

# Characteristics of mass distributions of aerosol particle and its inorganic water-soluble ions in summer over a suburb farmland in Beijing

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**Abstract** Agricultural activity is one of the most important sources of aerosol particles. To understand the mass distribution and sources of aerosol particles and their inorganic water-soluble ions in a suburb farmland of Beijing, particle samples were collected using a Microorifice uniform deposit impactor (MOUDI) cascade impactor in the summer of 2004 in a suburb vegetable field. The distribution of the particles and their inorganic water-soluble ions in the diameter range of 0.18–18  $\mu\text{m}$  were measured. The dominant fine particle ions were  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ . The association of day-to-day variation of the concentration of these ions with temperature, humidity, and solar radiation suggested that they are formed by the reaction of  $\text{NH}_3$  released from the vegetable field with the acid species produced from photochemical reactions. Fine particle  $\text{K}^+$  is likely from vegetation emission and biomass burning. Coarse particles like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  are suggested to come from the mechanical process by which the soil particle entered the atmosphere, and from the reaction of the acid species at the surface of the soil particle. The results show that fertilizer and soil are important factors determining the aerosol particle over agricultural fields, and vegetable fields in suburban Beijing contribute significantly to the aerosol particle.

**Keywords** mass size distribution, coarse particle, fine particle, source

## 1 Introduction

Atmospheric aerosol influences the atmosphere environment and the processes of climate change, which is an important

research area of present atmospheric chemistry. The size distribution and chemical compositions of aerosol particles are controlled by different sources and processes of atmospheric physical chemistry, and directly influence their effects on the atmosphere. Due to the different sources, the effects of atmospheric physical chemistry and deposition processes, atmospheric particles have special variability in chemical compositions and size distribution. Measurements of particle size and compositions in different ambient conditions would help reveal aerosols sources in different regions, and to estimate their environmental effects. At present, researches on aerosols typically focus on the city zones with the circumjacent countryside as reference sites [1,2]. However, Park et al. reported that biomass burning in farmlands would increase the concentrations of  $\text{PM}_{10}$ ,  $\text{K}^+$ , and  $\text{Cl}^-$ , and decrease those of secondary aerosols such as  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$  [3]. Xu investigated the aerosols in the countryside at Yangtze Delta and found that organic carbon was related to biomass burning, and the local anthropogenic sources and long-range transportation might play a crucial role in local aerosols [4]. Mechanical processes in farmlands could produce fine particles, and the wide application of nitrogenous fertilizer would cause the release of a lot of ammonia and the production of fine aerosol particles. However, there is lack of studies on aerosols over farmlands in China. The overload of fertilizers on vegetable fields, especially nitrogenous fertilizers, is likely to be an important source of fine particles. Thus, measurements on the distribution and compositions of atmospheric aerosols in vegetable fields are necessary to estimate the sources and transport of atmospheric aerosols [2].

This study describes the size distribution of atmospheric particles and their water-soluble ionic species collected in the summer of 2004, over suburban vegetable fields in Beijing. The source and forming mechanism of the particles were also discussed.

Translated from *Environmental Science*, 2006, 27(2): 193–199 [译自: 环境科学]

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## 2 Experimental method

### 2.1 Sampling

**Sampling site:** Xiangyang vegetable fields in Shaling Village, Yang Town, Shunyi county, Beijing (40°9'N, 116°52'E), about 50 km from the center of Beijing.

**Sampling period:** from August 7th to 15th, 2004 (2004-08-07–2004-08-15, Table 1). Lack of measurements on August 10th and 12th is due to instrumentation problem and precipitation, respectively. During the sampling period the dominant wind direction was northwest.

