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# The ion chemistry and the source of PM<sub>2.5</sub> aerosol in Beijing

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## Abstract

Daily PM<sub>2.5</sub> aerosol samples were collected at five sites in Beijing for a 3-year period from 2001 to 2003. Concentrations of the water-soluble ions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, NO<sub>2</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HCOO<sup>-</sup>, MSA, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>) and 23 elements were measured for a total of 334 samples. A relatively even spatial distribution throughout Beijing and a significant seasonal variation were observed. SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, and K<sup>+</sup> were the major ions and existed mainly in the form of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>, NaCl, KCl, and CaCl<sub>2</sub> in aerosol particles. Most ions showed high concentrations in winter and low in summer. Secondary ions, mainly SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, exhibited high concentrations in both summer and winter due to the secondary transformation accelerated under high humidity and strong solar radiation in summer and the higher concentration of SO<sub>2</sub> from coal burning and the lower removal rate in winter. The formations of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were determined largely by temperature and NH<sub>4</sub><sup>+</sup>, respectively. Temperature, relative humidity, rainwater frequency, and air mass origin might be the main factors regulating the aerosol distribution. Crustal ions exhibited sporadic but high peaks in spring due to the intrusion of dust from west and northwest of China. The Ca<sup>2+</sup>/Al ratio was used to indicate the mixing of different dust sources. Factor analysis showed that the secondary formation of coal/biomass burning products, crust, industrial and traffic emissions were the major sources of the fine aerosols in Beijing. Traffic source became more significant with motorization in recent years.

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**Keywords:** Water-soluble part; Ions; Speciation; Seasonal variation; Secondary transformation; Sources

## 1. Introduction

As the capital of China, Beijing (39.9N, 116.4E) with ~14.6 million inhabitants distributed over 16,800 km<sup>2</sup> has been facing serious particulate pollution in air

quality, has been listed as one of the top ten pollution cities in the world, as it has experienced a rapid increase in both energy consumption and vehicle quantities for the past two decades, plus the invaded dust from outside Beijing throughout the entire year, especially in spring. While many studies on Total Suspended Particulate (TSP, particle size smaller than 100 μm) and particle size smaller than 10 μm (PM<sub>10</sub>) have been reported since the 1980s (Winchester et al., 1981; Cheng et al., 2000; Kim et al., 2002; Xiao and Liu, 2004), there were much less studies on particle size smaller than 2.5 μm (PM<sub>2.5</sub>),

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which is commonly defined as fine particles. The first comprehensive study on  $PM_{2.5}$  in Beijing was done in 1989–1990 (Chen et al., 1994). The average concentration of  $PM_{2.5}$  for the four seasons was reported to be in the range of 70–90  $\mu\text{g m}^{-3}$ . He et al. (2001) and Ye et al. (2003) reported  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  to be the dominant ionic species in  $PM_{2.5}$ , which accounted for about one-third of the total  $PM_{2.5}$  mass in Shanghai and Beijing. Yao et al. (2002) investigated the formation of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in  $PM_{2.5}$  in understanding the origin of these species. They found that a large part of these species might be formed through the direct emissions of  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$ . Hu et al. (2002) studied the seasonal variation of ionic species in fine particles in Qingdao during 1997–2000. Their results showed that the concentrations of major ions,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ , and  $\text{K}^+$ , were higher in the heating season than in the non-heating season. Energy consumption and vehicle emission are found to be major sources of  $PM_{2.5}$ .

$PM_{2.5}$  particles can more readily penetrate into lungs and increase respiratory and mutagenic diseases (Shwartz et al., 1996; Hughes et al., 1998). There is a widely accepted hypothesis that chemical components of particles and their capacity to carry potentially toxic substances may be the main factors for health effects, but it is not yet clear as to which factors are determinant. It was reported that water-soluble ions such as sulfate, nitrate, and other acid-rain-related pollutants had severe effects on human health (Raizenne et al., 1996). Besides, some epidemiological data indicated that the possible seasonal effects of particulate, for example, there were larger number of deaths and hospitalizations with the same particulate exposition in summer rather than in winter (Ostro, 1995; Michelozzi et al., 1998). Therefore, understanding the composition, variation, sources, and the formation of secondary ionic species, with an emphasis on sulfate and nitrate, has been the key issue and hence the urgency in the study on air quality and its control policy.

Coal is used both industrially and domestically in Beijing and  $\text{SO}_2$  is mainly got from coal burning. In recent years, as the clean fuels such as natural gas and liquefied petroleum gas have replaced coal to be a part of the domestic heating, and also because low-sulfur coal is recommended for industrial use,  $\text{SO}_2$  emissions have been reduced. On the contrary,  $\text{NO}_x$  emissions and, in turn, nitrate as well as fine particle  $PM_{2.5}$ , have increased rapidly, as the amount of vehicles in Beijing has grown up at a rate of 15% per year since 1990, and has now exceeded 2.1 million. In addition, the industrial emissions from 4019 factories, currently in Beijing, may have worsened the surrounding environment.

With the development of economy and the control of pollutant emissions, the status of air quality in Beijing might be different from years ago. To understand the current air pollution and the characteristics of air

pollutants as well as their impact on air quality, we present a 3-year measurement of the aerosol components, their chemical forms, the seasonal variations at five sites in Beijing, and also investigated the possible factors determining the variation and the formation mechanisms of secondary ions to explain the observation, and the relative contribution of both natural and anthropogenic sources.

## 2. Experimental

### 2.1. Sampling

Aerosol samples of  $PM_{2.5}$  were collected in four seasons from 2001 to 2003 at five sampling sites, i.e. (1) a traffic site, located in the campus of the Beijing Normal University (BNU) between the 2nd and 3rd Ring Roads, (2) an industrial site near the Capital Steel Company (CS), (3) a residential site, Yihai Garden (YH), located near the South 4th Ring Road, and (4) the rural sites at Miyun (MY) and Pinggu (PG) in the suburban areas of Beijing, China, using a medium-volume sampler (model (TSP/ $PM_{10}$ / $PM_{2.5}$ )-2; ow rate, 77.59  $\text{L min}^{-1}$ ). The traffic site is located on the roof (~40 m high) of the Science and Technology Building at BNU. The industrial site is located on the roof (~4 m high) of a building, which is close to the Capital Steel Company. The residential site is located on the roof (~40 m high) of a residential building. The three sampling sites in urban areas could basically be the representatives over urban Beijing. The location of sampling sites was shown in Fig. 1 (a).  $PM_{2.5}$  were collected on Whatman<sup>®</sup> 41 filters (Whatman Inc., Maidstone, UK) for element and ion analysis. The sampling time was nominally 12 h with sampling starting at 8:00 a.m. every day. The samples were put in polyethylene plastic bags right after sampling and preserved in a refrigerator. All those filters were weighed before and after sampling with an analytical balance (Sartorius 2004MP, reading precision 10  $\mu\text{g}$ ) after stabilizing under constant temperature ( $20 \pm 5^\circ\text{C}$ ) and humidity ( $40 \pm 2\%$ ). A total of 334 aerosol samples were collected and used in this study. All the procedures were strictly quality-controlled to avoid any possible contamination of the samples.

