



Seasonal Variation of Physical and Chemical Properties in TSP, PM₁₀ and PM_{2.5} at a Roadside Site in Beijing and Their Influence on Atmospheric Visibility

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ABSTRACT

In Beijing, capital of China, decreasing visibility has become a serious problem on people's life, thus a hot environmental concern. An urban roadside site in Beijing was chosen to collect 24-h TSP, PM₁₀ and PM_{2.5} samples for one month each season from June 2009 to March 2010. The PM mass concentrations, and the concentrations of ions, EC, OC and metals in PM₁₀ and PM_{2.5} were measured, and their correlation with visibility, as well as the influence of weather factors on visibility were studied. The results showed that daily mean concentrations of TSP, PM₁₀ and PM_{2.5} were 75–1350 µg/m³ (mean 275.8), 29–448 µg/m³ (mean 187) and up to 300 µg/m³ (mean 92.6), with the number of days exceeding the secondary standard (GB3095-2012) representing 33.3%, 59.8% and 51.0%, respectively. All PM concentrations were higher in spring than in other seasons. Obvious seasonal variations were observed for certain ions, OC, EC and metal concentrations in PM₁₀ and PM_{2.5}. Average mean visibility was low (5.64 km), showing better visibility in summer than in other seasons. PM₁₀ and PM_{2.5} showed stronger negative correlation with visibility giving coefficients of –0.52 and –0.50. Almost all significant correlations were negative and occurred in autumn for visibility with TSP, PM₁₀ and PM_{2.5}, and with ions, EC and OC in both PM₁₀ and PM_{2.5}. The only positive and significant correlation was found between fine OC and visibility. Negative and significant correlations were also observed for visibility with humidity in autumn and winter, and with minimum temperature in all seasons but summer.

Keywords: PM; Anions; Cations; Metals; OC; EC; Weather; Visibility.

INTRODUCTION

Airborne particulate matter (PM) is broadly considered as a potent air pollutant in typical urban locations (Khan *et al.*, 2010), especially in most cities of China (Wang *et al.*, 2009), including Beijing. PM can be divided into total suspended particles (TSP), respirable particles (PM₁₀), fine particles (PM_{2.5}) and ultrafine particles (PM_{1.0}) with aerodynamic diameters less than 100, 10, 2.5 and 1.0 µm, respectively. High concentrations of PM have raised great concerns because of its adverse effects on human health and the environment (Raizenne *et al.*, 1996; IPCC, 2001; Gauderman *et al.*, 2004; Pope, 2004; Xiao and Liu, 2004; Cheung *et al.*, 2005; Kampa and Castanas, 2008; Wang *et al.*, 2008). It might cause human respiratory and cardiovascular

diseases (Berico *et al.*, 1997), and increase mortality rate (Sondreal *et al.*, 2004; Ulrich, 2005; Pope and Dockery, 2006), due to deposit of different sizes of particles on the respiratory system, especially PM_{2.5}, which can penetrate deeply into the human lung (Holgate *et al.*, 1999). Significantly positive association occurred between ambient PM (PM₁₀ and PM_{2.5}) concentrations and daily mortality counts or various indices of morbidity (IIASA, 2000a, b). Diverse sourced PM is composed of combinations of inorganic ions, elemental carbons (black soot), trace elements, crustal materials, organic compounds, and biological matter (Cheung *et al.*, 2011). It is these chemical components that being absorbed onto the surface of the recipients to hurt human and environment (Khan *et al.*, 2010). For example, organic carbon or polycyclic aromatic hydrocarbons (PAHs) and most trace elements are potential carcinogens (IPCC, 2007; Richter *et al.*, 2007); black carbon warms the atmosphere, whereas sulfate and most organic compounds lead to climate cooling.

PM can also degrade visibility, change radiation budget by absorbing or scattering solar radiation (Ramanathan and

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Crutzen, 2003), and affect global climate (Seinfeld and Pandis, 1998). In China, visibility condition has become an important issue for both the society and the scientific community. Decreased visibility has an effect on hospital admissions, which significantly associated with elevated death rates in Shanghai (Ge *et al.*, 2011). It also reduces crop yields by decreasing photosynthetic radiation, and affect regional climate by changing the radioactive properties of the atmosphere (Seinfeld and Pandis, 1998; Chameides *et al.*, 1999). Beijing is one of the highest haze cities within 31 provincial capitals in China between 1980 and 2005 (Che *et al.*, 2009a). Lower visibility occurred mainly in the urban areas of Beijing, where the number of haze days showed an increasing trend (Zhao *et al.*, 2011). Significant differences of aerosol optical properties might be affected by aerosol components under distinct weather conditions (Che *et al.*, 2008).

The Chinese government made a series of measures to decrease air pollution in Beijing before and after the Olympic Games in 2008 and new ambient air quality standard (GB3095-2012) was set up in 2012. This study aims to evaluate the pollution status of PM and to investigate their potential influence on visibility, through both physical and chemical measurements at an urban roadside site in Beijing from summer 2009 to spring 2010. The results will provide valuable information in future revision on governmental policy and technology procedures improving the atmospheric visibility and reducing adverse effect on human health.

METHODS AND MATERIALS

Site, Sampling, PM Mass Measurement

Influenced by the summer monsoon, Beijing experiences cold, relatively dry winter, hot and humid summer. The sampling site was located near a busy traffic line in Beijing (116°18'10"8E, 39°56'50"7N) (measured by GPS Etrex Vista HCX, made by GARMIN). Sampling equipments were set up on the roof of an office building with a height of 30 m aboveground and a distance about 30 m from the road/traffic. This is a very busy ring road with 6 fast tracks and 4 voeux roads; with 230–270 vehicles at the speed about 50 km/hour passing through per minute in the morning rush hour. 24-h TSP, PM₁₀ and PM_{2.5} were collected onto 90 mm diameter quartz microfiber filters (QMA, Whatman) at a flow rate 100 L/min, using the Smart TSP Volume Air Samplers (TH-150A type, made by Wuhan Tianhong Instrument Co., Ltd.), equipped with different PM head TSP, PM₁₀ and PM_{2.5} respectively. The filter was replaced at 10:00 a. m. Beijing time daily through the whole sampling period, and the measurement was carried out for one month every season. In detail, samples were collected from June 10 to July 10 in summer 2009, from September 10 to 30 in autumn 2009, from December 1 to 31 in winter 2009, and from March 1 to 31 for spring of 2010.

Filters were weighed using a balance (CP225D, with accuracy of 0.01 mg, made in Sartorius, Germany), and PM mass was calculated as the mass differences before and after sampling at unit sampling volume. Filters were heated for 4 hours at 550°C and preserved in desiccators with

humidity of 34% for 24 hours before pre-sampling weighing. After sampling, filters were kept in desiccators for 24 hours before re-weighing. During the weighing procedure, temperature was controlled at 20°C by air conditioning. Masses of PM_{coarse} were obtained as the difference between PM₁₀ and PM_{2.5}. Filters were then cut into quarters using stainless steel cutter for subsequent component analysis.

Samples Analysis

Ions

Ions were analyzed using the methods by Sun *et al.* (2010). One quarter of the filter was put in a 50 mL centrifuge tube, and 20 mL ultrapure water was added. After mechanic shaking for 48 h and ultrasonic bath for 1h, the extracted solution was diluted, filtered and then analyzed by ICS-2000 Ion chromatograph for both cations including Ca²⁺, K⁺, Na⁺, NH₄⁺, Mg²⁺, and anions including NO₃⁻, SO₄²⁻, Cl⁻, F⁻, NO₂⁻, HCOO⁻ and CH₃COO⁻.

Organic Carbon and Elemental Carbon

OC and EC were measured by DRI-2001A OC/EC Analyzer (Model 2001 A, Desert Research Institute) with the detection limit 0.2 µg/cm². A small piece of filter with 0.518 cm² was cut by Chung tool (circular cutter) and put into a small quartz boat, which was then added into a quartz furnace for measurement, using the IMPROVE heating procedure (Interagency Monitoring of Protected Visual Environment). At the end of each sample analysis, quantitative internal standard gas (CH₄) was injected into the system to calibrate the FID, thus the internal standard response peak area was obtained. For the sample analysis to be effective, the FID signal difference should be less than 3 before and after the measurement. The final results OC (OC1 + OC2 + OC3 + OC4 + OP) (OP is pyrolysis carbon) and EC (EC1 + EC2 + EC3 – OP) were determined based on the standard curve of the sucrose solution. At the first stage, OC1, OC2, OC3 and OC4 was released separately at the temperature of 140°C, 280°C, 480°C and 580°C. On the second stage, EC1, EC2 and EC3 were done separately at the temperature of 580°C, 740°C and 840°C. OP was decided by the equal reactive rate on the both stages. A repeat sample run was carried out for every 9 samples to check the instrument precision, for which a 10% or less is accepted, otherwise all 9 samples must re-run. The response deviation of the standard solution less than 5% indicates the instrument is stable for analysing samples. The standard curve was made by TC to the relative response of KHP solution (which was the ratio of KHP solution response peak area to internal standard response peak area, using CH₄ as the internal standard).