**Table 1** Observation and weather conditions

Date	Start time	End time	Mean temperature /°C	Mean wind speed /( $\text{m}\cdot\text{s}^{-1}$ )	Weather
2004-08-07	09:36	17:51	28.70	0.992	Cloudy
2004-08-08	07:16	19:24	30.62	0.736	Cloudy
2004-08-09	07:14	19:25	29.87	1.360	Cloudy
2004-08-10					Cloudy
2004-08-11	07:02	19:30	26.98	1.600	Overcast
2004-08-12					Rain
2004-08-13	07:12	19:31	23.29	0.849	Overcast then sunny
2004-08-14	06:50	18:41	24.32	0.602	Overcast then sunny
2004-08-15	06:57	17:34	22.42	0.926	Occasional light showers

**Instruments:** Microorifice uniform deposit impactor (MOUDI, Model 110, MSP Company, USA), which fractionates particles in cut-points of 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, and 0.18  $\mu\text{m}$  [5] at a stable flow rate of 30 L/min. Before sampling, the flow rate was calibrated with a gas meter, and was checked very 2 h during sampling. Nitrogenous fertilizer was applied to the sampling site. The gaseous ammonia released would react with acidic particles collected on filters, and affect measuring accuracy. Therefore, a glass annular denuder was installed upstream of MOUDI's inlet to absorb the ammonia. The glass annular denuder (inner diameter of 30 mm, outer diameter of 32 mm, total length of 300 mm) with a rough absorbing surface was used to hold more absorbent. The absorbent was  $\text{H}_3\text{PO}_3$  ( $w = 3\%$ ) in a methanol-water solution ( $v/v$ , 90:10) with an effective length of 220 mm. At the inlet, a smooth surface glass with 80 mm length without absorbent made air pass through the absorbing surface in laminar flow and avoid the loss of large particles from impacting the inlet [6]. Our previous experiments showed that absorbing efficiency of the annular denuder was 96% to ammonia. The inlet was around 1 m above ground level.

**Sampling filter:** PTFE (pore size of 2  $\mu\text{m}$ , diameter of 47 mm, Whatman Company, USA).

### 2.2 Sample analysis

Filter masses were determined with an electronic mass balance (AX105DR, Mettler-Toledo Company, Switzerland) located in a clean room (temperature ( $20 \pm 1$ )°C, humidity ( $45 \pm 5$ )%). Blanks were also collected and analyzed in order to quantify the level of contamination during filter handling, shipping, and analysis. Mass concentrations of aerosol particles were determined by the mass collected on each stage and sampling volume. Filters were then sonicated in a 10 mL ultrapure deionized water (Milli-Q Gradient, Millipore Company, USA) for 30 min. Ice was added into the water bath to keep water from warming. As PTFE is hydrophobic, 100  $\mu\text{L}$  ethanol was added into the ultrapure deionized water before extraction. The extracts were filtrated into plastic bottles through filters (pore size of 0.45  $\mu\text{m}$ ,  $\phi$  of 13 mm, Tengda Company of Tianjin). Samples from the denuder were washed off with ultrapure deionized water and diluted to 250 mL. All the samples were refrigerated in  $-18^\circ\text{C}$  until analysis.

Samples were analyzed by an ion chromatograph system (DX-2500 IC/ECD, Dionex Company, USA) for water-soluble inorganic ions. Dionex AS14 separator column and ASRS-4mm suppresser, with a mixture of sodium carbonate (3.5 mmol/L) and sodium bicarbonate (1.0 mmol/L) as an eluent passing at a flow rate of 1.2 mL/min, were used for anions; on the other hand, Dionex CS-12A separator column and CAES suppresser, with MSA (20 mmol/L) as an eluent passing at a flow rate of 1.0 mL/min, were used for cations. Each sample (25  $\mu\text{L}$ ) was injected. The lower detectable limits for  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  ( $S/N = 10$ ) were obtained as 6, 14, 12, 10, 19, 53, 169, and 154  $\text{ng}/\text{m}^3$ , respectively.

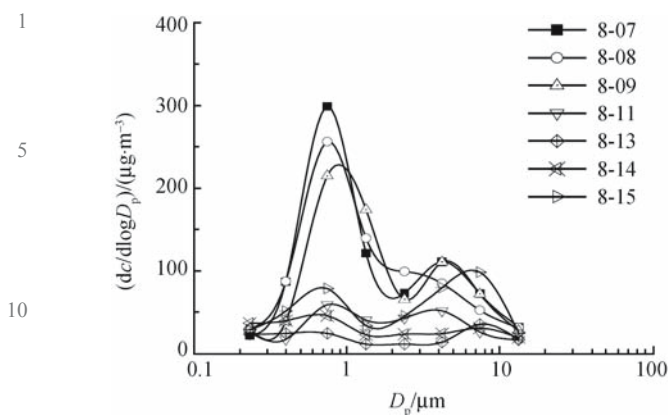
## 3 Results and discussion

### 3.1 Size distribution of particle mass concentration

There were different definitions between fine and coarse particles as reported [7]. Due to the cut points of MOUDI,  $\text{PM}_{1.8}$  (particles with size less than 1.8  $\mu\text{m}$ ) was defined as fine particles and  $\text{PM}_{10-1.8}$  (particles ranging between 1.8 and 10  $\mu\text{m}$ ) as coarse particles.

