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Size distributions and formation of ionic species in atmospheric particulate pollutants in Beijing, China: 1—inorganic ions

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Abstract

To study the formation of atmospheric sulfate, nitrate and chloride particulates in Beijing, China, 14 sets of measurements of the concentrations of SO_2, HNO_3, NH_3 and size-segregated particles were made in the summer of 2001 and the spring of 2002. Because of the very different humidity levels in Beijing in the summer and the spring, significant differences in the size characteristics and in the formation mechanisms of these ions were found. In the summer, the major fraction of sulfate was present in the fine mode with a mass median aerodynamic diameter (MMAD) of $0.7 \pm 0.1\,\mu m$. Its formation was attributed to in-cloud processing, which was supported by the observation of a large mole ratio of the sulfate at 0.54–1.0 μm to SO_2, with a maximum value of 3.0. The major fraction of nitrate sometimes appeared in the fine mode with an MMAD of $0.7 \pm 0.1\,\mu m$ and sometimes in the coarse mode with an MMAD of $6.0 \pm 1.5\,\mu m$. The coarse mode nitrate was associated with Ca^{2+}. The major peak of chloride, in most cases, appeared in the coarse mode. Chloride was expected to have formation mechanisms similar to nitrate formation in the coarse mode. In the spring, the major fraction of sulfate was present in the fine mode with an MMAD of $0.45 \pm 0.05\,\mu m$ and its formation was ascribed to non-cloud heterogeneous processes. A small mole ratio of the fine mode sulfate to SO_2, with a maximum value of only 0.06, was observed. Nitrate and chloride generally have a similar MMAD as sulfate in the fine mode, suggesting that both may originate from atmospheric processes similar to sulfate formation. Alternatively, they could be formed by gas condensation onto existing sulfate particles. Overall, much more efficient sulfate formation by cloud processing led to a higher sulfate concentration in the summer than in the spring, although the SO_2 concentration followed the reverse trend in Beijing.

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Keywords: Particle size; Sulfate; Nitrate; In-cloud processes; Gas-to-particle conversion

1. Introduction

Beijing is the capital and a major metropolis in China. In 2001, Beijing's population was 13 million and its annual coal consumption was 4.2×10^7 t (Beijing Environment Protection, Annual Report of 2001). The large energy consumption in Beijing led to serious air pollution there with respirable particles as the principal air pollutant. Moreover, a rapid increase of the number of vehicles (10–15% per year) and widespread construction activities exacerbate Beijing's air pollution problems. In the last decade, a lot of new tall buildings have been built. They hinder the dispersion of air pollutants. An eight-phase action plan to reduce air pollution has been implemented in Beijing since 1999.

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In the last two decades, a few short-term studies to characterize the chemical composition of atmospheric particles in Beijing have been reported in the literature (Huebert et al., 1988; Chen et al., 1994; Ning et al., 1996; Zhou et al., 1998). Between 1999 and 2000, a year-long PM2.5 study was conducted (He et al., 2001; Yao et al., 2002a). Secondary ionic species were found to contribute more than 40% of the PM2.5 mass. Yao et al. (2002a) also found that sulfate was well correlated with SO_2 and the mole ratio of sulfate to SO_2 was low (on average 0.2) in the winter, while sulfate was poorly correlated with SO_2 and had a much higher mole ratio (on average 3.7) in the summer. A seasonal dependence on the route of SO_4^{2-} formation was suggested.

Few studies on the size distributions of these secondary ionic species in the atmospheric particles in Beijing have been reported. The size distributions of ambient aerosols provide detailed information on mode distributions and also give evidence on the formation and transformation of particulate pollutants in the atmosphere (Whitby, 1978; Hering and Friedlander, 1982; John et al., 1990; Hering et al., 1997; Ondov and Wexler, 1998). For example, Whitby (1978) characterized the size distribution of sulfate with a trimodal model, consisting of the nucleation mode, the accumulation mode and the coarse mode. An accumulation mode of sulfate at 0.48±0.1 μm was reported. Hering and Friedlander (1982) and John et al. (1990) later observed that the accumulation mode of sulfate consisted of two modes. A small accumulation mode of sulfate at 0.2±0.1 μm was attributed to gaseous H_2SO_4 condensation. A larger accumulation mode (the droplet mode) of sulfate at 0.7±0.2 μm was attributed to aqueous phase reactions in fog and cloud droplets or to hygroscopic growth of aerosols from the smaller accumulation mode. More recently, Ondov and Wexler (1998) proposed that the accumulation mode of sulfate at 0.48 μm observed by Whitby (1978) was from the oxidation of SO_2 with subsequent hygroscopic growth, but the droplet mode of sulfate at 0.7 μm was formed in clouds. Because of the large water content in clouds, SO_2 is oxidized rapidly ($100\%\,h^{-1}$) by in-cloud processes (Meng and Seinfeld, 1994). The evaporation of cloud water results in droplet mode sulfate aerosols.