Metals

One quarter of the filter samples were digested with HNO₃ + H₂O₂ (2:0.5, v/v) by microwave assisted digestion (CEM Co., MARS), diluted with Milli-Q water (18.2 MΩ cm, Millipore) and analyzed by ICP-MS (Agilent 7500a) to determine metal concentrations. Standard metal solutions used for the analysis were obtained from National Center for Standard Materials (China). For quality assurance,

certified reference material, GBW 07408 (farmland soil) was used for the evaluation of measurement precision. Blanks were also used in each run both for the reagent and the sample. The precision of the analysis was generally < 5%.

Weather Data Collection and Data Statistical Analysis

Daily weather data were downloaded from wunderground.com website, including daily Maximum (Max), mean and minimum (Min) visibility, humidity and temperature, etc. Average max, mean and min visibility, humidity and temperature were obtained by averaging all daily max, mean and min value in an evaluated period. Excel 2007 and SPSS 17.0 were used to analyze all the measured data in this study.

RESULTS AND DISCUSSIONS

PM Concentration and Their Seasonal Variation

In a total of 388 daily collected samples of TSP, PM₁₀ and PM_{2.5} from June 2009 to March 2010, the TSP concentration ranged from 75 to 1350 µg/m³, with an average of 275.8 µg/m³. As a major air pollutant in Beijing, the annual average PM₁₀ concentrations in this study was higher than those measured from 2000 to 2008 (Table 1). The concentration of PM_{2.5} in this study was higher than that measured in Xi'an, in 2005–2006 (Table 1), and the concentrations of PM_{coarse}, ranged from 11 to 448 µg/m³ with an average of 94.8 µg/m³, cannot be compared due to lack of similar observation.

Further analysis indicates that concentration of aerosol particles has obvious seasonal variation. In March 2010, the TSP and PM_{coarse} concentrations were significantly higher than those of any other seasons in 2009 (Fig. 1). Similar seasonal concentration trends occurred for PM₁₀, which was significantly higher in spring of 2010 than summer in 2009. Previous investigation in 2003–2009 also showed high PM₁₀ concentrations, which always occurred in spring in Beijing, followed by autumn and winter, then summer (Zhu *et al.*, 2011).

PM₁₀ concentrations were the highest in spring 2010 from this study, which is lower than that measured previously in April, 2000 (Table 1; Xie *et al.*, 2005), and similar to that measured in spring 2006 (Table 1; Yu *et al.*, 2008; Sun *et al.*, 2010) in the same city. However, it is only one third of PM₁₀ concentration observed in spring 2008 in Xi'an, a western city of China that is more affected by sandstorm events (Table 1; Shen *et al.*, 2010). The lowest PM₁₀ concentration was observed in summer 2009, which was a little lower than those in summer 2000 (Table 1; Sun *et al.*, 2004), but higher than those in summer of 2006 (Table 1; Yu *et al.*, 2008). The decrease in PM₁₀ concentrations both in spring and summer from 2000 to 2009 indicated an improvement on air quality in the two seasons over the 10-year period.

PM₁₀ concentration in winter did not show a decreasing trend when compared with previous data for 1–15th January 2004 (Table 1; Zhang *et al.*, 2007), when PM₁₀ concentration was observed to be overlapped with those in winter 2009 from this study. This implies that winter PM₁₀ sources, coal combustion and heavy traffic etc., need further control.

Concentration of PM_{2.5} showed a different seasonal trend from that of PM₁₀. Instead of highest PM₁₀ concentration in spring, monthly mean concentration of PM_{2.5} was significantly higher in autumn and winter 2009 than that in summer 2009 (Fig. 1).

Similarly as PM₁₀, the daily PM_{2.5} concentration ranges in spring 2009 and 2010 (Table 1; Liu *et al.*, 2010) were lower than those measured in spring 2000 (Table 1; Xie *et al.*, 2005) and 2006 in Beijing (Table 1; Yu *et al.*, 2008; Sun *et al.*, 2010), except 2001 (Table 1; Zhang *et al.*, 2003), two dust storm samples, which implies that PM_{2.5} sources in spring have been controlled to some extent since 2000. On the contrary to PM₁₀ and with an exception for 2009, the spring PM_{2.5} levels in Beijing are all higher than that observed in 2005–2006 in Xi'an and in 2004 in Hong Kong (Table 1, Lee *et al.*, 2006), where different sources may exist. In the summer period, PM_{2.5} level from this study in 2009 was lower than those observed in 2003 (Table 1; Cao *et al.*, 2012) and similar to those in 2000 and 2006 in Beijing (Table 1; Sun *et al.*, 2004; Yu *et al.*, 2008), but slightly higher than that observed in the city of Xi'an in 2005–2006 (Table 1; Shen *et al.*, 2008). In autumn, the PM_{2.5} concentration level in 2009 was higher than both the levels in 2005–2006 in Xi'an and in 2006 in Beijing. In winter, there has been no obvious reduction observed in the daily PM_{2.5} mass concentrations in Beijing from 2003 to 2009 (Table 1; Yu *et al.*, 2008; Deng *et al.*, 2010; Cao *et al.*, 2012). These levels in Beijing were lower than that in 2007 from Tianjin, a northern Chinese city, but higher than that in 2005–2006 (Table 1; Shen *et al.*, 2008; Gu *et al.*, 2011) from Xi'an and in 2003 (Table 1; Lee *et al.*, 2006) from Hong Kong. It indicates that North China Plain is easier to be disturbed by fine particles than western and southeast coastal city in winter in China.

Within the Chinese Ambient Air Quality Standards (GB3095-2012), a second rate standard was suggested for dwelling and commercial regions, as 24h average upper limit value of 300 µg/m³ for TSP, 150 µg/m³ for PM₁₀, and 75 µg/m³ for PM_{2.5}. The current study site was located in the city area, which is regulated by the second rate standard. Over the one year measurement period, there were 33.3% observations for TSP, 59.8% for PM₁₀ and 51% for PM_{2.5} concentrations exceeded the second rate standard limit for TSP, PM₁₀ and PM_{2.5} respectively. Considering seasonal effect, the number of days exceeding the second rate standard limit were the highest in spring for TSP and PM₁₀, and in autumn and winter for PM_{2.5} (Fig. 2). The high percentage of PM concentration exceeding the standard limit requires strict control of the PM sources in Beijing.

Ion and Carbon Concentration and Their Seasonal Variation

Ion and Carbon Concentration in PM₁₀ and Their Seasonal Variation

There are 36–88 measurements for each component, for which daily PM₁₀ ion concentrations were processed and the average seasonal and annual mean values were calculated. In comparison with previous data in 2003 and 2006 in Beijing (Table 2; Song *et al.*, 2006; Cui *et al.*, 2008), similar

Table 1. Concentration variation of PM₁₀ and PM_{2.5} through years and seasons (unit: µg/m³).

PM Type	Time	Locality	Year	Concentration average (range)	references		
PM ₁₀	Yearly	Beijing	2000	162	Environmental Protection Bureau Annual Report 2000–2008 Zhang <i>et al.</i> , 2007 Environmental Protection Bureau Annual Report 2000–2008 this study		
			2001	165			
			2002	166			
			2003	141			
			2004	139			
			2005	149			
			2006	142			
			2007	161			
			2008	148			
			2009–2010	122			
	Spring	Beijing	2000	187 (29–448)	Xie <i>et al.</i> , 2005		
			2006	(66–728)	Sun <i>et al.</i> , 2010		
			2006	(289.9–421.6)	Yu <i>et al.</i> , 2008		
			2006	308	Shen <i>et al.</i> , 2010		
			2008	670.1	this study		
			2010	217.6(28.7–448.3)	Sun <i>et al.</i> , 2004		
			Summer	Beijing	2000	150.1–172.2 (23.9–461.5)	Yu <i>et al.</i> , 2008
					2006	104	this study
					2009	155.9 (54.8–362.1)	Yu <i>et al.</i> , 2008
			Autumn	Beijing	2006	75	this study
2009	194.4 (158.0–230.7)	Yu <i>et al.</i> , 2008					
Winter	Beijing	2004	172 (24.2–401.6)	this study			
		2009	193 (60.5–389.2)	Zhang <i>et al.</i> , 2007			
Yearly	Xi'an	2005–2006	45.0 ± 34.4	this study			
	Beijing	2009–2010	92.6 (–300)	Shen <i>et al.</i> , 2008			
PM _{2.5}	Spring	Beijing	2000	(29–262)	Xie <i>et al.</i> , 2005		
			2001	62.1, 54.1	Zhang <i>et al.</i> , 2003		
			2004	51.5 ± 17.0	Lee <i>et al.</i> , 2006		
			2005–2006	28.3 ± 29.3	Shen <i>et al.</i> , 2008		
			2006	(112.3–119.6)	Sun <i>et al.</i> , 2010		
			2006	165	Yu <i>et al.</i> , 2008		
			2009	9.3	Liu <i>et al.</i> , 2010		
			2010	88.6 (3.22–198.7)	this study		
			Summer	Beijing	2000	77.3–82.2 (12.2–216.2)	Sun <i>et al.</i> , 2004
					2003	131.6 ± 28.0	Cao <i>et al.</i> , 2012
	2005–2006	51.3 ± 35.1			Shen <i>et al.</i> , 2008		
	Autumn	Beijing	2006	69.4	Yu <i>et al.</i> , 2008		
			2009	73.8 (–261.0)	this study		
			2005–2006	52.5 ± 27.6	Shen <i>et al.</i> , 2008		
	Winter	Beijing	2006	52	Yu <i>et al.</i> , 2008		
			2009	103.9(17.0–220.2)	this study		
			2003	115.6 ± 46.6	Cao <i>et al.</i> , 2012		
	Yearly	HongKong	2003	54.1 ± 21.1	Lee <i>et al.</i> , 2006		
			2005–2006	94.7	Yu <i>et al.</i> , 2008		
			2005–2006	53.2 ± 39.2	Shen <i>et al.</i> , 2008		
2007			144.6 (48.2–319.2)	Gu <i>et al.</i> , 2011			
2008			94.24	Deng <i>et al.</i> , 2010			
2009	106.6 (23.0–300)	this study					

annual mean Na⁺, Mg²⁺, F⁻, Cl⁻ and NO₃⁻ concentrations were observed in this study, whilst the mean NH₄⁺ and SO₄²⁻ concentrations showed large increase, indicating the existence of large sources of nitrogen and sulfur. The reduction in the concentrations of K⁺, Ca²⁺ and OC was due

to the decrease in biomass combustion and construction activities through the years.