### 2.2. Chemical analysis

#### 2.2.1. Ion analysis

One-fourth of each sample and blank was extracted ultrasonically by 10 ml water, which was deionized to a resistivity of 18  $\text{M}\Omega\text{ cm}^{-1}$ . After passing through microporous membranes (pore size, 0.45  $\mu\text{m}$ ; diameter, 25 mm; made by the affiliated plant of Beijing chemical school), the filtrates were determined for pH with a pH meter (model, Orion 818). Each filtrate was stored at

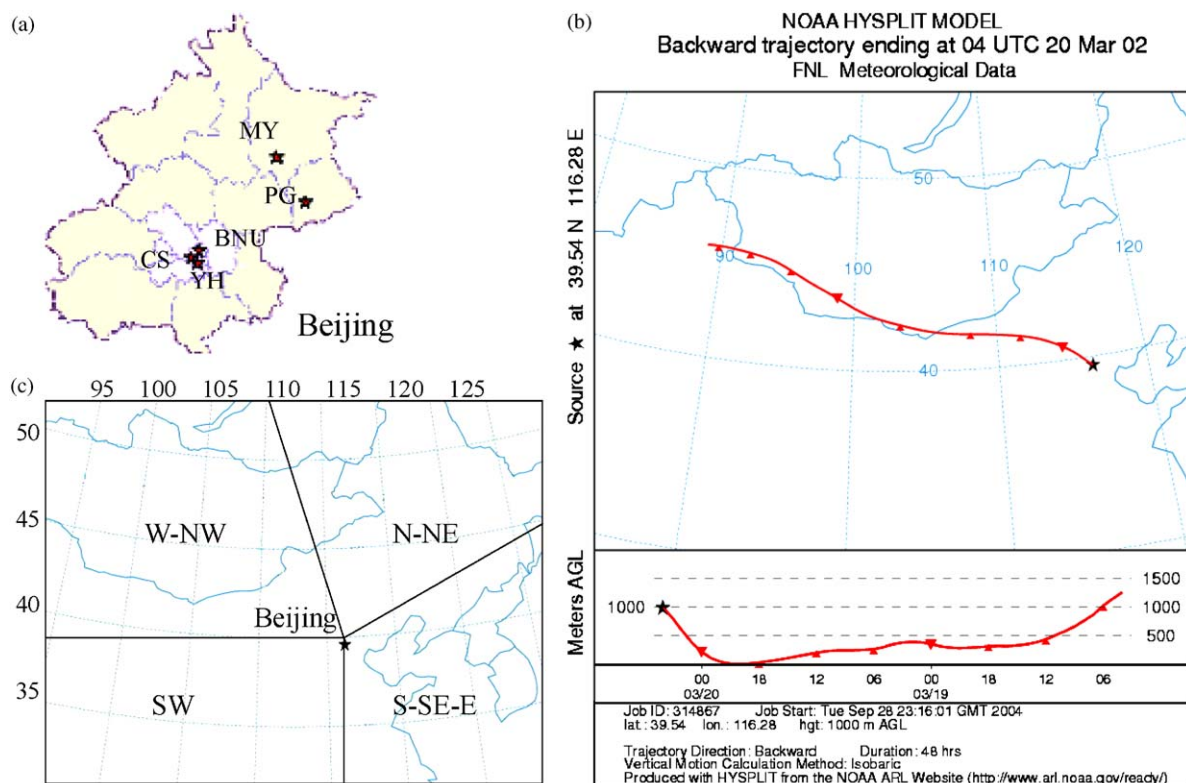


Fig. 1. (a) Sampling sites, (b) representative back trajectory on 20 March 2002 ending at Beijing; the triangles represent air mass locations at 6-h intervals and (c) the four sectors got from the classification of 2-day back trajectories ending at Beijing.

4 °C in a clean tube for analysis. Ten anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_2^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{HCOO}^-$ ,  $\text{MSA}$ ,  $\text{C}_2\text{O}_4^{2-}$ ) and five cations ( $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ) were analyzed by Ion Chromatography (IC, model, Dionex 600), which consists of a separation column (Dionex Ionpac AS11 for anion and CS12A for cation), a guard column (Dionex Ionpac AG 11 for anion and AG12A for cation), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50), and a gradient pump (Dionex Ionpac GP50). The gradient weak base eluent (76.2 mM NaOH + H<sub>2</sub>O) was used for anion detection, while the weak acid eluent (20 mM MSA) for cation detection. The recovery of each ion was in the range of 80–120%. The relative standard deviation (SD) of each ion was less than 5% for the reproducibility test. The limits of detection (S/N = 3) were less than 0.04 mg L<sup>-1</sup> for anions and 0.006 mg L<sup>-1</sup> for cations. The quality assurance was routinely carried out by using Standard Reference Materials (GBW 08606) produced by the National Research Center for Certified Reference Materials, China. Blank values were subtracted from sample determinations. The details are given elsewhere (Yuan et al., 2003).

### 2.2.2. Element analysis

The sample filters were digested at 170 °C for 4 h in a high-pressure Teflon digestion vessel with 3 ml concentrated HNO<sub>3</sub>, 1 ml concentrated HCl, and 1 ml concentrated HF. After cooling, the solutions were dried, and then diluted to 10 ml with deionized water (resistivity of 18 MΩ cm<sup>-1</sup>). Total 23 elements (Al, Fe, Mn, Mg, Ti, Sc, Na, Eu, Ce, Sr, Ca, Co, Cr, Ni, Cu, Pb, Zn, Cd, V, S, As, Se, and Sb) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, model, ULTIMA, made by JOBIN-YVON Company, France). The detailed analytical procedures are given elsewhere (Zhuang et al., 2001; Sun et al., 2004). Elements were used as the indicators of different sources in this study.

### 2.3. Meteorological data and the trace gases

The meteorological data, including temperature, atmospheric pressure, wind speed, relative humidity (RH), cloud cover, vapor pressure etc. was downloaded from National Climate Data Center (<http://cdc.cma.gov.cn>). Air Pollution Index (API = 100 corresponds to the Chinese air quality standard II) of PM<sub>10</sub>, SO<sub>2</sub>, NO<sub>2</sub>, CO, and O<sub>3</sub> in Beijing were collected from Beijing

Environmental Protection Bureau (<http://www.bjepb.gov.cn>) and converted to concentrations. The formulas used for converting API to concentration is

$$C = C_{\text{low}} + [(I - I_{\text{low}})/(I_{\text{high}} - I_{\text{low}})] \times (C_{\text{high}} - C_{\text{low}}),$$

where  $C$  is the concentration and  $I$  is the API value.  $I_{\text{high}}$  and  $I_{\text{low}}$ , the two values most approaching to value  $I$  in the API grading limited value table, stand for the value larger and lower one than  $I$ , respectively;  $C_{\text{high}}$  and  $C_{\text{low}}$  represent the concentrations corresponding to  $I_{\text{high}}$  and  $I_{\text{low}}$ , respectively.

Daily and seasonal variations of  $\text{SO}_2$  and  $\text{NO}_2$  from 2001 to 2003 are presented in Fig. 2. Based on their variations, four seasons were defined: spring (March, April, May), summer (June, July, August), autumn (September, October, November), and winter (December, January, February). The concentration of  $\text{SO}_2$  in winter (average  $163.65 \mu\text{g m}^{-3}$ ) was 11 times higher than that in summer (average  $14.84 \mu\text{g m}^{-3}$ ). As  $\text{SO}_2$  is mainly from coal burning in Beijing, the enhanced coal burning for heating might lead to the high concentration of  $\text{SO}_2$  in winter. The slight higher  $\text{NO}_2$  in winter might be due to burning activities, traffic, and industrial emissions.  $\text{O}_3$  showed high values in summer (average  $118.67 \mu\text{g m}^{-3}$ ) and low in winter (average  $30.47 \mu\text{g m}^{-3}$ ). As  $\text{O}_3$  indicates the oxidation ability of atmosphere, its high concentration in summer suggests that photochemical

oxidation might be an important process in the transformation of trace gases. Besides, there was a slight decrease of  $\text{SO}_2$  from 2001 to 2003, which appeared as a result of coal that has been replaced by clean fuels step-by-step in Beijing in recent years.

Based on the calculated data, in Beijing summer was relatively wet with monthly average amount of precipitation of 66.1, 57.7, 34.2 mm for June, July, and August, respectively, while winter was very dry with precipitation of 0.0, 9.6, 2.9 mm for December, January, and February, respectively. The ambient temperature in Beijing started to increase in April and reached a maximum in July–August (approximately  $27^\circ\text{C}$ ), then decreased to a minimum of  $-5^\circ\text{C}$  in January. In summer, the removal of aerosol particles by wet deposition is maximal and the possibility for photochemical formation of aerosol particles from their gaseous precursors is also at a maximum (high  $\text{O}_3$  concentration and high temperature), whereas in winter the primary emission is most efficient and may be accumulated in the atmosphere caused by the low inverse layer. The wind speed was higher in spring (average  $3.5 \text{ m s}^{-1}$ ) and autumn (average  $3.8 \text{ m s}^{-1}$ ) and lower in summer (average  $2.0 \text{ m s}^{-1}$ ) and winter (average  $1.8 \text{ m s}^{-1}$ ), indicating that the long-range transport of aerosols from outside Beijing is efficient in spring and autumn, especially in the spring dust periods (with the average wind speed of  $5.5 \text{ m s}^{-1}$ ).