During the sampling period, the size distribution was bimodal (Fig. 1), and the mass dominated in 0.56–1.0  $\mu\text{m}$  and 3.2–10  $\mu\text{m}$ . The mean mass concentrations of fine and coarse particles and  $\text{PM}_{1.8}$  were 70, 43, and 120  $\mu\text{g}/\text{m}^3$ , respectively. The ratio of the mass concentration of fine particle to  $\text{PM}_{10}$  was 59%, and the ratio of the mass concentration of  $\text{PM}_{1.8}$  to fine particle was 75%.  $R^2$  of the mass concentration of fine particles to  $\text{PM}_{10}$  was 0.974, and that of coarse particles to  $\text{PM}_{10}$  was 0.868, while  $R^2$  of the mass concentration of  $\text{PM}_{1.8}$  to fine particles was 0.970 and that of  $\text{PM}_{1.8-1}$  to fine particles was 0.884.

Typically, suburbs are studied as reference sites of city zone. For example, Wang [1] and Dong et al. [2] reported that



**Fig. 1** Mass size distributions of particulate matters during the sampling period

the particle concentration was lower in suburbs. Surprisingly, in our study, both mass concentrations of fine and coarse particles were higher, which was in good agreement with Hu's results [8] in summer in Beijing. Table 2 also shows that the mass concentrations of fine particles were higher than that of coarse ones. This suggests that sources of particles were different from those reported in previous literature. Keywood et al. found a strong relationship between the mass concentration of  $PM_{2.5}$  and  $PM_{10}$  in the city and a weak relationship between that of fine particles and  $PM_{10}$ , which indicate that  $PM_{10}$  was controlled by the fine particles in the city [9]. Dong et al. [2] reported that the concentration of fine particles was higher than that of coarse particles in Beijing suburbs with the same trend. The trend was different from that in the city, so atmospheric pollutants in the suburbs were primarily from atmosphere transportation. However, in this study, the concentrations of fine and coarse particles were not changing at the same trend. Despite the high relativity between the concentration of fine and coarse particles and that of  $PM_{10}$ , the different variabilities between the concentrations of fine and coarse particles were found by analyzing size distribution.

Figure 1 shows the day-to-day variability in both mass concentrations and size distributions of particles during the sampling period. From August 7th to 9th, the majority of the particles were fine ones. However, on August 11th and from

August 13th to 15th, the concentration of fine particles dropped significantly, and the concentrations of coarse particles were as high as that of fine particles. As shown in Table 1, the day-to-day variability in the mass concentrations of the particles is related to the weather condition. It was cloudy from August 7th to 9th with the mean temperature reaching as high as 29–31°C, when the maximum concentrations of  $PM_{18}$ , fine particles and coarse particles took place, and the fine particles contributed 67% to  $PM_{10}$ . On August 11th, the weather was overcast, and the temperature dropped nearly 3°C. At this time, the concentrations of  $PM_{18}$  and the fine particles decreased to about 30% of the preceding-3-day average, the concentration of the coarse particles to a half, and the percentage of fine particles to  $PM_{10}$  to 53%. After precipitation on August 12th, the temperature on August 13th dropped by nearly 4°C with the minimum concentrations of  $PM_{18}$ , fine particles and coarse particles. Then the temperature remained almost constant, and the concentration of  $PM_{10}$ , fine particles, and coarse particles increased gradually as well as the percentage of fine particles to  $PM_{10}$ , when the minimum of 45% was reached on August 15th. All of the above showed a relationship between the fine particles and the temperature. To a certain extent, temperature is influenced by solar radiation, so photochemical reaction was a major factor which influenced the concentrations of fine particles. Generally, coarse particles come from mechanical processes, and those produced from farmlands are related to wind speed, so a slight variability in wind speed would produce coarse particles at the same time during the sampling period. However, the maximum wind speed took place with the minimum concentration of the coarse particles on August 11th, which was possibly caused by the increase in humidity from irrigation on that day.