Seasonal variations were observed for most ions in this study (Fig. 3), showing different ions source features. In spring, the season with prevailing sandstorm weather and

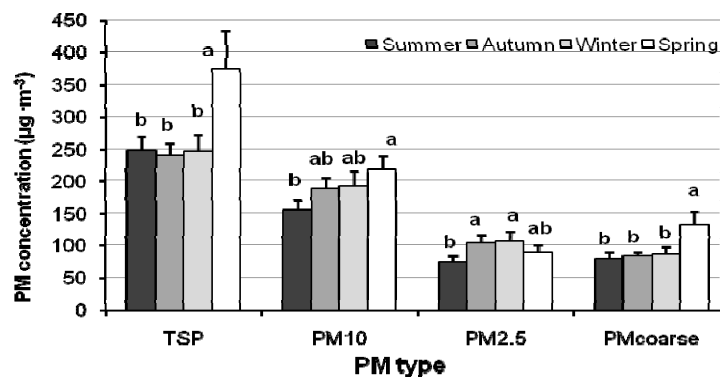


Fig. 1. Seasonal variance of TSP, PM₁₀, PM_{2.5} and PM_{coarse} concentration from Jun 2009–Mar 2010. Notes: Bar is standard error. Significant difference is conveyed between seasons' data for each kind of particulate matter.

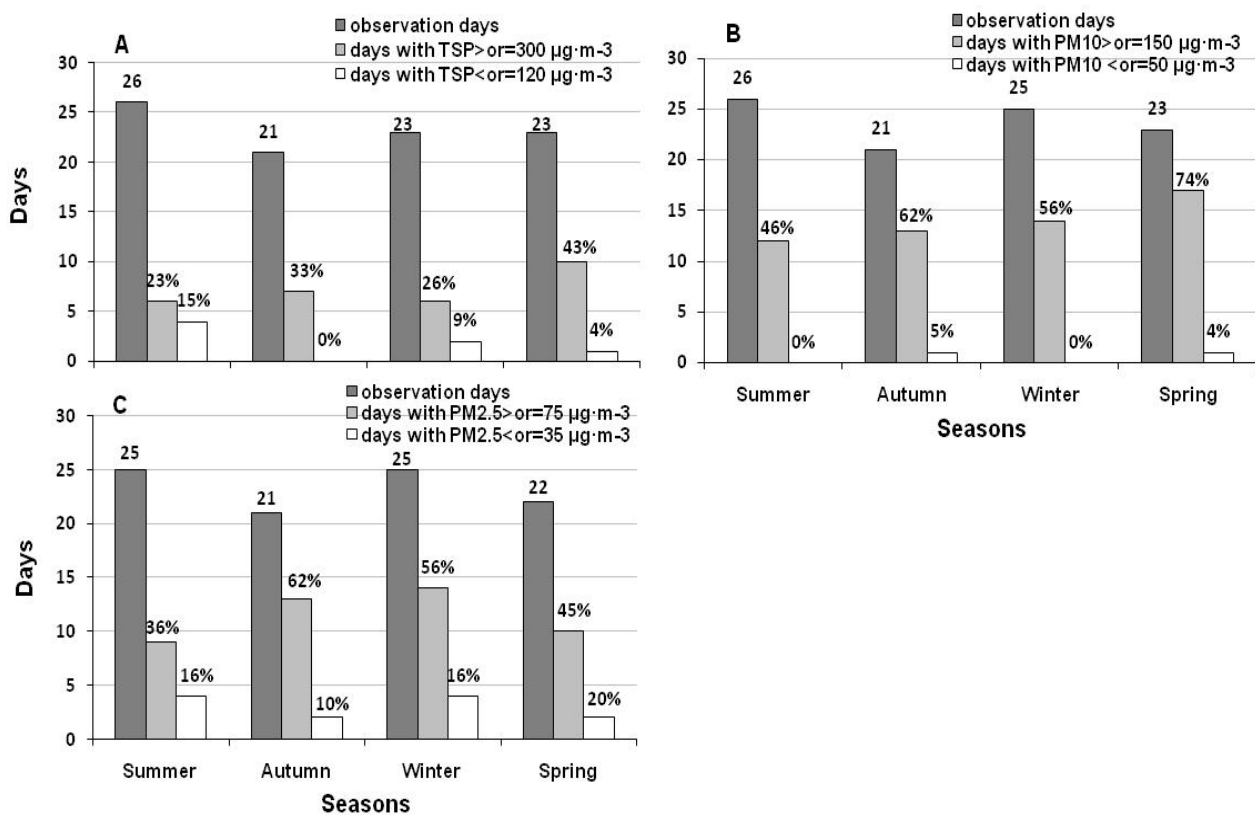


Fig. 2. Seasonal ambient air qualities variation of TSP, PM₁₀, PM_{2.5} and PM_{coarse} from June 2009 to March 2010.

northwest wind, ions Na⁺, Mg²⁺, F⁻ and HCOO⁻ showed higher concentrations. In comparison, the lowest concentrations occurred to Ca²⁺ and NO₃⁻, due to possibly local pollutants. The winter season, disturbed often by Siberia snap and fossil combustion, experienced higher ion concentrations include Na⁺, Mg²⁺, F⁻, Cl⁻, TC, OC and EC.

In spring, the mean concentrations of most ions except NH₄⁺ in PM₁₀ from this study were lower than that for both sandstorm and non sandstorm days in Beijing in spring 2004 and that in Xi'an in 2008 (Table 2; Shen *et al.*, 2010; Sun *et al.*, 2010). This implies the successful control on those ion elements, except ammonia which might be due to animals and human activities. In winter, concentrations of

OC and EC increased whilst other ions decreased, when comparing with those in winter 2003 (Table 2; Sun *et al.*, 2006; Zhang *et al.*, 2007). It reminds us that more work should be focused on the reduction of OC and EC sources. The PM₁₀ ion concentrations in winter 2005–2006 in Xi'an were 2–10 times higher than that in this study (Table 2, Shen *et al.*, 2011), showing worse air quality in this western city of China, relating to the respirable particle size fraction.

Ion and Carbon Concentrations in PM_{2.5} and Their Seasonal Variation

Ion concentrations appeared decreasing trend since 1999 (Table 2; He *et al.*, 2001; Duan *et al.*, 2006). Similar to

Table 2. Ions, TC, OC and EC concentrations in PM₁₀ and PM_{2.5} through years and seasons.