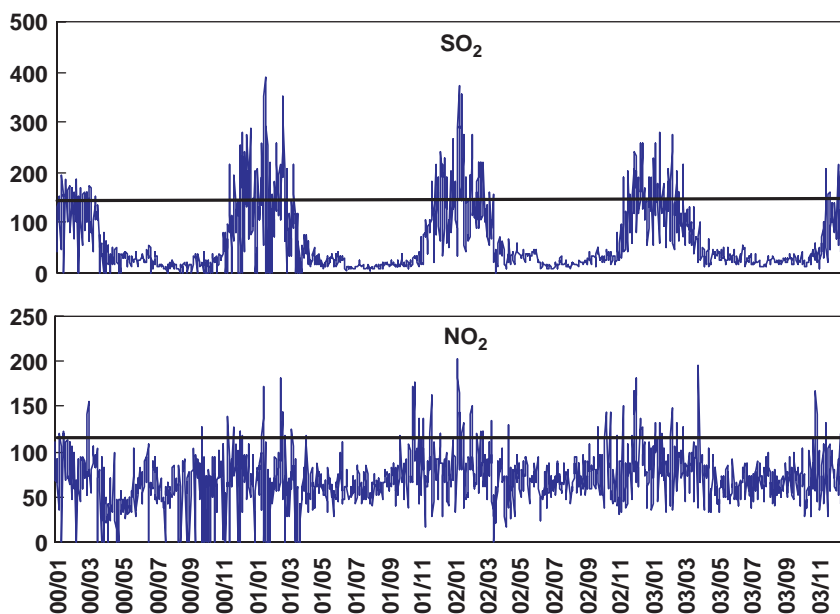


Fig. 2. Daily and seasonal variations of  $\text{SO}_2$  and  $\text{NO}_2$  from 2001 to 2003 in Beijing. (Unit:  $\mu\text{g m}^{-3}$ . The lines represent the Chinese standard level II: 150 for  $\text{SO}_2$ , and 120 for  $\text{NO}_2$ , respectively).

#### 2.4. Air mass trajectories

To identify the potential importance of different source regions on aerosol composition at the sampling sites, the air mass trajectories were calculated using the HYSPLIT 4 Model of the Air Resources Laboratory of NOAA (Draxler and Rolph, 2003). On every sampling day, a 2-day back trajectory was computed at 16:00 or 4:00 h UTC, and at 1000 m above the starting point, located at ground level. FNL Meteorological data have been used as the input. The model output is a set of latitude–longitude coordinates of the air parcel estimated position. A representative trajectory is shown in Fig. 1(b). With the statistical analysis of all these calculated trajectory directions, it has been found that the whole area could be classified into five sectors with different air . These sectors were shown in Fig. 1(c): (1) north–northeast (N–NE) sector represents the Northeast Plain, (2) south–southeast–east (S–SE–E) sector represents the eastern China as well as the western Pacific, (3) southwest (SW) sector represents the southwest China, (4) west–northwest (W–NW) sector represents the long fetch of dust air masses, and (5) an additional sector (local) represents the short trajectories that come from the local areas over Beijing, which are not shown in Fig. 1(c). These five sectors also represented long- or short-range transport. The first four sectors represent the long-range transport, while the last sector represents the short-range transport.

### 3. Results and discussions

#### 3.1. $PM_{2.5}$ mass concentrations

Mass concentrations of  $PM_{2.5}$  in Beijing were in the range of 11.1–1393.0  $\mu\text{g m}^{-3}$ , with a mean and SD of  $154.3 \pm 145.7 \mu\text{g m}^{-3}$  as shown in Table 1, which were higher than the values of  $77.5 \mu\text{g m}^{-3}$  in 1989 (Chen et al., 1994),  $129.0 \mu\text{g m}^{-3}$  in 1999 and 2000 (Yao et al., 2002), and  $109.6 \mu\text{g m}^{-3}$  in 2001 (Wang et al., 2004) measured in Beijing by other studies. Compared with the daily average of the standard value of  $65 \mu\text{g m}^{-3}$  for  $PM_{2.5}$  (US EPA, 1997), almost 79% of the daily  $PM_{2.5}$  mass concentrations in 2001–2003 were higher than the standard in this work, showing that fine particle pollution is extremely terrible in Beijing.

Strong temporal variations in  $PM_{2.5}$  mass concentrations were observed in Beijing. As illustrated in Table 1,  $PM_{2.5}$  mass concentrations were highest in winter, decreased through spring, autumn and tended to be lowest in summer. The  $PM_{2.5}$  mass averaged  $214.2 \mu\text{g m}^{-3}$  in winter, exceeding the  $154.3 \mu\text{g m}^{-3}$  annual average by 39%. The averages in spring, autumn, and summer were 162.1, 105.2, and  $93.3 \mu\text{g m}^{-3}$ , respectively.

The daily and seasonal variations of  $PM_{2.5}$ , trace gases, and meteorological parameters at BNU and their correlations were shown in Fig. 3. Generally,  $PM_{2.5}$  appeared weakly correlated with these parameters, as

Table 1  
Average concentrations ( $\mu\text{g m}^{-3}$ ) and the standard deviations (SD) of  $PM_{2.5}$  and ions in  $PM_{2.5}$  in four seasons in Beijing

PM <sub>2.5</sub>	Spring		Summer		Autumn		Winter		Total	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
No.	101	—	86	—	40	—	107	—	334	—
Mass	162.06	179.94	93.29	56.26	105.22	39.00	214.23	159.34	154.26	145.65
pH	5.99	0.87	5.48	0.49	5.92	0.54	5.10	0.89	5.57	0.84
Na <sup>+</sup>	0.61	0.64	0.24	0.17	0.21	0.15	0.88	0.52	0.55	0.54
NH <sub>4</sub> <sup>+</sup>	6.47	6.75	10.10	6.97	6.33	5.80	10.64	8.83	8.72	7.66
K <sup>+</sup>	1.09	0.97	1.29	1.25	0.76	0.74	2.48	2.16	1.55	1.63
Mg <sup>2+</sup>	0.24	0.20	0.10	0.07	0.06	0.06	0.20	0.17	0.17	0.16
Ca <sup>2+</sup>	2.54	2.46	0.73	0.60	1.16	1.70	1.68	1.67	1.63	1.90
F <sup>-</sup>	0.25	0.22	0.10	0.09	0.09	0.09	0.55	0.36	0.29	0.31
CH <sub>3</sub> COO <sup>-</sup>	0.21	0.57	0.15	0.26	0.06	0.10	0.22	0.39	0.18	0.41
HCOO <sup>-</sup>	0.04	0.05	0.08	0.08	0.07	0.07	0.13	0.12	0.08	0.10
MSA	0.07	0.32	0.06	0.07	0.02	0.03	0.01	0.03	0.04	0.18
Cl <sup>-</sup>	2.92	2.19	1.41	1.31	1.09	0.99	5.28	3.99	3.07	3.13
NO <sub>2</sub> <sup>-</sup>	0.64	0.70	0.27	0.26	0.12	0.13	0.40	0.42	0.41	0.51
NO <sub>3</sub> <sup>-</sup>	11.92	11.79	11.18	10.37	9.14	10.27	12.29	12.12	11.52	11.37
SO <sub>4</sub> <sup>2-</sup>	13.52	13.95	18.42	15.28	12.69	12.91	20.96	19.72	17.07	16.52
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	0.43	0.36	0.25	0.16	0.32	1.01	0.36	0.28	0.35	0.44
PO <sub>4</sub> <sup>3-</sup>	0.17	0.24	0.43	0.41	0.28	0.25	0.21	0.16	0.26	0.29

No. means the number of samples measured.

