S., Huang, C., Streets, D. G., Huang, H. Y., Zhang, G. F., Wang, Y. J., Jang, C. J., Wang, H. L., Chen, Y. R., and Fu, J. M.: Air quality and emissions in the Yangtze River Delta, China, *Atmos. Chem. Phys.*, 11, 1621–1639, doi:10.5194/acp-11-1621-2011, 2011.
- Li, X. R., Wang, L. L., Wang, Y. S., Wen, T. X., Yang, Y. J., Zhao, Y. N., and Wang, Y. F.: Chemical composition and size distribution of airborne particulate matters in Beijing during the 2008 Olympics, *Atmos. Environ.*, 50, 278–286, 2012.
- Liu, J., Zhang, X. L., Xu, X. F., and Xu, H. H.: Comparison analysis of variation characteristics of SO₂, NO_x, O₃ and PM_{2.5} between rural and urban areas, Beijing, *Environ. Sci.*, 29, 1059–1065, 2008 (in Chinese).
- Liu, Y., Shao, M., Lu, S. H., Chang, C. C., Wang, J. L., and Chen, G.: Volatile Organic Compound (VOC) measurements in the Pearl River Delta (PRD) region, China, *Atmos. Chem. Phys.*, 8, 1531–1545, doi:10.5194/acp-8-1531-2008, 2008.
- Louie, P. K. K., Chow, J. C., Antony Chen, L.-W., Watson, J. G., Leung, G., and Sin, D. W. M.: PM_{2.5} chemical composition in Hong Kong: urban and regional variations, *Sci. Total Environ.*, 338, 267–281, 2005.
- Lv, S. L., Chen, X. H., Wu, M. H., Jiao, Z., Wen, T. Q., Bi, X. H., Sheng, G. Y., and Fu, J. M.: Physicochemistry and Bioreactivity Characterization of Fine Particles (PM_{2.5}) in Shanghai Air, *Environ. Sci.*, 28, 472–477, 2007 (in Chinese).
- Ma, N., Zhao, C. S., Nowak, A., Müller, T., Pfeifer, S., Cheng, Y. F., Deng, Z. Z., Liu, P. F., Xu, W. Y., Ran, L., Yan, P., Göbel, T., Hallbauer, E., Mildenerger, K., Henning, S., Yu, J., Chen, L. L., Zhou, X. J., Stratmann, F., and Wiedensohler, A.: Aerosol optical properties in the North China Plain during HaChi campaign: an in-situ optical closure study, *Atmos. Chem. Phys.*, 11, 5959–5973, doi:10.5194/acp-11-5959-2011, 2011.
- Ma, N., Zhao, C. S., Müller, T., Cheng, Y. F., Liu, P. F., Deng, Z. Z., Xu, W. Y., Ran, L., Nekat, B., van Pinxteren, D., Gnauk, T., Müller, K., Herrmann, H., Yan, P., Zhou, X. J., and Wiedensohler, A.: A new method to determine the mixing state of light absorbing carbonaceous using the measured aerosol optical properties and number size distributions, *Atmos. Chem. Phys.*, 12, 2381–2397, doi:10.5194/acp-12-2381-2012, 2012.
- Pathak, R. K., Wu, W. S., and Wang, T.: Summertime PM_{2.5} ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere, *Atmos. Chem. Phys.*, 9, 1711–1722, doi:10.5194/acp-9-1711-2009, 2009.
- Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd edition,

- John Wiley & Sons, New Jersey, 2006.
- Shen, X. J., Sun, J. Y., Zhang, Y. M., Wehner, B., Nowak, A., Tuch, T., Zhang, X. C., Wang, T. T., Zhou, H. G., Zhang, X. L., Dong, F., Birmili, W., and Wiedensohler, A.: First long-term study of particle number size distributions and new particle formation events of regional aerosol in the North China Plain, *Atmos. Chem. Phys.*, 11, 1565–1580, doi:10.5194/acp-11-1565-2011, 2011.
- Song, Y., Zhang, Y. H., Xie, S. D., Zeng, L. M., Zheng, M., Salmon, L. G., Shao, M., and Slanina, S.: Source apportionment of PM_{2.5} in Beijing by positive matrix factorization, *Atmos. Environ.*, 40, 1526–1537, 2006.
- Sun, Y. L., Zhuang, G. S., Wang, Y., Han, L. H., Guo, J. H., Dan, M., Zhang, W. J., Wang, Z. F., and Hao, Z. P.: The air-borne particulate pollution in Beijing-concentration, composition, distribution and sources, *Atmos. Environ.*, 38, 5991–6004, 2004.
- Turpin, B. J. and Huntzicker, J. J.: Identification of secondary organic aerosol episodes and quantification of primary and secondary organic aerosol concentrations during SCAQS, *Atmos. Environ.*, 29, 3527–3544, 1995.
- Vega, E., Reyes, E., Ruiz, H., García, J., Sánchez, G., Martínez-Villa, G., González, U., Chow, J. C., and Watson, J. G.: Analysis of PM_{2.5} and PM₁₀ in the Atmosphere of Mexico City during 2000–2002, *J. Air Waste Manage. Assoc.*, 54, 786–798, 2004.
- Wang, Q., Shao, M., Zhang, Y., Wei, Y., Hu, M., and Guo, S.: Source apportionment of fine organic aerosols in Beijing, *Atmos. Chem. Phys.*, 9, 8573–8585, doi:10.5194/acp-9-8573-2009, 2009.