PM Type	Time	Locality	Year	Concentration (unit: $\mu\text{g}/\text{m}^3$)											References		
				Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	OC	EC			
PM ₁₀	Yearly	Beijing	2003	NA	NA	NA	NA	NA	0.45	2.75	NA	NA	3.21	20.56	NA	Song et al., 2006	
			2006	0.71	3.76	4.82	0.69	6.81	NA	2.54	12.02	12.61	NA	NA	NA	NA	Cui et al., 2008
			2009–2010	0.91	10.2	1.39	0.46	3.92	0.32	2.43	14.1	18.1	18.1	6.88	1.34	NA	this study
	Spring	Xi'an	2004	1.4/2.0	NA	3.1/3.4	1.06/1.22	10.1/11.4	0.53/0.52	NA	29.7/13.9	29.3/24.2	NA	NA	NA	NA	Sun et al., 2010
			2008	3.8	5.6	2.9	1.7	27.8	1	8.6	16.4	24.5	66.7	21.3	5.83	NA	Shen et al., 2010
	Summer	Beijing	2010	1.21	12.6	1.5	0.62	2.01	0.43	0.68	2.05	19.1	26.1	19.8	6.75	NA	this study
			2009	0.38	7.82	1.21	0.37	4.45	0.14	1.01	14.8	17.8	19.8	19.8	6.75	NA	this study
	Autumn	Beijing	2009	0.75	12.6	1.45	0.33	4.64	0.21	2.38	28.3	24.5	22.5	7.4	NA	NA	this study
			2003	NA	NA	NA	NA	NA	NA	NA	NA	21.2 ± 16.0	8.9 ± 5.1	3.0–72.3	(1.7–20.1)	NA	Zhang et al., 2007
	Winter	Xi'an	2005–2006	NA	29.2 ± 12.9	6.9 ± 2	1.3 ± 0.6	10.5 ± 4.9	4.1 ± 1.2	14.2 ± 3.5	60.8 ± 27.7	122.3 ± 51.2	73.7 ± 20.1	15.2 ± 5.2	35.2	11.1	NA
2004			NA	14	NA	NA	NA	NA	NA	24	39	NA	NA	NA	NA	NA	Sun et al., 2006
2009			1.37	7.76	1.43	0.52	4.62	0.51	5.85	13.53	12.3	9.3–95.9	(2.1–42.5)	NA	NA	NA	this study
PM _{2.5}	Yearly	Beijing	1999–2000	NA	7.8	NA	NA	NA	NA	NA	4.61	15.35	24.87	NA	NA	NA	He et al., 2001
			2001	NA	7.13	NA	NA	NA	NA	NA	10.72	9.88	NA	NA	NA	NA	Duan et al., 2006
			2001–2003	0.61	6.47	1.09	0.24	2.54	0.25	2.92	11.92	13.52	NA	NA	NA	NA	Wang et al., 2005
	2002–2003	Beijing	2002	NA	15.5	NA	NA	NA	NA	6.77	16.6	27.8	NA	NA	NA	NA	Sun et al., 2004
			2003	NA	NA	NA	NA	NA	0.14	2.2	2.38	16.98	NA	NA	NA	NA	Song et al., 2006
	2005–2006	Xi'an	2005	0.8 ± 0.6	8.7 ± 7.0	1.8 ± 1.5	0.2 ± 0.2	1.7 ± 1.6	0.4 ± 0.5	2.5 ± 2.8	8.3 ± 7.4	19.5 ± 15.7	NA	NA	NA	NA	Shen et al., 2008
			2006	1.18	6.03	3.83	0.29	0.68	NA	4.61	9.06	9.11	NA	NA	NA	NA	Deng et al., 2010
	2008–2009	Beijing	2008	0.47	8.33	1.24	0.11	0.63	0.11	2.84	9.73	14.6	18.8	5.92	NA	NA	this study
			2009	0.47	8.33	1.24	0.11	0.63	0.11	2.84	9.73	14.6	18.8	5.92	NA	NA	this study
	2004	Beijing	2004	0.68/0.60	7.2	2.1/2.3	0.11/0.35	3.9/2.4	NA	NA	14.9	19.6/21.6	NA	NA	NA	NA	Sun et al., 2010
2004			NA	NA	NA	NA	NA	NA	NA	NA	10.0 ± 3.7	12.7 ± 4.2	NA	NA	NA	Lee et al., 2006	
Spring	Xi'an	2006	0.8 ± 0.7	4.7 ± 5.2	1.1 ± 1.3	0.3 ± 0.2	2.7 ± 2.8	0.6 ± 0.5	2.0 ± 1.6	5.0 ± 7.0	11.4 ± 12.7	NA	NA	NA	NA	Shen et al., 2009	
		2006	NA	NA	NA	NA	NA	NA	NA	NA	NA	14.0 ± 8.3	2.1 ± 1.3	NA	NA	Zhang et al., 2012	
2009	Beijing	2009	0.44	9.62	1.17	0.087	0.075	0.11	4.76	16.2	13.8	16.9	5.11	NA	NA	this study	
		2003	0.5 ± 0.3	9.8 ± 4.2	2.5 ± 0.6	NA	NA	NA	1.3 ± 0.6	13.7 ± 6.4	22.6 ± 9.2	19.7 ± 4.7	5.7 ± 4.1	NA	NA	Cao et al., 2012	
Summer	Xi'an	2006	0.5 ± 0.3	12.2 ± 8.2	1.6 ± 0.9	0.2 ± 0.2	1.9 ± 1.9	0.3 ± 0.4	1.4 ± 1.1	8.3 ± 6.5	25.1 ± 18.8	NA	NA	NA	NA	Shen et al., 2010	
		2006	0.44	2.81	3.29	0.44	4.61	NA	1.36	7.78	9.16	NA	NA	NA	NA	Cui et al., 2008	
2009	Beijing	2009	0.18	6.94	1.21	0.099	0.18	0.044	0.38	8.01	15.9	12.5	4.9	NA	NA	this study	
		2005	1.0 ± 0.7	10.2 ± 6.7	2.5 ± 1.6	0.2 ± 0.1	1.3 ± 0.8	0.4 ± 0.4	2.6 ± 1.7	11.1 ± 6.7	23.3 ± 13.1	NA	NA	NA	NA	Shen et al., 2011	
Autumn	Beijing	2009	0.53	10.7	1.31	0.13	0.43	0.082	1.6	1.42	18.7	17.1	7.16	NA	NA	this study	
		2001–2003	NA	10.64	NA	NA	NA	NA	12.29	20.96	10.64	NA	NA	NA	NA	Wang et al., 2005	
Winter	HongKong	2003	NA	NA	NA	NA	NA	NA	NA	NA	NA	13.2 ± 6.0	11.0 ± 4.7	NA	NA	Lee et al., 2006	
		2004	NA	NA	NA	NA	NA	NA	NA	NA	NA	27.8	5.12–6.7	NA	NA	Huan et al., 2006	
		2005	1.1 ± 0.8	9.5 ± 7.5	2.8 ± 2.0	0.3 ± 0.3	1.5 ± 1.1	0.6 ± 0.7	5.2 ± 4.6	11.7 ± 9.7	21.3 ± 15.9	NA	NA	NA	NA	Shen et al., 2008	
2005–2006	Xi'an	2005	4.8 ± 1	28 ± 13	6.5 ± 2.2	0.6 ± 0.3	3.0 ± 1.6	2.6 ± 0.8	12.9 ± 3.3	48.9 ± 23.7	107.3 ± 48.6	73.4 ± 24.7	12.0 ± 4.5	NA	NA	Shen et al., 2011	
		2009	0.73	6.66	1.26	0.14	0.11	0.202	4.53	12.2	10.8	27.8	6.7	NA	NA	this study	

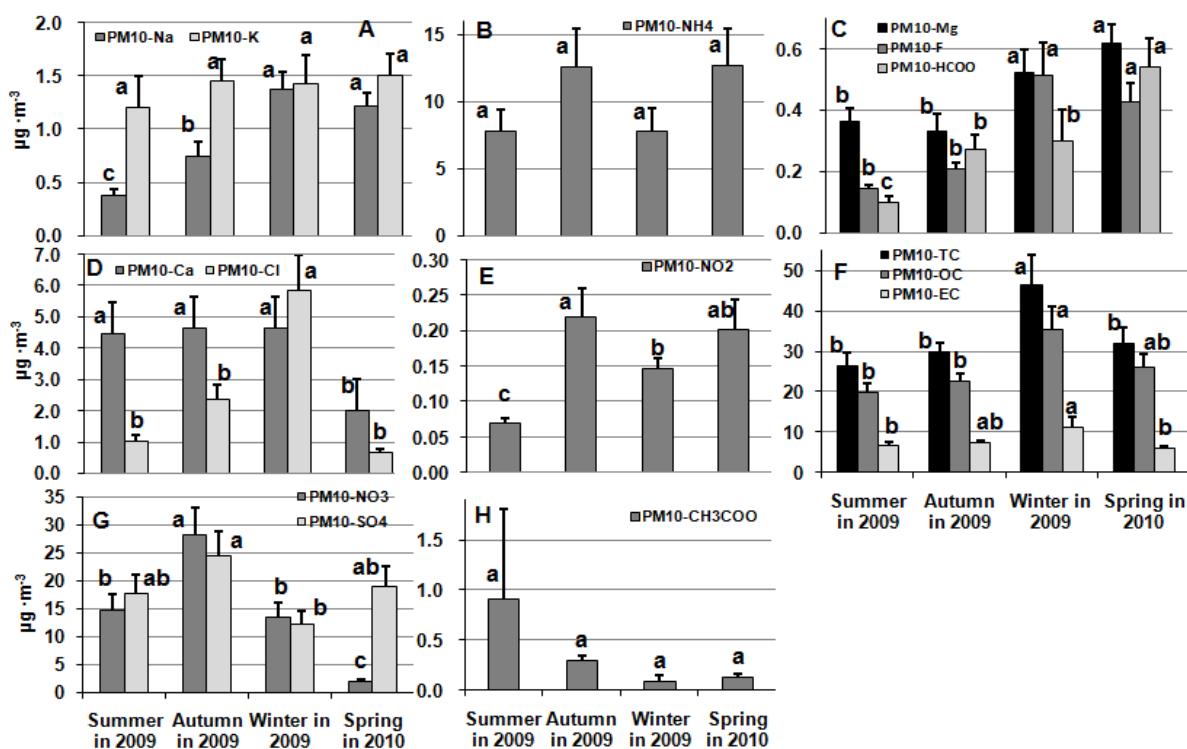


Fig. 3. Seasonal variations of cations, anions, OC and EC of PM_{10} from June 2009 to March 2010. Notes: Bar is standard error. Letter above column refers to the difference for same ions through seasons.