### 3.2 Water-soluble ion compositions and size distributions

Ion concentrations in the sample of 0.18–0.32 µm on August 14th were abnormal, which was a contradiction to the mass concentration. This sample might have been contaminated when extracted or analyzed, and therefore was abandoned.

During the sampling period, mean concentrations of water-soluble  $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Cl^-$ ,  $NO_3^-$ , and

**Table 2** Comparison of mass concentrations of fine particles and  $PM_{10}$  in Beijing

Particles	Fine/( $\mu\text{g}\cdot\text{m}^{-3}$ )	$PM_{10}$ /( $\mu\text{g}\cdot\text{m}^{-3}$ )	Fine/ $PM_{10}$	Reference
Suburb (1991, Spring)	–10 ( $PM_2$ )	–30	0.314	1
City (1991, Spring)	–15 ( $PM_2$ )	–48	0.294	1
Suburb (1995–1996, Annually)	31.2 ( $PM_2$ )	58	–2	
City (2001, Summer)	46 ( $PM_{2.5}$ )	68	0.68	10
Peking University				
2001, Summer	52 ( $PM_{1.8}$ )	113	0.44	8
2002, Winter	64.6 ( $PM_{1.8}$ )	159.1	0.41	8
2002, Summer	70.4 ( $PM_{1.8}$ )	130.9	0.51	8
2003, Winter	41.8 ( $PM_{1.8}$ )	71.6	0.58	8
Our results				
2004, Summer	70 ( $PM_{1.8}$ )	113	0.59	

SO<sub>4</sub><sup>2-</sup> in fine mode were 1.21, 13.0, 2.86, 0.65, 1.83, 1.03, 5.91, and 25.0 μg/m, and in coarse mode were 0.97, 0.51, 0.33, 0.92, 3.58, 0.97, 2.92, and 3.36 μg/m, respectively. Table 3 shows the percentages of fine and coarse particle water-soluble ions. SO<sub>4</sub><sup>2-</sup> had the highest concentration in the fine mode, followed by NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>. These three ions accounted for 52.7% of PM<sub>1.8</sub>, which were dominated in fine particles.

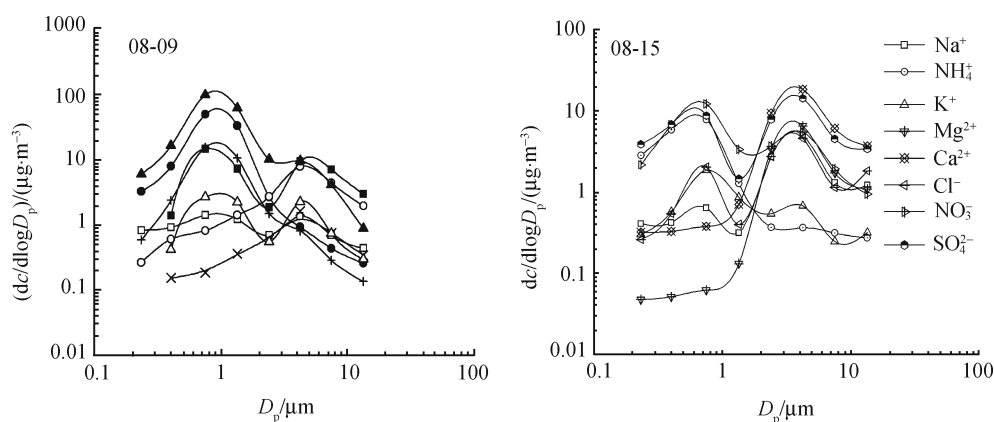
Figure 2 shows unimodal distributions of NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> concentrations, and bimodal distributions of Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> concentrations. The majority of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were in 0.56–1.0 μm in the fine mode, and there was a second highest peak for NO<sub>3</sub><sup>-</sup> in 3.2–5.6 μm in coarse mode. The majority of Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Cl<sup>-</sup> were in

3.2–5.6 μm, and there was a second highest peak for both Na<sup>+</sup> and Cl<sup>-</sup> in 0.56–1.0 μm. There was an obvious difference between size distributions of ions in different days from August 9th to 15th. On August 9th, the majority of K<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> were in fine mode, and they dropped significantly on August 15th. This could be related to two possible factors: one was the precipitation on August 12th which wiped off some particles from the atmosphere; the other was the less active photochemical reaction on August 15th which produced fewer fine particles.