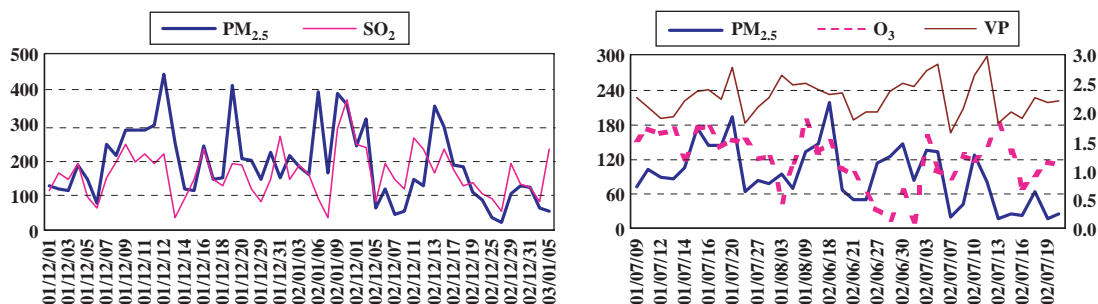


Fig. 3. The correlations between  $\text{PM}_{2.5}$  and  $\text{SO}_2$  in winter (left), and between  $\text{PM}_{2.5}$ ,  $\text{O}_3$ , vapor pressure (VP) in summer (right) at BNU during 2001–2003. (left axis:  $\text{PM}_{2.5}$ ,  $\text{SO}_2$  and  $\text{O}_3$  in  $\mu\text{g m}^{-3}$ , right axis: vapor pressure in kPa).

there might be many processes contributing to the formation of  $\text{PM}_{2.5}$ , and the measured  $\text{PM}_{2.5}$  mass measured could be the combination of all these processes. However, they showed clear correlations when the data were investigated seasonally. For example,  $\text{PM}_{2.5}$  was well correlated with  $\text{SO}_2$  in winter, with  $\text{O}_3$  and vapor pressure in summer. The high  $\text{PM}_{2.5}$  mass concentration in winter was most likely due to the combination of increased emissions from heating sources and the meteorological factors that limited dispersion; while in summer  $\text{PM}_{2.5}$  might be partially from the photochemical transformation and its low concentration was likely related to the high wet deposition. Besides, several severe high  $\text{PM}_{2.5}$  episodes occurred in spring due to the intrusion of dust from the west or northwest of China. For example, the highest value of daily average  $\text{PM}_{2.5}$  mass ( $1393.0 \mu\text{g m}^{-3}$ ) occurred when a super dust storm attacked Beijing on 20 March 2002. This was verified by the backward trajectory shown in Fig. 1(b), in which the air mass was shown to come from the northwest of China. Therefore, it must be noted that the air pollution in Beijing might be under the influence of local emissions as well as long-range transport from outside areas.

### 3.2. Ion composition and speciation of $\text{PM}_{2.5}$

#### 3.2.1. Ionic composition of $\text{PM}_{2.5}$

Water-soluble ions comprise a large part of aerosol particles and play an important role in the atmosphere. The concentrations of various ionic species in the whole sampling period are shown in Table 1. The sum of ions contributed an average of 30% of  $\text{PM}_{2.5}$  mass concentration. The sum of the major cations (ammonium (19%), calcium (6%), potassium (4%)) and the major anions (sulfate (34%), nitrate (23%), chloride (7%)) contributed more than 90% of the total ion concentration, which were the most important alkaline and acidic species in  $\text{PM}_{2.5}$ , respectively.

The mass ratio of  $\text{NO}_3^-/\text{SO}_4^{2-}$  has been used as an indicator of the relative importance of mobile vs. stationary sources of sulfur and nitrogen in the atmo-

sphere (Arimoto et al., 1996; Yao et al., 2002; Xiao and Liu, 2004). The seasonal variation of  $\text{NO}_3^-/\text{SO}_4^{2-}$  shown in Fig. 4 ranged from 0.01 to 2.94 (mean = 0.71, SD = 0.48), comparable with the value of 0.67 measured during 2001–2003 in Beijing, higher than the value of 0.58 measured during 1999–2000 in Beijing (Yao et al., 2002), much higher than that in Shanghai (0.43; Yao et al., 2002), Qingdao (0.35; Hu et al., 2002), Taiwan (0.20; Fang et al., 2002), and Guiyang (0.13; Xiao and Liu, 2004). Arimoto et al. (1996) ascribed high  $\text{NO}_3^-/\text{SO}_4^{2-}$  mass ratios to the predominance of mobile source over stationary source of pollutants (Arimoto et al., 1996). In China, gasoline and diesel fuel contain 0.12% and 0.2% sulfur (by weight), respectively (Kato, 1996). The estimated ratios of  $\text{NO}_x$  to  $\text{SO}_x$  from the emission of gasoline and diesel fuel burning are 13:1 and 8:1, respectively. The sulfur content in coal is 1% and the estimated ratio of  $\text{NO}_x$  to  $\text{SO}_x$  is 1:2 from coal burning. It is reasonable to use  $\text{SO}_4^{2-}$  as an indicator of stationary emission and  $\text{NO}_3^-$  of mobile emission. The results indicated that air pollution from vehicle emissions (mobile source) in Beijing has become sever compared with that to a few years ago. Seasonally  $\text{NO}_3^-/\text{SO}_4^{2-}$  showed low values in winter (0.49) and summer (0.63) compared with that in autumn (0.93) and in spring (0.84). As shown in Fig. 2,  $\text{NO}_2$  was almost evenly distributed all the year round, while  $\text{SO}_2$  was higher in winter. The lower  $\text{NO}_3^-/\text{SO}_4^{2-}$  value in winter could be due to the high  $\text{SO}_2$  emission. In summer, high temperature, high RH, and high radiation are more favorable for the formation of  $\text{SO}_4^{2-}$ , and hypothetically the lower ratio of  $\text{NO}_3^-/\text{SO}_4^{2-}$  could be due to the higher  $\text{SO}_4^{2-}$  in summer.

Fig. 5 showed the comparison of the ion concentrations in different locations. The y-axis represented the ratio of the concentrations in the other sites to those we got in Beijing. It could be seen clearly that the aerosol pollution was more serious in Beijing than those sites in East Asia and Africa. Crustal species ( $\text{Ca}^{2+}$  as a representative) exhibited higher concentrations in Beijing than most of other cities. Pollution aerosol, such as sulfate, in Beijing was the highest amongst those

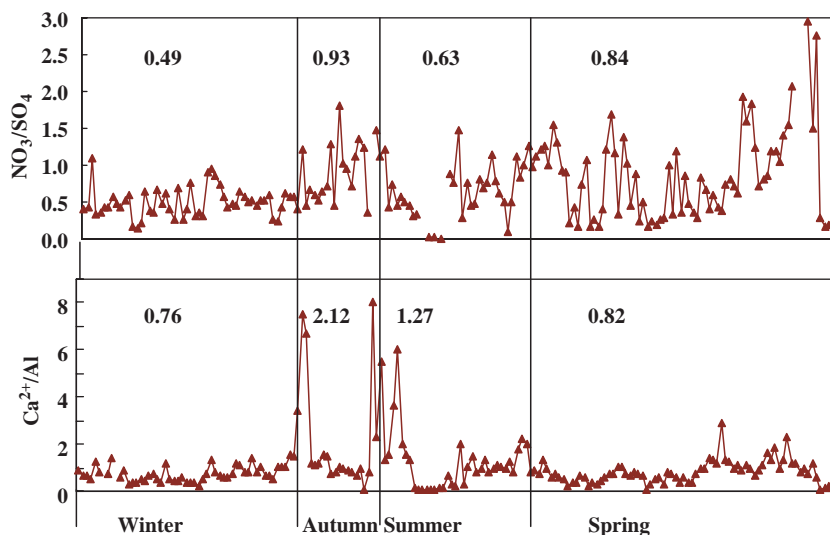


Fig. 4. Seasonal variations of  $\text{NO}_3^-/\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}/\text{Al}$  ratios at BNU during 2001–2003. (All the samples were grouped to the four seasons. The last five points denoted samples collected during dust storm. The average values in each season were shown in the figure).

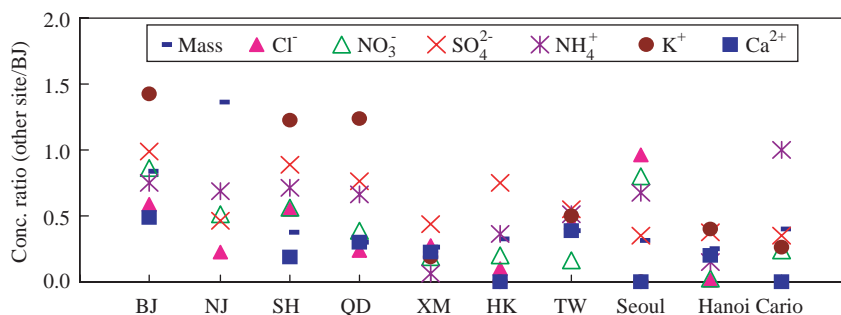


Fig. 5. Comparison of concentrations of  $\text{PM}_{2.5}$  and the major ions in various urban sites. (BJ: Beijing, China, (Yao et al., 2002); NJ: Nanjing, China, (Wang et al., 2003); SH: Shanghai, China, (Yao et al., 2002); QD: Qingdao, China, (Hu et al., 2002); XM: Xiamen, China, (Gao et al., 1996); HK: Hong Kong, (Ho et al., 2003); TW: Taiwan, (Fang et al., 2002); Seoul, Korea, (Park et al., 2004); Hanoi, Vietnam, (Hien et al., 2004); Cairo, Egypt, (Mahmoud et al., 2002))

urban areas reported in literature. The higher coal consumption combined with poor dispersion in winter, and the high photochemical reaction in summer could account for the very high concentrations of sulfate. Levels of nitrate and ammonium in Beijing were higher by a factor of 3–4, compared to those at other sites, which was likely due to heavy traffic and other local anthropogenic activities in Beijing. Such high levels of ammonium, nitrate, and sulfate indicated that pollution from acidic and secondary aerosol pollutants in Beijing has been a critical issue in the control of air quality.