PM_{10} , concentrations of NH_4^+ , K^+ and Mg^{2+} in $PM_{2.5}$ have no significant differences through seasons (Fig. 4). In spring, higher mean concentration values were found for NO_3^- , Cl^- and $HCOO^-$, but lowest value for Ca^{2+} in current study. The high Ca^{2+} concentration observed in Xi'an (Shen *et al.*, 2009) was due to dust outbreaks. The fact that the lowest Cl^- concentration in PM_{10} and highest in $PM_{2.5}$ in spring indicated that Cl^- presented mainly in the fine particle fraction rather than PM_{10} . In summer, most ions showed lower average daily mean concentrations than other seasons, likely due to wet weather conditions and dense flora, which could wash off or reduce the pollutants. In autumn, SO_4^{2-} , NH_4^+ and Ca^{2+} concentrations were higher than those in other seasons, similar to those in PM_{10} . Mean K^+ concentration was the highest in autumn, might related to straw burning (Shen *et al.*, 2009). NO_3^- concentration in autumn appeared to be the highest in PM_{10} , but lowest in $PM_{2.5}$, indicating that NO_3^- is mostly in the form of PM_{10} rather than in $PM_{2.5}$.

In general, Ca^{2+} , NO_3^- , SO_4^{2-} concentrations after 2008 were lower than that obtained in the previous years (Table 2; He *et al.*, 2001; Sun *et al.*, 2004; Wang *et al.*, 2005; Duan *et al.*, 2006; Song *et al.*, 2006; Shen *et al.*, 2008; Deng *et al.*, 2010). This is likely due to reductions in both building construction and factory activities. The average daily mean concentrations of SO_4^{2-} , Ca^{2+} , K^+ , Na^+ and Mg^{2+} in spring from this study were lower than those in spring 2004 for both storm and non-storm days (Table 2; Sun *et al.*, 2010), presumably due to positive controls of these ion sources in the capital city. Nevertheless, higher concentrations of NH_4^+ , NO_3^- and SO_4^{2-} were observed in spring 2010 in Beijing when compared with those measured in 2006 in Xi'an

(Table 2; Shen *et al.*, 2009). In summer, most available ions showed lower concentrations in comparison with those measured earlier in 2003 and 2006 both in Beijing and Xi'an (Table 2; Cui *et al.*, 2008; Cao *et al.*, 2012; Shen *et al.*, 2010). Lower concentrations were also observed in autumn from this study for most ions except NH_4^+ when compared to those in Xi'an in 2005 (Table 2; Shen *et al.*, 2011), due to more possible animals and humans activities in Beijing. In winter 2009, most ion concentrations were lower than those measured previously in 2005–2006 in Xi'an and 2001–2003 in Beijing, apart from SO_4^{2-} , OC and EC, for which similar concentrations were found between the current measurement and the earlier data from 2001–2003 in Beijing (Table 2; Wang *et al.*, 2005; Huan *et al.*, 2006; Shen *et al.*, 2008, 2011), due to efficient source control except fossil combustion and vehicle emission. In comparison with carbon data measured in 2004 in Hong Kong, OC concentrations were higher but EC concentrations lower in both spring and winter in Beijing (Table 1; Lee *et al.*, 2006), due to both vehicular and ship emissions' contribution to raise EC level in Hong Kong (Lee *et al.*, 2006). Whilst fine EC concentrations were lower in semi-arid area of Northeastern China than those measured in spring in Beijing (Table 1; Zhang *et al.*, 2012), due to a different geological features and crustal matters.

Metal Concentration and Their Seasonal Variation

There are 53–91 daily measurements from which the annual and seasonal mean concentrations were calculated shown in Fig. 5. All measured metal concentrations of PM_{10} and $PM_{2.5}$ in spring from this study showed higher

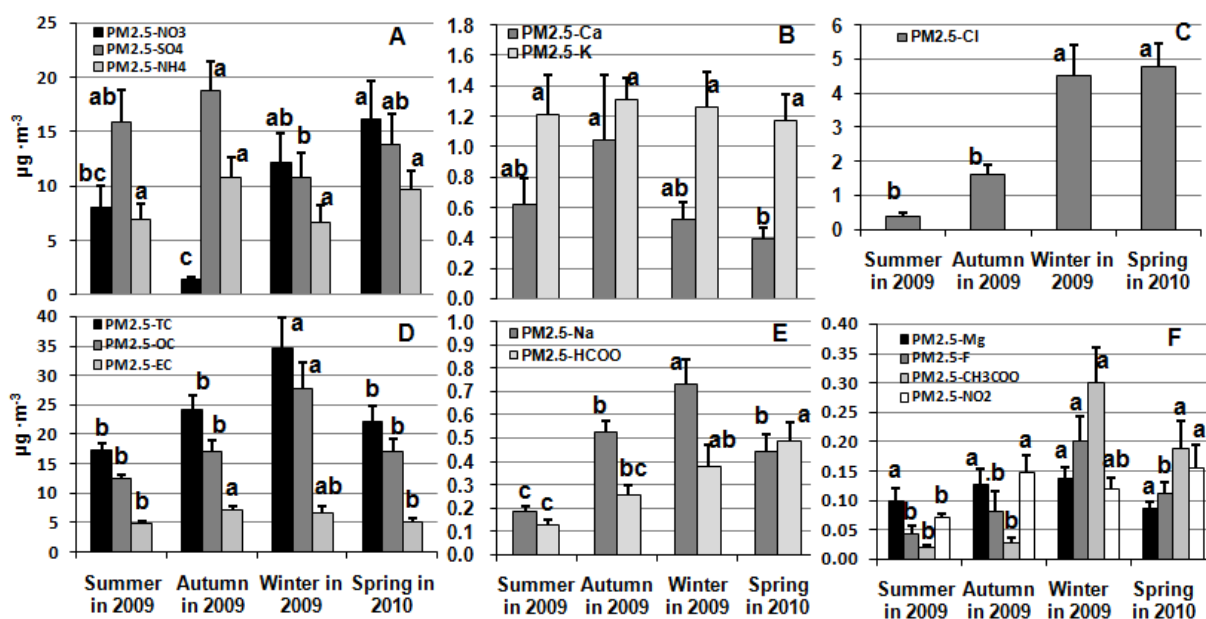


Fig. 4. Seasonal variations of cations, anions, OC and EC of $PM_{2.5}$ from June 2009 to March 2010. Notes: Bar is standard error. Letter above column refers to the difference for same ions through seasons.

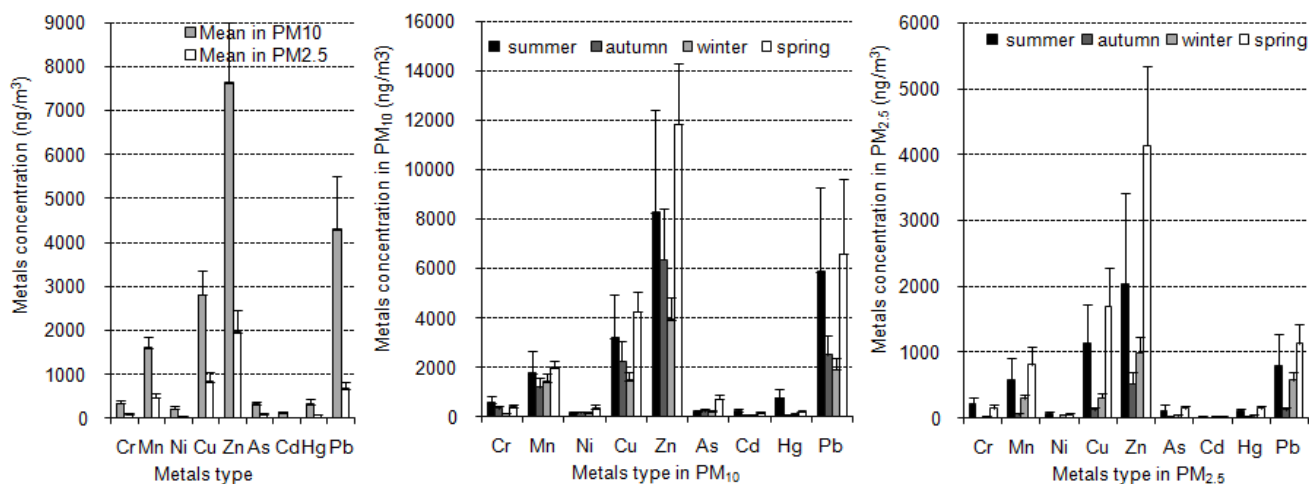


Fig. 5. Metals concentration and their seasonal variations both in PM_{10} and $PM_{2.5}$. Notes: Bar is standard error.

values than those in spring 2006 (Sun *et al.*, 2010). This might be due to pollution from increasing transportation. Much higher concentrations of Cr, Mn, Ni, Cu, Zn, As, Cd, Hg and Pb in PM_{10} than in $PM_{2.5}$ implies that these metals are mostly in form of coarse particle fraction (Fig. 5(A)). Metals Cr in both PM_{10} and $PM_{2.5}$ and Hg in PM_{10} showed higher values in summer than in other seasons, and the latter may be due to low vaporization temperature, whilst Zn and As in PM_{10} and Zn, Mn, Cu, Pb, Hg in $PM_{2.5}$ were observed with higher concentrations in spring (Figs. 5(B) and 5(C)), showing the feature of local crustal matters.

Considering that no significant correlations exist between metals and visibility, the metal data was not used in the following visibility analysis.