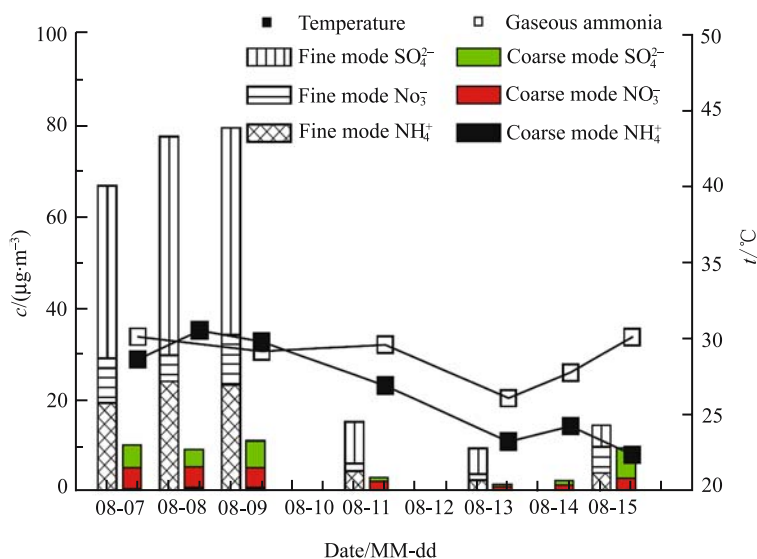
More evidences about the relationship between weather conditions and day-to-day variability of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and gaseous NH<sub>3</sub> concentrations are given in Fig. 3. From August 7th to 9th, there was plenty of sunlight with high

**Table 3** Inorganic water-soluble ions in fine and coarse particles, wt-%

Ions	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Fine mode	1.85	15.40	3.39	1.09	3.04	1.64	7.84	29.50
Coarse mode	2.28	1.22	0.76	1.91	7.88	2.40	6.64	6.76



**Fig. 2** Mass size distribution of inorganic water-soluble ions in particulate matter



**Fig. 3** Time course of the mass concentrations of the dominant inorganic water-soluble ions during the sampling period

temperature and high concentration of gaseous ammonia and ions in both fine and coarse mode. On August 11th after irrigation, it turned overcast, and there was less sunlight accompanied by low temperature and low concentrations of ions in both fine and coarse mode, but the ammonia concentration did not change much. After the precipitation on August 13th, the soil and air humidity increased as the temperature continued decreasing, when ammonia concentration decreased and ion concentrations in both fine and coarse mode dropped to a minimum. After that, the temperature did not change much, and the concentrations of ammonia and ions in both fine and coarse mode increased gradually. Temperature was lower after August 11th, and concentrations of  $\text{NH}_4^+$  in particles were several times lower than those on days with higher temperatures. However, ammonia did not change much, which contradicted with the relationship between temperature and the thermodynamic balance of gaseous ammonia and  $\text{NH}_4^+$  in particles. However, low temperature on overcast days produces less  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  by photochemical reaction, which decreases  $\text{NH}_4^+$  produced by their neutralization.