- Wang, W., Wu, M. H., Li, L., Zhang, T., Liu, X. D., Feng, J. L., Li, H. J., Wang, Y. J., Sheng, G. Y., Claeys, M., and Fu, J. M.: Polar organic tracers in PM_{2.5} aerosols from forests in eastern China, *Atmos. Chem. Phys.*, 8, 7507–7518, doi:10.5194/acp-8-7507-2008, 2008.
- Watson, J. G. and Chow, J. C.: Comparison and Evaluation of In Situ and Filter Carbon Measurements at the Fresno Supersite, *J. Geophys. Res.*, 107, 8341, doi:10.1029/2001JD000573, 2002.
- Wu, S. W., Deng, F. R., Niu, J., Huang, Q. S., Liu, Y. C., and Guo, X. B.: Association of Heart Rate Variability in Taxi Drivers with Marked Changes in Particulate Air Pollution in Beijing in 2008, *Environ. Health Perspect.*, 118, 87–91, 2010.
- Wu, Z. J., Hu, M., Liu, S., Wehner, B., Bauer, S., Ma Biling, A., Wiedensohler, A., Petäjä, T., Dal Maso, M., and Kulmala, M.: New particle formation in Beijing: China Statistical analysis of a 1-year data set, *J. Geophys. Res.*, 112, D09209, doi:10.1029/2006JD007406, 2007.
- Wu, Z. J., Hu, M., Lin, P., Liu, S., Wehner, B., and Wiedensohler, A.: Particle number size distribution in the urban atmosphere of Beijing, China, *Atmos. Environ.*, 42, 7967–7980, 2008.
- Yan, P., Tang, J., Huang, J., Mao, J. T., Zhou, X. J., Liu, Q., Wang, Z. F., and Zhou, H. G.: The measurement of aerosol optical properties at a rural site in Northern China, *Atmos. Chem. Phys.*, 8, 2229–2242, doi:10.5194/acp-8-2229-2008, 2008.
- Yang, F., He, K., Ye, B., Chen, X., Cha, L., Cadle, S. H., Chan, T., and Mulawa, P. A.: One-year record of organic and elemental carbon in fine particles in downtown Beijing and Shanghai, *Atmos. Chem. Phys.*, 5, 1449–1457, doi:10.5194/acp-5-1449-2005, 2005.
- Yao, X. H., Chan, C. K., Fang, M., Cadle, S., Chan, T., Mulawa, P., He, K. B., and Ye, B. M.: The water-soluble ionic composition of PM_{2.5} in Shanghai and Beijing, China, *Atmos. Environ.*, 36, 4223–4234, 2002.
- Yao, X. H., Lau, A. P. S., Fang, M., Chan, C. K., and Hu, M.: Size distributions and formation of ionic species in atmospheric particulate pollutants in Beijing, China: 1-inorganic ions, *Atmos. Environ.*, 37, 2991–3000, 2003.
- Ye, B. M., Ji, X. L., Yang, H. Z., Yao, X. H., Chan, C. K., Cadle, S. H., Chan, T., and Mulawa, P. A.: Concentration and chemical composition of PM_{2.5} in Shanghai for a 1-year period, *Atmos. Environ.*, 37, 499–510, 2003.
- Yue, D. L., Hu, M., Wu, Z. J., Wang, Z. B., Guo, S., Wehner, B., Nowak, A., Achtert, P., Wiedensohler, A., Jung, J., Kim, Y. J., and Liu, S. C.: Characteristics of aerosol size distributions and new particle formation in the summer of Beijing, *J. Geophys. Res.*, 114, D00G12, doi:10.1029/2008JD010894, 2009.
- Yue, D. L., Hu, M., Zhang, R. Y., Wu, Z. J., Su, H., Wang, Z. B., Peng, J. F., He, L. Y., Huang, X. F., Gong, Y. G., and Wiedensohler, A.: Potential contribution of new particle formation to cloud condensation nuclei in Beijing, *Atmos. Environ.*, 45, 6070–6077, 2011.
- Zhang, J. L., Song, H. Q., Tong, S. L., Li, L., Liu, B. Y., and Wang, L. H.: Ambient sulfate concentration and chronic disease mortality in Beijing, *Sci. Total Environ.*, 262, 63–71, 2000.
- Zhang, X. Q. and McMurry, P. H.: Evaporative Losses of Fine Particulate Nitrates During Sampling, *Atmos. Environ.*, 26A, 3305–3312, 1992.
- Zhang, Y. M., Zhang, X. Y., Sun, J. Y., Lin, W. L., Gong, S. L., and Shen, X. J.: Characterization of new particle and secondary aerosol formation during summertime in Beijing, China, *Tellus*, 63B, 382–394, 2011.
- Zhao, P. S., Zhang, X. L., Xu, X. F., and Zhao, X. J.: Long-term visibility trends and characteristics in the region of Beijing, Tianjin, and Hebei, China, *Atmos. Res.*, 101, 711–718, 2011.
- Zhao, P. S., Xu, X. F., Meng, W., Dong, F., He, D., Shi, Q. F., and Zhang, X. L.: Characteristics of hazy days in the region of Beijing, Tianjin, and Hebei, China *Environmental Science*, 32, 31–36, 2012 (in Chinese).
- Zhao, P. S., Dong, F., Yang, Y. D., He, D., Zhao, X. J., Zhang, W. Z., Yao, Q., and Liu, H. Y.: Characteristics of carbonaceous aerosol in the region of Beijing, Tianjin, and Hebei, China, *Atmos. Environ.*, 71, 389–398, 2013.
- Zhao, X. J., Zhang, X. L., Xu, X. F., Xu, J., Meng, W., and Pu, W. W.: Seasonal and diurnal variations of ambient PM_{2.5} concentration in urban and rural environments in Beijing, *Atmos. Environ.*, 43, 2893–2900, 2009.