Visibility and the Influence Factors

Visibility Variation

The 29-year average visibility in Beijing, Tianjin, and Hebei from 1998 to 2008 was 19.4 and 14.4 km for non-urban and urban stations respectively (Zhao *et al.*, 2011). Worse situation was observed in this study, where average mean visibility was less than 10 km, only 5.64 km, which really becomes a serious problem. Days with visibility less or equal to 6 km (low visibility days) were counted separately from those with higher or equal to 10 km (high visibility days), and then the percent of the two type visibility days was calculated. In summary, higher percentages of low visibility days were found, representing around 50% or more of the total observations for all seasons. High visibility days were only occurred in summer for 32% of the total measurements, and 0% was observed for autumn, winter 2009 and spring 2010 (Fig. 6(A)).

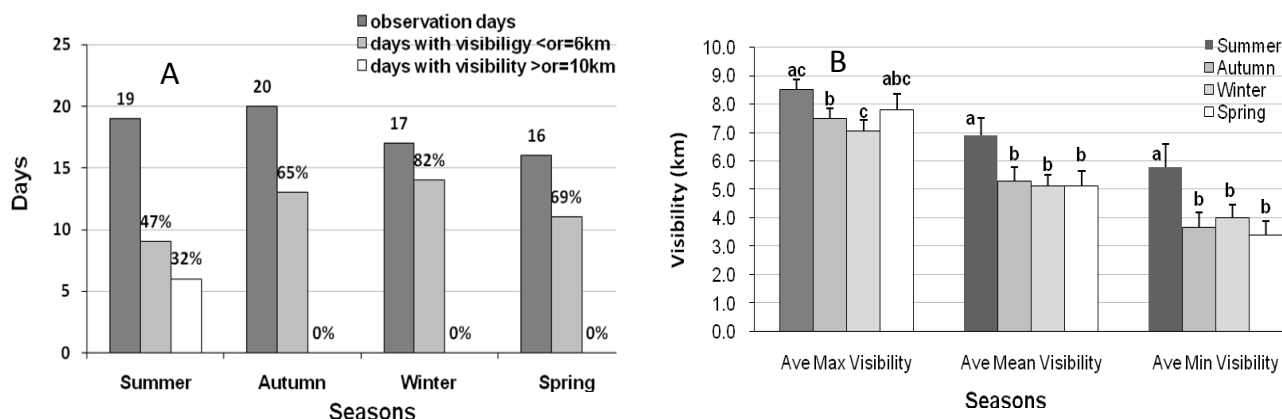


Fig. 6. Visibility through seasons from June 2009 to March 2010 (A) Days of different visibility observation; (B) Variation of visibility. Notes for Fig. 4(B): Bars stand for standard error. Significant difference is conveyed between seasons' data for each kind of particulate matter or visibility. Letter above column refers to the difference for same ions through seasons

Looking into the bad visibility situation, monthly average max, mean and min visibility were calculated through summer 2009 to spring 2010 by using daily max, mean and min visibility data respectively. The average mean and min visibility in summer was significantly higher than that at any other seasons (Fig. 6(B)). In case of the average max visibility, both spring and summer showed higher values, most likely due to high wind speed and high temperature having a dilution effect on the polluted air masses over the city. Different pictures were observed in the Grand Canyon and the Big Bend National Parks in the western United States, where the visibility was the best during winter months, worst during summer season and intermediate during spring and fall (Malm, 1989). Within China, similar visibility situations were found over the years of 1973–2007, when visibility was the best in spring in the northern regions (Beijing and Shenyang) and in summer in the southern and mid-western China (Chang, 2009). Other report on the seasonal mean aerosol optical depth, a positively related parameter to visibility, also showed higher values in spring and summer, and smaller values in autumn and winter from March 1993 to March 1995 (Li and Lu, 1997). Seasonal visibility variation indicates that in Beijing low visibility days appear mostly in autumn and winter, with the lowest average min visibility observed was 3.38 km and 3.65 km in spring 2010 and autumn 2009, respectively. This also agrees with previous observations, showing that the haze is most severe during winter and lightest during summer, due to fossil fuel combustion in winter and wet removal from precipitation in summer (Che *et al.*, 2009a).

PM, Ions and Carbons under Different Visibility Conditions

In order to analyze factors that influencing the atmospheric visibility, the measured parameters were compared under the two type visibility days, including PM, ion and carbon concentrations (Fig. 7). Concentrations of TSP, PM₁₀, PM_{2.5} and PM_{coarse} were all significantly higher in low visibility days than in high visibility days. Most mean component concentrations were higher worse visibility days, though significant differences between the two type visibility days

were observed for Na⁺, K⁺, Mg²⁺, HCOO⁻, NO₂⁻, NH₄⁺, and NO₃⁻ in PM₁₀, but only for Na⁺ and Mg²⁺ in PM_{2.5}. Mean Ca²⁺ and EC concentrations in PM₁₀ appeared to be similar for the two types of visibility days. Previous study also showed that secondary ions (NO₃⁻, SO₄²⁻, and NH₄⁺) were most abundant in the haze events (Shen *et al.*, 2009).

Correlations

Correlations between Visibility and PM Concentration

The concentrations of TSP, PM₁₀, PM_{2.5} and PM_{coarse} were significantly and negatively related to the mean visibility for the annual data (Fig. 8(A)). PM₁₀ and PM_{2.5} are both negatively related with visibility at a similar extent, with the correlation coefficients -0.52 and -0.50 , which are stronger than that observed for TSP and coarse particle, with lower correlation coefficients -0.33 and -0.30 . This indicates that the finer particles PM₁₀ and PM_{2.5} have larger contributions to low visibility than coarse particles. Previous studies also found that concentrations of PM₁₀, PM_{2.5} and PM_{10-2.5} showed strongest correlations with visibility (Huang *et al.*, 2009), and visibility was observed to be negatively correlate with PM_{2.5} at two stations in Beijing (Zhao *et al.*, 2011). Xu *et al.* (2005) found that the concentration of PM_{2.5} had greater influence on visual range than PM₁₀ in Hangzhou. Data collected in 1999–2000 also indicated that scattering of PM contributed to low visibility, especially for PM_{2.5}, which closely related with visibility (Song *et al.*, 2003). Visual range also showed stronger correlation with the concentrations of PM_{2.5} than the concentrations of PM₁₀ (Wang *et al.*, 2003; Song *et al.*, 2003). The similar degree of correlation between visibility and PM_{2.5} and PM₁₀ in this study might be site specific, that suffered high flow of traffic all the time. Seasonal analysis showed significant negative correlations for mean visibility with TSP and PM₁₀ concentrations in both summer and autumn, showing coefficients, -0.53 and -0.62 in summer and -0.70 and -0.62 in autumn respectively. The highest correlation was observed between visibility and PM_{2.5}, with coefficient up to -8.0 in autumn 2010 (Fig. 8(B)), and only in autumn, PM_{2.5} showed significant correlation with visibility.

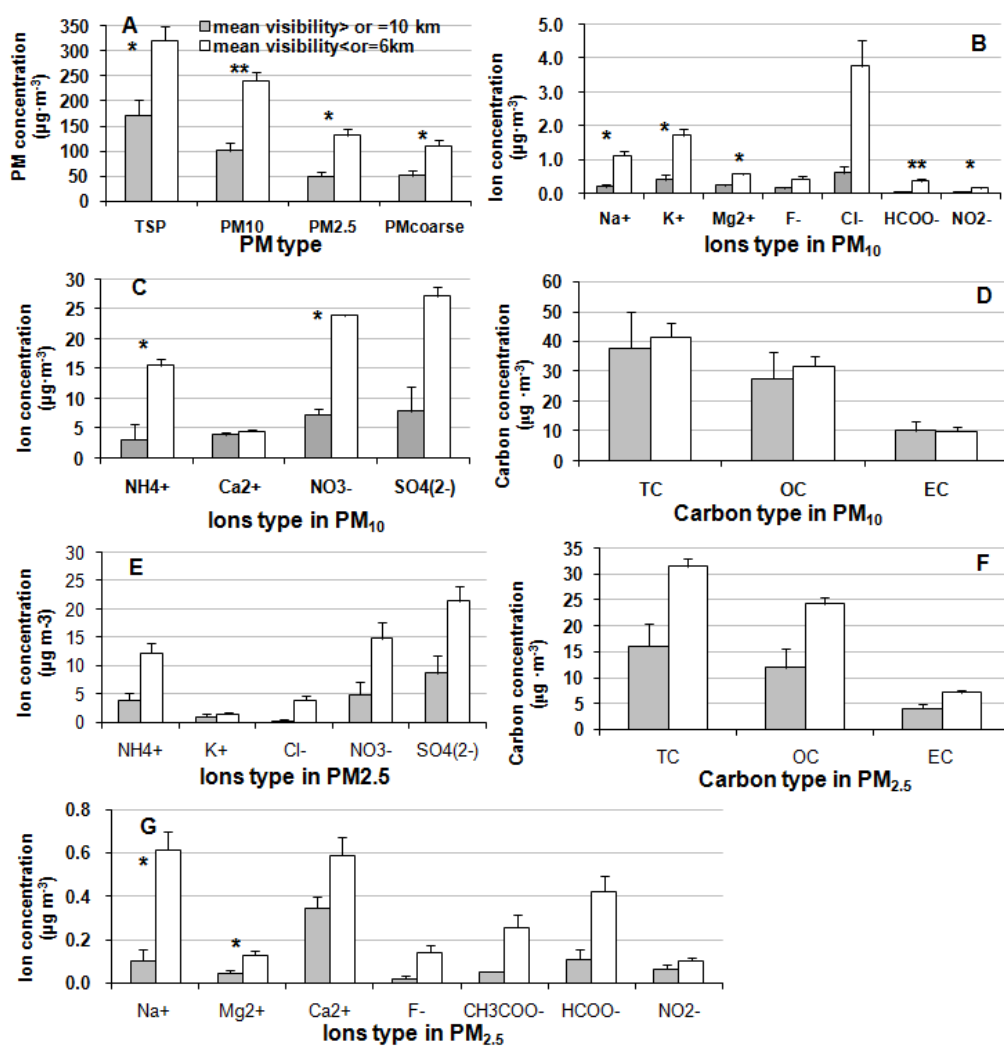


Fig. 7. PM, ions and carbons concentration under the different visibility conditions. Notes: Bars stand for standard error. Letter above column refers to significant difference for same ions between two levels of visibility.