### 3.2.2. Acidity of $\text{PM}_{2.5}$

The pH of  $\text{PM}_{2.5}$  aerosols at Beijing ranged from 3.94 to 7.65 (mean = 5.57, SD = 0.84) with a blank value of 5.74 as shown in Table 1. pH of the aerosol filtrate was a

parameter used to denote the acidity of the aerosols directly. It is well known that low pH values of aerosols result from acidic matters such as sulfate, nitrate, chloride, and carboxylic anions, whereas basic water-soluble matters such as ammonium, calcium, and magnesium result in the increase in pH values. The mean value of 5.57, a little lower than the blank value, indicated that although Beijing was not in the state-controlled zone of acid rain, it would face the acid problem in the near future.

The ion balance expressed by the sum of the equivalent concentration ( $\mu\text{eq m}^{-3}$ ) ratio of cation to anion (C/A) was an indicator to study the acidity of the environment. The ratio calculated from all the measured ionic species ranged from 0.63 to 3.28 (mean = 1.09, SD = 0.48). The mean ratio of 1.09, which was close



to 1, indicated that almost all of the ion components had been quantified. When the total equivalents of anions were plotted against the total equivalents of cations, the slope of the regression line was slightly lower than unity (slope = 0.87,  $R = 0.92$ ), which might be attributed to  $H^+$ , which was not counted in the calculation, or due to parts of  $NH_4^+$  that was probably vaporized into the gas phase. The highest values of both pH and C/A were on 20 March 2002 when a super dust storm attacked Beijing, which indicated clearly that the dust from West/Northwest China brought a large amount of crustal species and could alleviate the acidity of the local environment. With a closer consideration of the regression between cations and anions, an anion de (slope = 1.61,  $R = 0.80$ ) was found in the dust storm period, which might be attributed to the presence of bicarbonate or carbonate in the samples that was not measured with IC in this study. A positive correlation ( $R = 0.90$ ) was found when  $Ca^{2+}$  was plotted against the anion de, indicating that bicarbonate or carbonate could indeed account for the missing anion during the dust period. The interaction between carbonate and the pollutant gases ( $SO_2$ ,  $NO_x$ , HCl) or acidic particles ( $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ ) might be a major route to alleviate the acidifying processes.

### 3.2.3. The speciation of major ions

The chemical forms of those major ions, i.e.  $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ ,  $NH_4^+$ ,  $Ca^{2+}$ , and  $K^+$ , in aerosols in Beijing were identified by bivariate correlations. Table 2 showed the correlation coefficients and linear regression equations among these major ions. It could be seen that  $NH_4^+$  was closely correlated with  $SO_4^{2-}$ . The slope of the regression between  $NH_4^+$  and  $SO_4^{2-}$  ( $\mu eq$  vs.  $\mu eq$ ) for the whole data set was 1.14, which indicated the complete neutralization of  $SO_4^{2-}$  by  $NH_4^+$ , and suggested that  $(NH_4)_2SO_4$ , instead of  $NH_4HSO_4$ , was the major species formed by  $SO_4^{2-}$  and  $NH_4^+$ . In addition,  $NH_4NO_3$ , NaF, NaCl, and KCl were found to be the major chemical species in the aerosol particles based on their correlation coefficients. The concentrations of these species have been calculated based on the individual ion concentrations and their mutual relationships. For example, the

correlation coefficients decreased from 0.92 for  $NH_4^+ - SO_4^{2-}$ , 0.88 for  $NH_4^+ - NO_3^-$  to 0.71 for  $Na^+ - F^-$ . Therefore, the  $(NH_4)_2SO_4$  concentration was calculated first, then to  $NH_4NO_3$  and NaF, successively. The concentrations of the succeeding species were calculated based on the concentrations of the formed ions and the foregoing species. Table 3 showed the calculated concentrations of those major species in  $PM_{2.5}$ . Without counting the samples from the period of dust storm, the average concentrations of  $(NH_4)_2SO_4$  and  $NH_4NO_3$  ranged from 16 to 30 and from 5 to  $10 \mu g m^{-3}$ , respectively. The total secondary aerosol (TSA, refer to  $(NH_4)_2SO_4$  and  $NH_4NO_3$  here only) comprised a major part of the total water-soluble ions (TWSI), from 52.3% in spring to 72.0% in summer. However, during dust days, TSA only comprised 11.8% of TWSI. This indicated that the formation of the secondary aerosols due to the conversion of gaseous precursors was significant in summer, but inhibited under dry weather in the dust season.

Sulfur oxidation ratio defined as  $SOR = n-SO_4^{2-} / (n-SO_4^{2-} + n-SO_2)$  and nitrogen oxidation ratio defined as  $NOR = n-NO_3^- / (n-NO_3^- + n-NO_2)$  could be the indication of the secondary transformation processes. Fig. 6 showed the SOR and NOR obtained for  $PM_{2.5}$  aerosols in Beijing. The average values of SOR were 0.08, 0.12, 0.39, 0.19, and 0.07 in the dust storm, spring, summer, autumn, and winter periods, respectively. The corresponding values for NOR were 0.00, 0.05, 0.08, 0.04, and 0.05, respectively. SOR expresses the degree of oxidation of sulfur in terms of the ratio of the sulfur in sulfate to the total sulfur (in sulfate and sulfur dioxide). Similarly, the NOR expresses the degree of oxidation of nitrogen in terms of the ratio of the nitrogen in nitrate to the total nitrogen (in nitrate and nitrogen dioxide). Higher SOR and NOR suggest that the oxidation of gaseous species would occur and more secondary aerosols can exist in the atmosphere. Earlier studies (Pierson et al., 1979; Truex et al., 1980) have reported that in the primary pollutant the value of SOR is lower than 0.10. Ohta and Okita (1990) suggested that when the ratio value was greater than 0.10, photochemical oxidation of  $SO_2$  would occur in the atmosphere. SOR

Table 2  
The correlation coefficients ( $R$ ) and the linear regression equations between major ions

$R$	$F^-$	$Cl^-$	$NO_3^-$	$SO_4^{2-}$	$NH_4^+ = 0.08 + 1.14SO_4^{2-}$
$Na^+$	0.71	0.55	0.27	0.35	$NH_4^+ = 0.11 + 2.03NO_3^-$
$NH_4^+$	0.43	0.65	0.88	0.92	$NH_4^+ = 0.06 + 0.78(SO_4^{2-} + NO_3^-)$
$K^+$	0.50	0.52	0.51	0.53	$Na^+ = 0.01 + 1.02F^-$
$Mg^{2+}$	0.45	0.30	0.18	0.22	$Na^+ = 0.01 + 0.15Cl^-$
$Ca^{2+}$	0.26	0.08	0.02	0.02	$K^+ = Mg^{2+} + Ca^{2+} = 0.10 + 0.37Cl^-$

Table 3

The concentrations ( $\mu\text{g m}^{-3}$ ) of major species in particles in four seasons in Beijing

	Spring	Summer	Autumn	Winter	Dust
No. <sup>a</sup>	96	86	40	107	5
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	17.190	25.847	15.769	27.983	4.181
NH <sub>4</sub> NO <sub>3</sub>	8.683	9.527	5.284	9.566	0.000
NaF	0.512	0.183	0.178	1.113	0.536
Chloride <sup>b</sup>	4.157	2.378	1.844	6.616	2.983
TSA <sup>c</sup> /TWSI <sup>d</sup>	0.523	0.720	0.648	0.591	0.118

<sup>a</sup>No.: number of samples measured.