### 3.3 Source analysis

#### 3.3.1 Terrestrial and marine sources

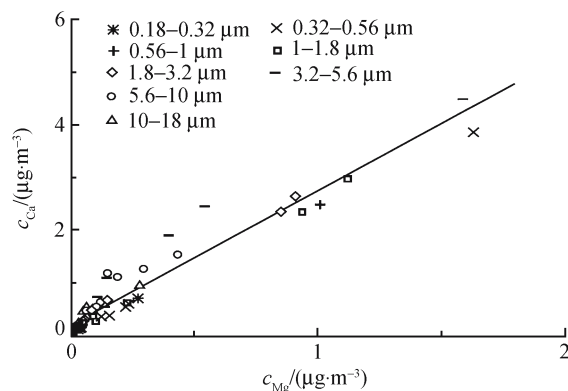
Typically,  $\text{Cl}^-$  and  $\text{Na}^+$  come from long-distance transportation of sea salt aerosols. Sea salt ratios were calculated using Na as reference element assuming all of  $\text{Na}^+$  to be of marine origin. The ratios are given in Table 4.  $[\text{Cl}^-]/[\text{Na}^+]$  in both fine and coarse mode was less than that of sea water. The reason was likely the reactions between  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{NaCl}$  during transportation. The reaction caused a loss of  $\text{Cl}^-$  by producing gaseous  $\text{HCl}$  [11], and also caused an adsorbance of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  on fine particles [12].  $[\text{K}^+]/[\text{Na}^+]$ ,  $[\text{Ca}^{2+}]/[\text{Na}^+]$ ,  $[\text{Mg}^{2+}]/[\text{Na}^+]$ , and  $[\text{SO}_4^{2-}]/[\text{Na}^+]$  were higher while  $[\text{Cl}^-]/[\text{Na}^+]$  was lower, which suggested that the sea salt contributed insignificantly to the particles in the sampling site.

**Table 4** Ratios of inorganic water-soluble ions to  $\text{Na}^+$

	$[\text{Cl}^-]/[\text{Na}^+]$	$[\text{K}^+]/[\text{Na}^+]$	$[\text{Ca}^{2+}]/[\text{Na}^+]$	$[\text{Mg}^{2+}]/[\text{Na}^+]$	$[\text{SO}_4^{2-}]/[\text{Na}^+]$
Coarse mode	1.07	0.40	3.55	0.80	3.60
Fine mode	1.02	2.50	1.36	0.45	20.80
$\text{PM}_{10}$	0.97	1.51	2.44	0.67	13.20
Sea water [11]	1.80	0.037	0.038	0.12	0.25

During the sampling period, the strong evident relativity ( $R^2 = 0.9364$ ) of  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  (Fig. 4) showed that the source of  $\text{Ca}^{2+}$  was the same as that of  $\text{Mg}^{2+}$ , and that the source was likely related to soil humidity. From August 7th to 9th, the mean concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the coarse mode were 4.27 and 0.95  $\mu\text{g}/\text{m}^3$ , respectively. After irrigation on August 11th, they decreased to 1.52 and 0.22  $\mu\text{g}/\text{m}^3$ ,

respectively. After the precipitation on August 12th, they decreased to the minimum of 1.01 and 0.19  $\mu\text{g}/\text{m}^3$  on August 13th, respectively, and then increased gradually. The evident influence of irrigation and precipitation on both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations indicated that these two elements were possibly released from local soil.



**Fig. 4** Correlation of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in the particles of each diameter range during sampling period

Soil particles could be blown by wind into the atmosphere [13] and become a primary source of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  in coarse particles in the atmosphere. Parmar et al. reported that low concentrations of particles and ions in monsoons were caused by precipitation, which wipes particles off the atmosphere and reduces the release from terrestrial source [11]. In our study, the wind speed did not change much before and after precipitation except for the high value on August 11th, with low concentrations of both coarse particles and coarse mode ions from August 11th to 14th. The reason might be that the irrigation on August 9th and precipitation increased soil humidity and made it difficult to bring the soil particles into the atmosphere by wind. After August 15th, soil humidity decreased gradually, which caused the increase in the concentration of the coarse particles and coarse mode ions.

Reactions of gaseous  $\text{SO}_2$  on the surface of humid alkali soil particles might be another source of  $\text{SO}_4^{2-}$  in coarse mode. Moreover,  $\text{SO}_2$  and gaseous  $\text{H}_2\text{SO}_4$  could turn into  $\text{SO}_4^{2-}$  and be adsorbed on large particles by heterogeneous nucleation [12]. Besides the contribution of soil particles directly brought into the atmosphere, soil particle surface absorb water, form liquid droplets, capture  $\text{HNO}_3$  and  $\text{NO}_2$ , and then produce  $\text{NO}_3^-$  particles [14]. This might be another source of  $\text{NO}_3^-$  in coarse mode. Ali-Mohamed et al. reported that the coarse particles could be produced by airplane exhaust during landing and take off [15]. Beijing Capital Airfield is near our sampling site, so airplane exhaust might be another source of coarse particles in our study.