Correlations between Visibility and ion and Carbon Concentrations in PM₁₀ and PM_{2.5}

Aerosol optical depth was considered to be affected by chemical composition (Che *et al.*, 2009b), which is also observed in this study in the annual data. NH₄⁺, SO₄²⁻, NO₃⁻ concentrations are significantly and negatively related to visibility both in PM₁₀ and PM_{2.5}, showing correlation coefficient stronger than -0.30 (Fig. 8(A)). This partly agrees with the data from two urban sites in Korea, where the worst visibility condition was well correlated with increasing SO₄²⁻, NO₃⁻ and EC mass concentrations from August 2002 to August 2004 (Kim *et al.*, 2006). As an important contributor to visibility, PM_{2.5} composes of the major species including sulfate, nitrate, ammonium, particulate organic matter and black carbon, which can degrade visual range (Tsai and Cheng, 1999; Cheung *et al.*, 2005). Na⁺, K⁺, Mg²⁺ and HCOO⁻ concentrations in PM₁₀ and Na⁺, Cl⁻, HCOO⁻, OC and EC in PM_{2.5} were also significantly and negatively related with visibility though the coefficient values were lower. Previous report showed that black (or elemental) carbon is the principal light-absorbing component

in atmospheric aerosols (Horvath, 1993, 1997). Meanwhile, concentrations of K⁺, Mg²⁺ in PM_{2.5}, Cl⁻, OC and EC in PM₁₀ and Ca²⁺, F⁻, CH₃COO⁻ and NO₂⁻ in both PM₁₀ and PM_{2.5} have no significant correlation with visibility (Fig. 8(B)). It partially agrees with the report by Yang *et al.* (2007), who showed that seasonal variation of crustal elements (Ca²⁺, Mg²⁺) has no apparent correlation with seasonal variation of visual range, the farthest distance that a person with normal eyesight can see in the current weather conditions (Yang *et al.*, 2007).

Further analysis on the correlation between ion, OC and EC concentrations and visibility through seasons indicates that no significant correlation exists for concentrations of CH₃COO⁻, NO₂⁻, Ca²⁺, F⁻, Cl⁻ in PM₁₀ and of Na⁺, K⁺, Mg²⁺, HCOO⁻, Ca²⁺, F⁻, NO₂⁻ and HCOO⁻ in PM_{2.5} with visibility in any season, therefore these parameters have not been included in Figs. 9(A) and 9(B). For both PM₁₀ and PM_{2.5}, significant correlations between parameter concentrations and visibility occurred only in autumn, when ions, OC and EC showed greater contribution to low visibility. These components included NH₄⁺, NO₃⁻, SO₄²⁻,

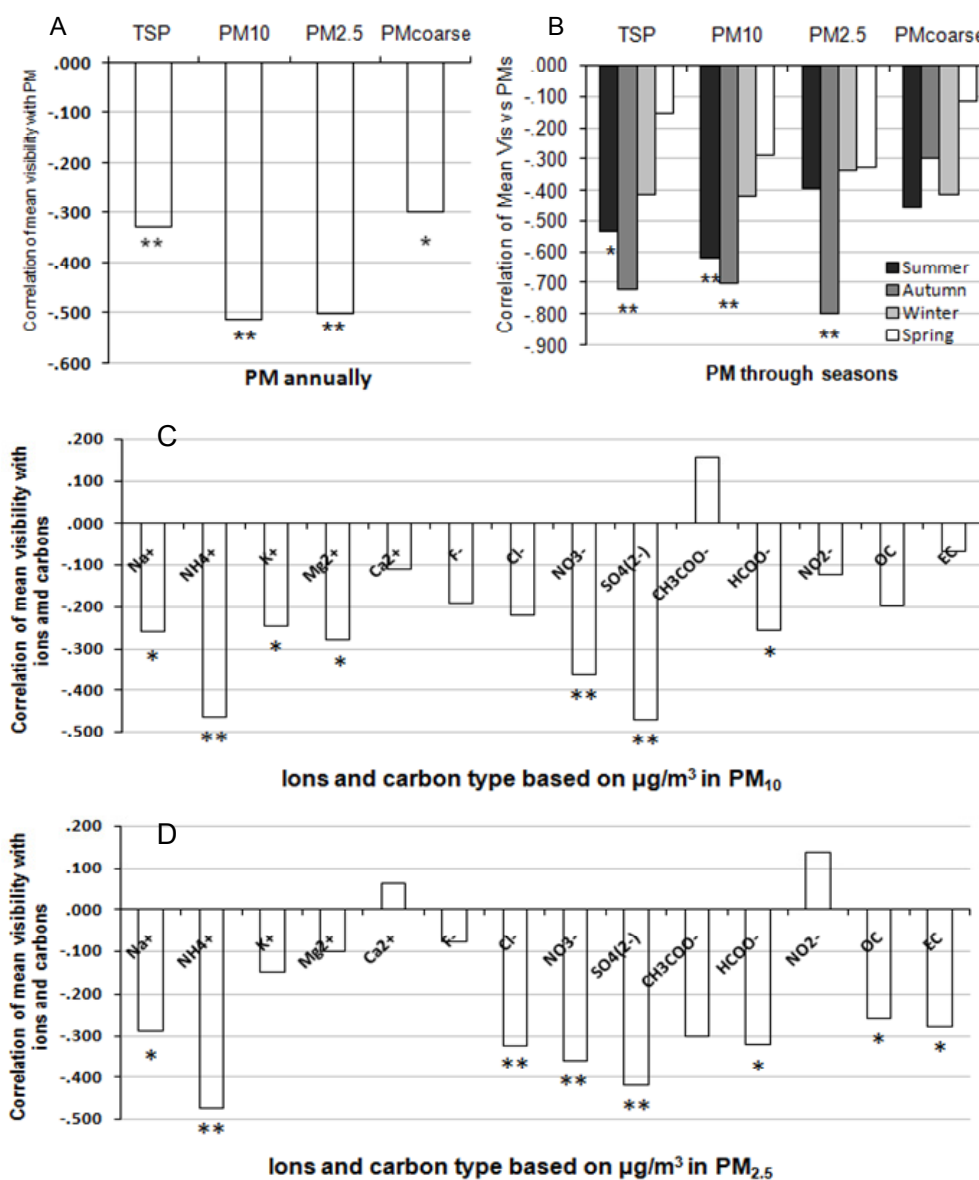


Fig. 8. Correlations between visibility and PM concentration annually and seasonally, between visibility and ions & carbons concentration in PM₁₀ and PM_{2.5} annually. Notes: Asterisk stands for significant correlation with ** at $\alpha = 0.01$ level and * at $\alpha = 0.05$ level.

OC and EC in both PM₁₀ and PM_{2.5}, Na⁺, K⁺, Mg²⁺ and HCOO⁻ in PM₁₀, and Cl⁻ in PM_{2.5}, possibly co-reacting to form into extinction matters at adaptable humidity and temperature. Except OC in PM_{2.5}, which was significantly positively correlated with visibility, other parameters were all negatively correlated with visibility (Figs. 9(A) and 9(B)). The positive correlation between fine OC and visibility might be related to chemical reactions between OC and other chemical pollutants, which produces certain catalysts that enhance visibility.

Both current and previous studies within China indicated that chemical parameters contributing to visibility are varied at different locations and seasons, but SO₄²⁻, NH₄⁺, NO₃⁻, OM and EC are always strong contributors. In April, 2007, PM_{2.5} sulfate was found to be the dominant species that affected visibility in urban Guangzhou, south China,

whilst nitrate, organics and elemental carbon also contributed a lot (Tao *et al.*, 2009). One year measurement of PM_{2.5} from March 2006 to February 2007 indicated that large sized (NH₄)₂SO₄ and organic mass were the most important contributors to visibility impairment at urban and rural sites (Yang *et al.*, 2012). (NH₄)₂SO₄, particulate organic matter, NH₄NO₃ and EC are main contributors to visibility during November–December 2010 in a rural site of southern China (Wang *et al.*, 2012). Zhang *et al.* (2012) observed that organic mass, (NH₄)₂SO₄, NH₄NO₃ and EC contributed to low visibility, in June 2009–May 2010, Xiamen, southern China. Tao *et al.* (2012) also concluded that fine (NH₄)₂SO₄, NH₄NO₃, OM were the most important contributors to light extinction coefficients in winter in urban Guangzhou, China.