<sup>b</sup>Chloride: NaCl, KCl, MgCl<sub>2</sub> and CaCl<sub>2</sub>.

<sup>c</sup>TSA: total secondary aerosol ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> plus NH<sub>4</sub>NO<sub>3</sub>).

<sup>d</sup>TWSI: total water soluble ions.

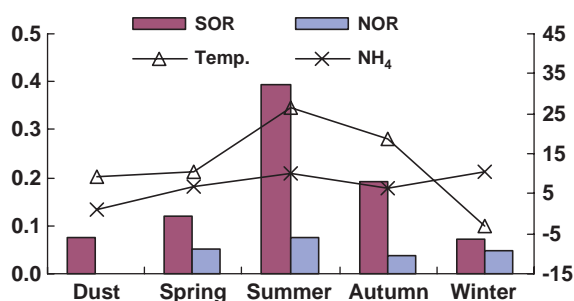


Fig. 6. Seasonal variations of SOR, NOR, and their relations to temperature (temp.) and ammonium. (Left axis: SOR, NOR; Right axis: temperature °C, ammonium  $\mu\text{g m}^{-3}$ ).

of Beijing PM<sub>2.5</sub> aerosols were higher than 0.10 in summer and autumn, comparable or lower than 0.10 in dust period, spring, and winter. The result clearly showed that secondary formation of SO<sub>4</sub><sup>2-</sup> from SO<sub>2</sub> occurred in summer and autumn, but inhibited in dust period and winter. The distribution of NOR in the four seasons was similar to those of SOR. NOR were generally lower than SOR. The lower NOR in Beijing PM<sub>2.5</sub> aerosols suggested that the secondary formation of NO<sub>3</sub><sup>-</sup> from NO<sub>2</sub> weakly occurred in Beijing compared to that of SO<sub>4</sub><sup>2-</sup>.

To identify the factors controlling the formation of secondary ions (SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>), the correlation coefficients between SOR, NOR and other parameters were calculated and the results were shown in Table 4 and Fig. 6. SOR positively correlated with temperature and negatively correlated with atmospheric pressure. NOR showed correlations with NH<sub>4</sub><sup>+</sup>. There are many mechanisms reported for the formation of SO<sub>4</sub><sup>2-</sup> from SO<sub>2</sub>, such as gas phase reaction of SO<sub>2</sub> and OH radical, aqueous transformation processes (metal catalyzed oxidation or H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> oxidation), and in-cloud processes, etc. Since the gas-phase oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> by OH radical is a strong function of temperature

Table 4

The correlation coefficients between SOR, NOR, and other parameters

	NH <sub>4</sub> <sup>+</sup>	O <sub>3</sub>	Temperature	Atmospheric pressure	RH
SOR	0.43	0.47	<b>0.64</b>	-0.56	0.38
NOR	<b>0.76</b>	0.08	0.13	-0.18	0.38

Note: boldface indicates that the correlation coefficient is higher than 0.60.

(Seinfeld, 1986), the positive correlation of SOR with temperature would suggest a possible oxidation mechanism of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> as that the local gas phase oxidation of SO<sub>2</sub> by OH radical followed by the condensation or absorption into the particle phase. The positive correlation of NOR with NH<sub>4</sub><sup>+</sup> would suggest that NH<sub>4</sub>NO<sub>3</sub> might be the main chemical form of NO<sub>3</sub><sup>-</sup>. The correlation among those factors shown in Table 4 indicated evidently that strong solar radiation (high temperature), high O<sub>3</sub> concentration, high RH, low atmospheric pressure, along with high ammonia emission in summer might accelerate the secondary conversion, while the dry weather during the dust period and high atmospheric pressure during the winter might drive this process to the lowest degree. The dominant controlling factors for the oxidation of SO<sub>2</sub> and NO<sub>2</sub> might be temperature and NH<sub>4</sub><sup>+</sup>, respectively.

### 3.3. The spatial distribution of ions

The five sampling sites in studying the spatial distribution of aerosols in Beijing were classified into two groups, the urban sites of BNU, CS, and YH and the rural sites of MY and PG. The paired samples *t*-test (SPSS 11.0 for Windows) and a parameter of CD (coefficient of divergence) were used to judge the similarity or difference because there was a large spread in the concentrations of the various chemical components. CD was defined as follows (Park and Kim, 2004):

$$CD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left( \frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2}$$

where,  $x_{ij}$  represents the average concentration for a chemical component  $i$  at site  $j$ ,  $j$  and  $k$  represent two sampling sites, and  $p$  is the number of chemical components. The chemical components include particle mass concentration, pH, and 15 ionic species. If the CD approaches zero, the data from the two sites are considered to be similar. If the CD approaches one, they are considered to be very different. Based on the results from *t*-test for paired samples used in this

comparison, the concentrations of all those components in  $PM_{2.5}$  were not statistically different at the  $p < 0.05$  level for urban and rural sites. Concentrations of  $PM_{2.5}$  chemical components for the paired rural–urban samples showed similarities with CD of 0.40, indicating that the concentrations of the chemical species in  $PM_{2.5}$  were similar among the sites, i.e. there was no obvious regional difference between urban and rural areas over the entire city. As fine particles could be transported to a much longer range for its longer residence time in the atmosphere,  $PM_{2.5}$  fine particles could likely inter-mix or intra-mix well with each other in the atmosphere and lead to a more even spatial distribution.

### 3.4. Seasonal variation of ions

The seasonal variations for water-soluble ionic components were shown in Table 1. Clear seasonal patterns for all the ionic species in  $PM_{2.5}$  were observed. The sum of the concentrations for cations was in the order of 0.81, 0.65, 0.60, and  $0.43 \mu\text{eq m}^{-3}$  for winter, summer, spring, and autumn, respectively. Concentrations dropped in a similar extent for the sum of anions

(0.85, 0.67, 0.62, and  $0.49 \mu\text{eq m}^{-3}$  for winter, summer, spring, and autumn, respectively). Compared with the seasonal trend of  $PM_{2.5}$  mass concentrations as winter > spring > autumn > summer, it was clear that more ions were formed and attached to particles in the summer period.

Fig. 7 showed the seasonal variations of several typical ions in  $PM_{2.5}$ . As the tracers of soil/dust,  $Ca^{2+}$  and  $Mg^{2+}$  were frequently observed in lower concentrations in summer (average:  $0.73 \mu\text{g m}^{-3}$  for  $Ca^{2+}$ ,  $0.10 \mu\text{g m}^{-3}$  for  $Mg^{2+}$ ), which could be due to more precipitation in this season, while in spring they were in higher concentrations (average:  $2.54 \mu\text{g m}^{-3}$  for  $Ca^{2+}$  and  $0.24 \mu\text{g m}^{-3}$  for  $Mg^{2+}$ ), which could be due to the intense episodic peaks of mineral dust that originated from west–northwest often observed as shown in the air mass trajectories. The concentrations of  $Ca^{2+}$  and  $Mg^{2+}$  in non-dust peaks days in spring (average:  $2.22 \mu\text{g m}^{-3}$  for  $Ca^{2+}$ ,  $0.22 \mu\text{g m}^{-3}$  for  $Mg^{2+}$ ) were comparable to those days of a relative high level in winter (average:  $1.68 \mu\text{g m}^{-3}$  for  $Ca^{2+}$ ,  $0.20 \mu\text{g m}^{-3}$  for  $Mg^{2+}$ ), as the dry season was favorable for the re-suspension of soil particles.