$\text{NH}_4^+$  in coarse mode might partly come from the reactions of excessive ammonia with  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in sea salt and soil particles [16]. In this study, the higher  $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$  and  $[\text{NH}_4^+]/[\text{NO}_3^-]$  in fine mode but the lower ratios

in coarse mode indicated the reaction between excessive ammonia and humid soil particles.

$K^+$  in fine mode might come from vegetation release and biomass burning. In hot and humid conditions,  $K^+$  in soil solution would pass through roots and leaves, then be emitted in sub-micrometer size though the stoma by respiration [11]. Chemical fertilizers contain plenty of  $K^+$ , which might be an important source of  $K^+$  in coarse mode.

### 3.3.2 Release of ammonia and photochemical reactions

Compared with the reports in literature, the concentrations of  $SO_4^{2-}$ ,  $NO_3^-$ , and  $NH_4^+$  in fine and coarse mode were higher in our study (Table 5), indicating a strong source nearby. Day-to-day variability in ion concentrations indicates a relationship between the emission of major sources, ammonia and weather conditions.

Measurements on ammonia flux over farmlands had verified that the application of chemical fertilizers could cause emission of ammonia to the atmosphere [19]. A relationship between fine particle and ammonia emissions has been reported [20]. Investigations on the atmosphere near a pig farm suggested that  $(NH_4)_2SO_4$  in fine mode came from a strong local source of  $NH_3$  [21]. Both distributions between  $NH_3$  and  $NH_4^+$  in liquid and ammonia balance between gas and liquid phases depended on temperature. When temperature rose, gaseous ammonia increased, and the emission of ammonia from manure, soil and vegetables became stronger, which made the formation of  $NH_4^+$  in fine mode easier. Thus, ammonia emitted by agriculture influences the concentration of  $PM_{2.5}$  and  $NH_4^+$  in local aerosols [22].

Photochemical reaction turned  $SO_2$  and  $NO_x$  to  $H_2SO_4$  and  $HNO_3$  by homogeneous reaction in the atmosphere, which produced  $(NH_4)_2SO_4$  and  $NH_4NO_3$  by homogeneous nucleation with ammonia, thus the majority of these three ions existed in fine mode [14,17]. Reaction of ammonia took place on the surface of acidic aerosol particles and produced  $NH_4NO_3$ ,  $(NH_4)_2SO_4$ , and  $NH_4Cl$ . The stabilities of these productions were different in the atmosphere.  $(NH_4)_2SO_4$  was the most stable, and  $NH_4Cl$  was the most inclined to volatilize and decompose, so  $NH_3$  was inclined to combine with  $H_2SO_4$

[11]. In summer, atmosphere humidity was higher before and after raining, which is helpful for the formation of  $NH_4NO_3$  [23]. At high temperatures, the balance between  $NO_x$ ,  $NO_3^-$ ,  $HNO_3$ , and  $NH_4NO_3$  make it difficult to form  $NO_3^-$ , so the minimum  $[NO_3^-]$  is in summer and the maximum in winter. Lee [18] showed that the maximum  $[SO_4^{2-}]/([SO_2] + [SO_4^{2-}])$  was in summer and the minimum in winter, indicating that photochemistry was a primary reason that caused the production of  $SO_4^{2-}$ .

In our sampling site, one kind of compound fertilizer abundant in nitrogen was applied to fields, containing 21% nitrogen, 65% of which was ammonium. In hot summers, it would emit gaseous ammonia into the atmosphere. Soil humidity and temperature were different before and after raining. From August 7th to 9th, the temperature was higher, which helped the fertilizer to emit ammonia, so ammonia concentration was higher at that time. On August 13th, the temperature was low and soil humidity was high, which was not helpful for ammonia to emit, so ammonia concentration was lower than before. The change of ammonia concentration influence reactions of ammonia with  $H_2SO_4$  and  $HNO_3$  and change the concentrations of  $NH_4^+$ ,  $NO_3^-$ , and  $SO_4^{2-}$  in fine mode (Fig. 3). The neutralization factor, i.e. the ratio of actual  $[NH_4^+]$  to assumed  $[NH_4^+]$  that completely converted to  $(NH_4)_2SO_4$ ,  $NH_4NO_3$ , and  $NH_4Cl$  (completely neutralized with a factor over 0.8 [24]), in  $PM_{1.8}$  was 1.08, so  $NH_3$  in fine mode was completely neutralized.