International comparisons also indicate that SO₄²⁻, NO₃⁻, OM and NH₄⁺ are major contributors to low visibility.

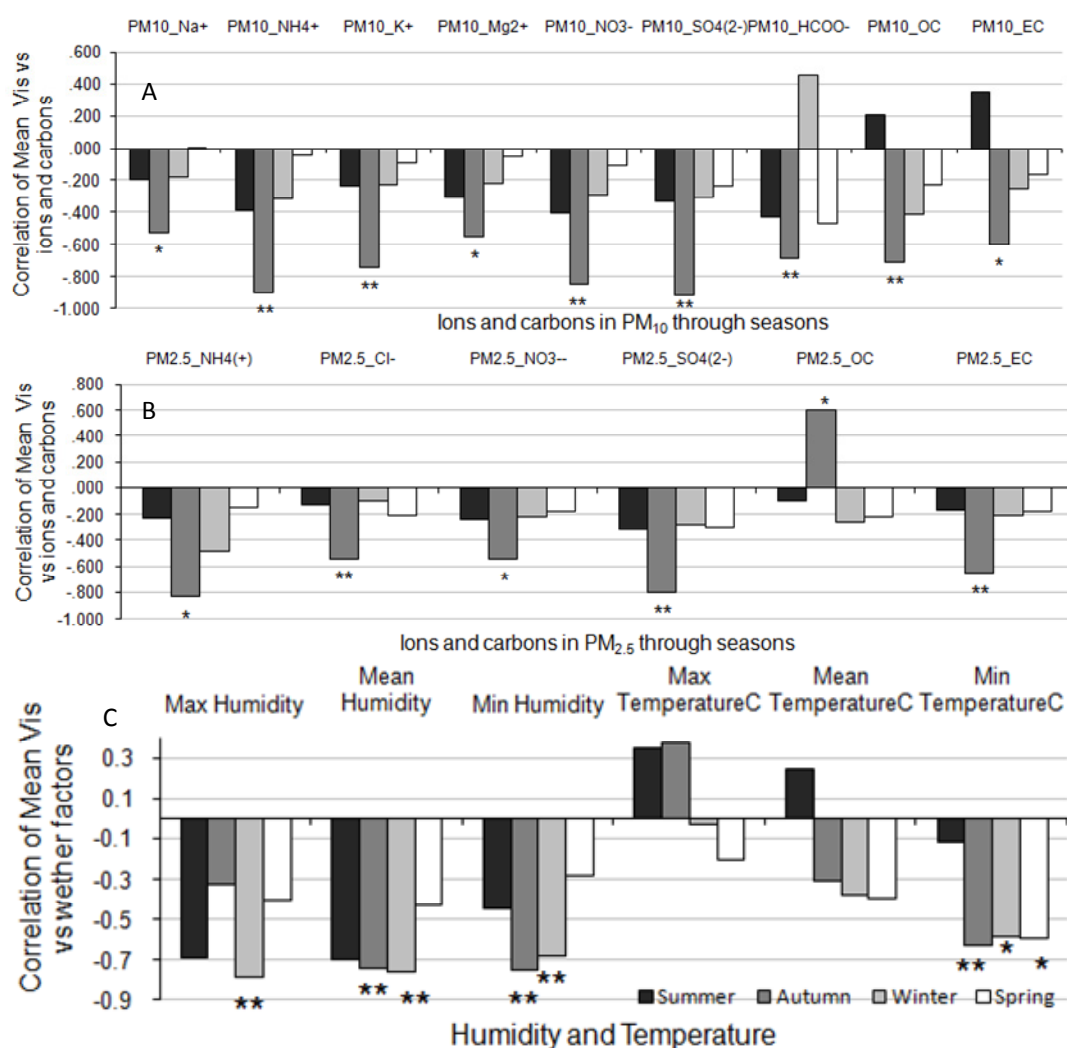


Fig. 9. Correlations between visibility and ions & carbons concentration in PM₁₀ and PM_{2.5}, between visibility and humidity or temperature through seasons. Notes: Asterisk stands for significant correlation. ** refers to $\alpha = 0.01$ level and * at $\alpha = 0.05$ level.

Sulfate associated with anthropogenic emissions of sulfur dioxide, is the single largest contributor to visibility reduction, except in the northwestern United States, where organic aerosols contribute the most (Malm, 1989). Particulate water, NO₃⁻, organic matter and NH₄⁺ were the major particulate species contributing to light scattering in the San Joaquin Valley in California between December 25, 2000 and January 7, 2001 (Chen *et al.*, 2009). In an Asian city, metropolitan Kaohsiung of Korea, PM_{2.5} measurement in November 1998 to December 2001 showed that sulfate was the most sensitive species to the visibility variation, suggesting that the reduction of fine sulfate could effectively improve the visibility of metropolitan Kaohsiung (Yuan *et al.*, 2006). Tao *et al.* (2012) also concluded that fine (NH₄)₂SO₄, NH₄NO₃, OM were the most important contributors to light extinction coefficients in winter in urban Guangzhou, China.

Correlations between Visibility and Weather Factors

High relative humidity and low wind speed were found

to be the main factors affecting visual range in Beijing in a previous study (Song *et al.*, 2003). However, no significant correlation was observed in this study between wind speed and visibility, so that only humidity and temperature was showed in Fig. 9(C) to evaluate weather influence on visibility. Negative correlations occurred between daily max, mean, min humidity and daily mean visibility at all seasons, but significant correlations were observed only in autumn and winter, indicating the important effect of humidity on visibility during the colder seasons. Previous results also showed that the influence of meteorological factors on visual range was varied in different seasons (Xu *et al.*, 2005). Another study on regression analysis indicated humidity as a dominant factor affecting remote visibility in the coastal area of central Taiwan (Cheng and Tsai, 2000); whilst Yan *et al.*, (2004) found that very high humidity in summer also lead to a short term low visibility in Beijing. The latter phenomenon was also observed in the current study, which showed correlation coefficients about -0.7 in summer, although they were not significant. The reason lies in

the fact that those secondary ions possess strong moisture absorption ability, which leads to scattering of light, then to low air visibility. Some scientists thought that meteorological factors, such as wind speed and humidity, can also play a role in the variation of the visual range by influencing the concentration of PM_{2.5} (Larson and Cass, 1989; Xu *et al.*, 2005). Only minimum temperature was negatively and significantly correlated with visibility in autumn, winter and spring. No significant correlation was observed for temperature with visibility in summer (Fig. 9(C)), when maximum and mean temperatures even positively correlated with visibility, due to that very high temperatures in summer may decompose the chemicals having negative effects on visibility.

CONCLUSIONS

Based on the investigation in this study, we have concluded as the follows:

- (1) There is a large percentage of PM exceeding the second rate of Ambient Air Quality Standards (GB3095-2012) in China. Seasonal variations have been observed in the concentrations of PM with TSP, PM₁₀ concentration were in the order spring > winter > autumn, while higher PM_{2.5} concentrations were observed in autumn and winter than in spring. This indicates that further controls of PM concentrations are needed especially for PM₁₀ in spring and PM_{2.5} in autumn and winter.
- (2) Seasonal variation was observed for the measured chemical components due to different pollution source features and meteorological conditions. Higher component concentrations occurred for CH₃COO⁻ in PM₁₀ in summer and for NO₃⁻, SO₄²⁻, NO₂⁻, NH₄⁺ in PM₁₀ and SO₄²⁻, NH₄⁺, Ca²⁺, EC in PM_{2.5} in autumn. Winter months showed higher concentrations of OC, EC, Cl⁻ and Na⁺ in PM₁₀ and of Cl⁻, NO₃⁻, OC, EC, Na⁺, F⁻, CH₃COO⁻ and NO₂⁻ in PM_{2.5}. In spring, concentrations of NH₄⁺, Mg²⁺, HCOO⁻ in PM₁₀ and Cl⁻, HCOO⁻ and NO₂⁻ in PM_{2.5} was higher, whilst Ca²⁺ and NO₃⁻ in PM₁₀ showed the lowest levels.
- (3) The percentage of low visibility (no more than 6 km) days is higher in comparison with high visibility days (no less than 10 km). Summer showed better visibility than any other seasons. Concentrations of TSP, PM₁₀, PM_{2.5}, PM_{coarse}, ions, OC, EC and metals were significantly higher in low visibility days than that in high visibility days. PM₁₀ and PM_{2.5} are both negatively related with visibility at a similar extent, and the correlations were stronger than for TSP and coarse particles. This indicates that finer particles PM₁₀ and PM_{2.5} are strong contributors to low visibility.
- (4) Visibility was also affected by different chemical components and appeared the obviously seasonal pattern. In summer, high TSP, PM₁₀ concentrations contributed significantly to low visibility. In autumn, high concentrations of TSP, PM₁₀, PM_{2.5}, SO₄²⁻, NO₃⁻, NH₄⁺, K⁺, HCOO⁻, OC, EC, Mg²⁺, Na⁺ in PM₁₀, and SO₄²⁻, NH₄⁺, NO₃⁻, Cl⁻, EC in PM_{2.5} showed stronger effect on visibility. High humidity and low temperatures contribute to low visibility in winter and autumn, and whilst in spring, low temperature easily leads to low visibility.

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