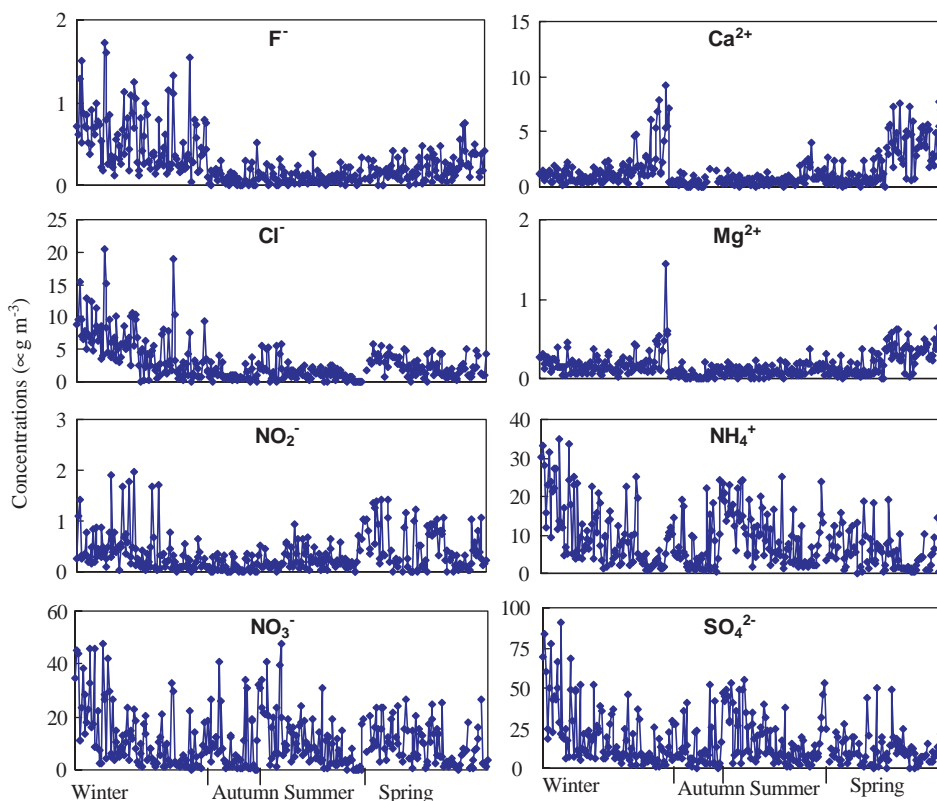


Fig. 7. Seasonal variations in the concentrations of representative ions of different sources (soil:  $Mg^{2+}$ ,  $Ca^{2+}$ ; secondary:  $NH_4^+$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ; combustion:  $F^-$ ,  $Cl^-$ ; traffic activities:  $NO_2^-$ ). (All the samples in 3 years were grouped to the four seasons. The last five points denoted samples collected during the dust storm).

$\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  did not show the same seasonal variations as those of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , indicating that they were of different sources. Concentrations of  $\text{NH}_4^+$  in spring, summer, autumn, and winter were 6.47, 10.10, 6.33, 10.64  $\mu\text{g m}^{-3}$ , of  $\text{SO}_4^{2-}$  were 13.52, 18.42, 12.69, 20.96  $\mu\text{g m}^{-3}$ , of  $\text{NO}_3^-$  were 11.92, 11.18, 10.27, 12.12  $\mu\text{g m}^{-3}$ , respectively. The results showed clearly that the concentrations of these secondary ions were generally higher in summer and winter and lower in spring and autumn. As the average concentration of  $\text{SO}_2$  was 163.65  $\mu\text{g m}^{-3}$  in winter, 11 times than that of 14.84  $\mu\text{g m}^{-3}$  in summer, the high  $\text{SO}_4^{2-}$  concentration in winter could be attributed to the higher concentration of  $\text{SO}_2$  in this season, which was due to the higher coal burning combined with the poor dispersion and the lower rate of removal via wet deposition. The good correlation between  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  ( $R = 0.35$ ,  $n = 107$ ) in winter supported such an explanation. In summer, there were higher SOR and lower  $\text{SO}_2$ , which would suggest that the high  $\text{SO}_4^{2-}$  could be mainly from the secondary transformation instead of the direct local emissions. The average concentrations of  $\text{NO}_2$  were 92.16 and 64.22  $\mu\text{g m}^{-3}$  in winter and summer, respectively.  $\text{NO}_3^-$  is from  $\text{NH}_4\text{NO}_3$  that is generally formed by the oxidation of  $\text{NO}_x$  to form the gas phase of nitric acid and then with the reaction with  $\text{NH}_3$ . The lower temperature in winter would favor the shift from the gas phase of nitric acid to the particle phase of ammonium nitrate, which could lead to the high concentration of  $\text{NO}_3^-$  in winter. In summer, both the higher NOR and the higher emission of  $\text{NH}_3$  contributed to the high concentration of  $\text{NO}_3^-$ .

High  $\text{Cl}^-$  concentrations averaged of 5.28  $\mu\text{g m}^{-3}$  were observed in winter, which was  $\sim 4$  times higher than that in summer of 1.41  $\mu\text{g m}^{-3}$ . As Beijing is  $\sim 150$  km from the sea, it has been demonstrated that the contribution to the aerosols from the sea could be ignored here (Yuan et al., 2004). The major source of  $\text{Cl}^-$  in Beijing might be coal burning, which could reasonably explain the higher  $\text{Cl}^-$  concentration in winter, because of the enhanced burning activities in this season. The seasonal variation of  $\text{F}^-$  was similar to  $\text{Cl}^-$ , indicating that both  $\text{F}^-$  and  $\text{Cl}^-$  were primarily related to the burning activity. Low concentration of  $\text{NO}_2^-$  was observed in summer, which might be related to the faster decay rate of  $\text{NO}_2^-$  under high solar radiation plus more precipitation in summer, as the traffic exhaust was likely to be the major source of nitrite at urban locations.

### 3.5. Source of $\text{PM}_{2.5}$ fine particles

#### 3.5.1. Source apportionment by factor analysis

Table 5 presents the results of the factor loadings from the factor analysis (SPSS for window 11.0). Six of the major components of the variation in the ionic concentrations were identified on the basis of the

magnitude of eigenvalues (greater than one), and these six factors accounted for 80.03% of total variance in the entire set of the data. The factor was highly loaded in  $\text{NH}_4^+$ , S,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and moderately loaded with  $\text{Cl}^-$ ,  $\text{K}^+$ , Se,  $\text{F}^-$ , and it explained 26.24% of the total system variance. This factor appears to represent the secondary pollution sources from the fossil fuel combustion, traffic emission, plus the possible biomass burning. Se,  $\text{Cl}^-$ , and  $\text{F}^-$  might be mainly from coal burning.  $\text{K}^+$  was likely from biomass burning, as in Beijing suburban areas, wheat straws and maize stalks are burned in field during the autumn and winter. The second factor had strong factor loadings for Fe, Al, Mn,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$ , which accounted for 22.00% of the total variance. This factor could be identified as a crustal source, including air-borne road dust, construction dust, and fugitive dust. The third factor was highly loaded in Ni, Cu, and Zn, which explained a further 12.20% of the variance. This factor could be attributed to the source from the smelting industry and partially from incineration. The fourth factor grouped MSA and  $\text{F}^-$  together, which explained another 7.29% of the total variance. As a considerable amount of MSA had been detected in Beijing aerosol, which has been demonstrated not to be from the sea source (Yuan et al., 2004), but was suspected to be from the unknown industrial emissions. The fifth factor grouped  $\text{C}_2\text{O}_4^{2-}$  and  $\text{NO}_2^-$  together.  $\text{C}_2\text{O}_4^{2-}$  was well correlated with  $\text{O}_3$  in spring ( $R = 0.40$ ,  $n = 49$ ) and summer ( $R = 0.31$ ,  $n = 86$ ), which indicated that the photochemical formation was a source of  $\text{C}_2\text{O}_4^{2-}$  (Kawamura and Ikushima, 1993). It was also reported that  $\text{C}_2\text{O}_4^{2-}$  could be originating directly from vehicle exhausts (Kawamura and Kaplan, 1987).  $\text{NO}_2^-$  could be one of the oxidation products of  $\text{NO}_x$  that was mostly from vehicular emissions. Thus, this factor could be attributed to the photochemical products related to vehicle emissions. The sixth factor only showed a high loading of  $\text{PO}_4^{3-}$ , whose source was not clear at this stage and further study is needed. Overall, the secondary formation of coal/biomass burning products, crust, industrial and traffic emissions were the major sources of the fine aerosols in Beijing.