To some degree, temperature reflected solar radiation. In our study, the concentration of  $NO_3^-$  and  $SO_4^{2-}$  in fine mode had the same trend as the change in temperature, indicating that  $NO_3^-$  and  $SO_4^{2-}$  primarily came from photochemical oxidation. From August 11th to 15th, weak sunlight could not help  $SO_2$  and  $NO_x$  to convert  $H_2SO_4$  and  $HNO_3$ , which could not convert all the ammonia to  $NH_4^+$ , thus the concentrations of  $NH_4^+$ ,  $NO_3^-$ , and  $SO_4^{2-}$  in fine mode were much lower.

Hu et al. reported that sulfate, nitrate, and ammonium directly influence fine particles in summer in Beijing. By controlling the precursor of secondary ions such as  $SO_2$ ,  $NO_x$ , and ammonia, fine particles could be decreased effectively [8]. Our results showed that  $NH_4^+$ ,  $NO_3^-$ , and  $SO_4^{2-}$  were main components in fine particles in vegetable fields in the suburb of Beijing, and the neutralization of ammonia released

**Table 5** Comparison of the concentrations of  $NO_3^-$ ,  $NH_4^+$ , and  $SO_4^{2-}$  in fine and coarse particle

Area and season	Coarse mode/ $(\mu g \cdot m^{-3})$			Fine mode/ $(\mu g \cdot m^{-3})$			Fine mode percentage/%			Reference
	$NO_3^-$	$NH_4^+$	$SO_4^{2-}$	$NO_3^-$	$NH_4^+$	$SO_4^{2-}$	$NO_3^-$	$NH_4^+$	$SO_4^{2-}$	
Inland city, summer	0.61	0.04	0.18	0.40	1.07	2.98	40	97	94	17
Inland city, winter	0.38	0.02	0.20	0.94	0.95	2.32	71	98	92	17
City, summer				1.11	3.13	9.87				18
City, whole year				3.63	2.84	8.22				18
Inland farmland, monsoon							49.6	63.7	51.8	2
Beijing, summer 2001							60	97	80	8
Beijing, winter 2002							83	91	72	8
Beijing, summer 2002							70	83	80	8
Beijing, winter 2003							82	91	84	8
Inland suburb, summer	2.92	0.51	3.36	5.91	13.0	25.0	62	95	82	Our results

1 from the soil with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  produced by photochemical reaction was a primary source of fine particles in such areas.

## 4 Conclusions

(1) During the sampling period, aerosol particles were bimodal, and the concentration of fine mode was higher than the coarse mode.

(2) Water-soluble ions  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  were unimodal, while the concentration of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  were bimodal. The majority of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were in fine mode, and those of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$  were in coarse mode. The majority of  $\text{K}^+$  and  $\text{SO}_4^{2-}$  were in fine mode before precipitation, and the concentration of fine mode decreased after precipitation. There was a relationship between weather conditions and day-to-day variability in the concentration of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and gaseous ammonia in both fine and coarse mode.

(3)  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  in coarse mode came from the mechanical processes by which soil particles entered the atmosphere, and from the reaction of the acid species on the surface of soil particle.  $\text{NH}_4^+$  of coarse mode might partly come from the reaction between ammonia and  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  in sea salt, and between ammonia and the soil particles when excessive ammonia exists.

(4) The dominant ions in fine particles were  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ . The fine particles were formed by the reaction of  $\text{NH}_3$  with acid species such as  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , in which the  $\text{NH}_3$  was released from vegetable fields and  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  were produced by photochemical reactions.  $\text{K}^+$  in the fine particle was likely from vegetation emission and biomass burning.

(5) Sea salt might contribute little to  $\text{Cl}^-$  and  $\text{Na}^+$  in the aerosol particles in the suburb of Beijing and insignificantly to the other components. The results showed that vegetable fields in the suburb of Beijing could contribute significantly to aerosol particles.

**Acknowledgements** This study was supported by the National Basic Research Program of China (Grant No. 2002CB410802).

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