#### 3.5.2. The source identification by $\text{Ca}^{2+}/\text{Al}$ ratio

Crustal components have been a major part of  $\text{PM}_{2.5}$  aerosol in Beijing. Al is a typical crustal component and it has been used widely as a tracer for suspended soil and long-range-transported mineral aerosols.  $\text{Ca}^{2+}$  could be derived from soil dust and construction materials in urban aerosols.  $\text{Ca}^{2+}$  was used as an indicator for construction dust in Beijing (Zhang and Iwasaka, 1999).  $\text{Ca}^{2+}/\text{Al}$  ratio could be seen as a good tracer for the mixing of soil dust with the suspended construction materials in urban aerosols. Fig. 4 showed the seasonal variation of  $\text{Ca}^{2+}/\text{Al}$  ratio at one of the sampling sites, BNU, in Beijing. The ratio of  $\text{Ca}^{2+}/\text{Al}$  was low in winter

Table 5  
Varimax rotated factor matrix for the complete data set

Factor	1	2	3	4	5	6	Communality
NH <sub>4</sub> <sup>+</sup>	<b>0.92</b>	−0.09	0.23	−0.06	0.05	0.14	0.93
S	<b>0.90</b>	0.06	0.24	−0.08	−0.01	0.12	0.90
SO <sub>4</sub> <sup>2−</sup>	<b>0.90</b>	0.02	0.20	−0.06	0.17	0.12	0.90
NO <sub>3</sub> <sup>−</sup>	<b>0.87</b>	−0.04	0.21	−0.04	0.17	0.11	0.84
Cl <sup>−</sup>	<b>0.75</b>	0.10	0.22	0.26	−0.01	−0.37	0.83
K <sup>+</sup>	<b>0.66</b>	0.15	0.08	0.26	−0.13	−0.07	0.55
Se	<b>0.59</b>	0.09	0.30	0.34	−0.26	−0.01	0.62
F <sup>−</sup>	<b>0.58</b>	0.24	0.10	<b>0.56</b>	−0.10	−0.32	0.83
Fe	−0.07	<b>0.95</b>	−0.03	−0.13	−0.06	0.04	0.92
Al	−0.12	<b>0.94</b>	−0.03	−0.12	−0.02	0.03	0.92
Mn	0.22	<b>0.90</b>	0.12	−0.06	−0.11	0.00	0.89
Ca <sup>2+</sup>	−0.04	<b>0.86</b>	0.10	0.16	0.14	−0.01	0.80
Mg <sup>2+</sup>	0.16	<b>0.80</b>	0.18	0.29	0.15	−0.06	0.82
Na <sup>+</sup>	0.37	<b>0.66</b>	0.18	0.48	0.01	−0.19	0.87
Ni	0.29	0.18	<b>0.89</b>	0.09	0.11	0.05	0.93
Cu	0.30	0.19	<b>0.87</b>	0.11	0.15	0.01	0.92
Zn	0.41	−0.05	<b>0.75</b>	−0.06	−0.16	0.00	0.76
MSA	−0.03	−0.05	0.03	<b>0.70</b>	0.17	0.22	0.58
C <sub>2</sub> O <sub>4</sub> <sup>2−</sup>	0.02	0.10	0.06	0.19	<b>0.80</b>	0.07	0.70
NO <sub>2</sub>	0.08	−0.06	0.03	−0.10	<b>0.64</b>	−0.46	0.64
PO <sub>4</sub> <sup>3−</sup>	0.16	−0.01	0.06	0.10	−0.06	<b>0.79</b>	0.67
Eigenvalue	5.51	4.62	2.56	1.53	1.35	1.23	
% of variance	26.24	22.00	12.20	7.29	6.44	5.86	
Cumulative %	26.24	48.24	60.44	67.73	74.17	80.03	

Extraction method: principal component analysis.

Rotation method: varimax with Kaiser normalization.

Note: Boldface indicates that the factor loading is higher than 0.50.

and spring, and high in autumn and summer. The low ratio in winter could be because that the construction activities decreased in the cold season. In spring, the low ratio of Ca<sup>2+</sup>/Al denoted the great increase of soil dust, which was transported to Beijing from the west or the northwest of China. The high ratio of Ca<sup>2+</sup>/Al in autumn and summer could attribute to increasing construction activities in warm days as well as increased removal of suspended soil dust by precipitation in the wet season.

### 3.5.3. Influence of air mass parcels on the levels of fine particles

Air mass origin could influence the levels of the fine particles because different air masses traveling through different regions bring aerosols with different chemical components. Dust air parcels, which often attack Beijing in spring, are mainly from the west or northwest of China, so air masses from W–NW sector could bring a large amount of crustal species. As the industrial factories are largely located in the south and southwest areas of Beijing, the air masses from S–SE–E and SW sectors could bring much pollution. Table 6 presented the distribution of five species (NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2−</sup>,

NO<sub>3</sub><sup>−</sup>, Cl<sup>−</sup>) for each sector identified in Fig. 1(c). The results showed that a large number of air parcels were from the W–NW sector in the spring and winter season, while more samples prevailed in the SW sector in the summer and autumn season. It showed clearly that in spring, which are characterized by Asian dust outbreaks, the Ca<sup>2+</sup> levels associated with the long-range transport from W–NW sector were higher, while the NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>−</sup>, Cl<sup>−</sup> levels were lower, compared to other sectors. This indicated that the dust from the long-range transport could bring lots of crustal species to Beijing in spring. In summer, the frequencies of air masses from each sector were comparable, but the highest concentrations of ionic species (NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2−</sup>, NO<sub>3</sub><sup>−</sup>, Cl<sup>−</sup>) were associated with the transport from SW sector, which could be due to more industrial factories located in the SW sector of Beijing.

## 4. Conclusions

A 3-year campaign from 2001 to 2003 measuring organic and inorganic constituents of PM<sub>2.5</sub> was conducted at five sites in Beijing, China. Concentrations

Table 6  
Concentrations of ions ( $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) from different air-mass origin in four seasons ( $\mu\text{g m}^{-3}$ )

Season	Ion species					
	No.	$\text{NH}_4^+$	$\text{Ca}^{2+}$	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{Cl}^-$
<i>Spring</i>						
Local	12	5.25	1.45	8.62	10.30	3.49
N-NE	7	7.87	1.06	17.79	13.52	3.94
S-SE-E	9	11.89	1.63	21.90	22.33	4.05
SW	24	10.21	2.26	19.12	18.86	4.04
W-NW	49	3.75	3.32	9.83	6.78	1.88
<i>Summer</i>						
Local	14	9.85	0.90	17.78	11.28	1.35
N-NE	11	4.53	0.39	7.05	5.74	0.90
S-SE-E	13	13.64	0.68	24.56	14.92	1.41
SW	28	14.83	0.81	27.44	16.52	2.10
W-NW	20	4.40	0.72	8.49	4.19	0.77
<i>Autumn</i>						
Local	2	2.88	0.08	5.59	3.77	0.86
N-NE	6	2.33	0.23	5.33	3.58	0.67
S-SE-E	6	8.39	1.27	18.95	9.71	1.28
SW	12	10.91	1.07	22.33	16.00	1.70
W-NW	14	3.72	1.76	5.92	6.16	0.70
<i>Winter</i>						
Local	19	9.32	1.40	16.71	11.72	5.84
N-NE	1	7.27	1.09	3.36	1.09	1.69
S-SE-E	1	8.41	0.50	17.55	10.36	5.06
SW	12	19.19	1.60	41.77	22.03	5.63
W-NW	74	9.66	1.79	18.96	11.04	5.13

No. means the number of samples measured.

of the water-soluble ions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_2^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{HCOO}^-$ ,  $\text{MSA}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ) and 23 elements were measured for a total of 334 samples. A relatively even spatial distribution throughout Beijing and a significant seasonal variation were observed.  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$  were the major ions and existed mainly in the form of  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NaCl}$ ,  $\text{KCl}$ , and  $\text{CaCl}_2$  in aerosol particles. Most ions showed high concentrations in winter and low in summer. Secondary ions, mainly  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , exhibited high concentrations in both summer and winter due to the secondary transformation that is accelerated under high humidity and strong solar radiation in summer and the higher concentrations of  $\text{SO}_2$  from coal burning and the lower removal rate in winter. The formations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were determined largely by temperature and  $\text{NH}_4^+$ , respectively. Temperature, relative humidity, rainwater frequency, and air mass origin might be the main factors regulating the aerosol distribution. Crustal ions exhibited sporadic but high peaks in spring due to the

intrusion of dust from west and northwest of China. The  $\text{Ca}^{2+}/\text{Al}$  ratio indicated the mixing of different dust sources. Factor analysis showed that the secondary formation of coal/biomass burning products, crust, industrial and traffic emissions were the major sources of the fine aerosols in Beijing. Traffic sources became more significant with the motorization in recent years. Compared with studies in other areas, it could be seen clearly that aerosol pollution is a more serious issue in China than other East Asian sites.

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