Nitrate, chloride and some low molecular weight water-soluble organic acids are semi-volatile species. Their partitioning in the gas and particulate phases is determined by the gas–particle equilibrium (solid or aqueous) (Wexler and Seinfeld, 1990, 1991; Meng and Seinfeld, 1996). Evaporation of these semi-volatile species and subsequent condensation on other particles alter their size distributions (Meng and Seinfeld, 1996; Song and Carmichael, 1999; Yao et al., 2002b). In this study, the size distribution and the formation of sulfate in Beijing are investigated in two seasons. Using sulfate, K^+ and Ca^{2+} as references, the size distributions and the partitioning of nitrate and chloride in different sizes of particles are examined. The size distributions of oxalic, succinic and malonic acids are discussed in a companion paper (Yao et al., 2003).

2. Experimental method

In the summer of 2001 and the spring of 2002, two sampling studies were carried out in Beijing and 14 sets of size-segregated samples were collected in total. Beijing is located at the northwestern border of the Great North China Plain, surrounded by mountains in all directions except the south. The mountains extend several hundred kilometers and the highest peak is more than 3000 m in elevation. The prevailing wind is from the north and from the northwest, in particular, in the winter and the spring, leading to a low concentration of PM2.5 despite a large emission of air pollutants due to coal consumption for heating (He et al., 2001). The mountains block air pollutants from the west and the north except during strong dust storms, which did not occur during the sampling periods.

The sampling site was on the roof of an academic building (about 15 m above the ground level) on the campus of Peking University in a northwestern suburb of Beijing. In the summer, a MOUDI-100 (MSP Corporation, USA), equipped with nominal cut-sizes of 18 (inlet), 10, 5.6, 3.2, 1.8, 1.0, 0.54, 0.32, 0.18 μm (Marple et al., 1991) and a Harvard honeycomb PM2.5 sampler (Koutrakis et al., 1992) were simultaneously used for 24 h of sampling. The honeycomb PM2.5 sampler was equipped with a Na_2CO_3-coated denuder to measure SO_2, HNO_3, HNO_2 and HCl and a citric acid-coated denuder to measure NH_3, followed by a Teflon filter, a nylon filter and a citric acid-coated Teflon filter to measure PM2.5. Each sampling usually started at 6:30 p.m. and ended at 6:15 p.m. the next day. In the spring of 2002, a MOUDI-110 (MSP Corporation, USA), equipped with nominal cut-sizes of 18 (inlet), 10, 5.6, 3.2, 1.8, 1.0, 0.54, 0.32, 0.18, 0.10 and 0.056 μm, was used. Measurements of the size-segregated aerosols, gases and PM2.5 (with a honeycomb PM2.5 sampler) were carried out simultaneously. Each sampling usually started at 7:00 p.m. and ended at 6:30 p.m. the next day. The meteorological data were obtained from the local meteorological stations.

The extraction method used on the samples has been reported by Yao et al. (2002a, b). The ionic concentrations of the aqueous extracts were determined by ion chromatography. An AS11 column (4 mm) with an AG11 guard column and an Anion Trap column (4 mm) were used for anion detection with an eluent of 0.4–6 mM NaOH (gradient). A CS12 column and an eluent of 20mM MSA were used for cation detection. The detection limits in μg/ml were 0.004 for SO_4^{2-}, 0.01

for NO_3^- and 0.004 for Cl^- in aqueous extracts. Uncertainties were ±5% for SO_4^{2-}, Cl^- and NO_3^-.

3. The size distributions of sulfate, nitrate and chloride in the summer

3.1. The size distribution of sulfate

There are major differences in the size distributions of sulfate, nitrate and chloride in the summer and in the spring. We will first discuss the measurements in the summer. In this study, fine and coarse particles are defined as particles smaller than 1.8 μm and larger than 1.8 μm, respectively. The size distributions of various ionic species, in terms of the geometric mean aerodynamic diameter, in the summer are shown in Fig. 1(a)–(h). In Fig. 1(a), sulfate has a major fraction in the droplet mode with a mass median aerodynamic diameter (MMAD) of 0.7±0.1 μm. The MMAD was determined by fitting the impactor data with log-normal distribution functions using the DISTFIT software (TSI, USA). Meng and Seinfeld (1994) attributed the formation of sulfate at 0.7 μm to in-cloud processes because the growth of condensation mode particles by the accretion of water vapor or by gas phase and/or aqueous aerosol phase sulfate production cannot explain the existence of the droplet mode. They estimated that droplet mode particles of 0.6 and 0.8 μm were obtained after water evaporated from cloud droplets of 5 μm in diameter for initial SO_2 concentrations at 1 and 10 ppb, respectively. Kerminen and Wexler (1995) verified that other processes, such as growth by condensation, coagulation or aerosol phase reactions, would take a much longer time than the atmospheric residence time of the particles and therefore would not contribute to the formation of droplet mode sulfate. In this study, the SO_2 concentrations were generally in the range of 1–2 ppb as listed in Table 1. The mole ratio of sulfate at 0.54–1.0 μm to SO_2 ranged from 0.2 to 3.0, suggesting that in-cloud formation of sulfate can be important in sulfate formation, especially when large sulfate-to-SO_2 ratios were obtained. The total cloud coverage (high-cloud + low cloud) and the low-cloud coverage (%) at 8:00 a.m., 2:00 p.m. and 8:00 p.m. are shown in Fig. 2(a). Clouds (high-cloud and/or low-cloud) generally existed in the daytime during the sampling periods. Although the total cloud coverage and the low-cloud coverage (%) at night are not available, clouds were expected to exist because of the higher relative humidity (RH) at night as shown in Fig. 2(b). Sulfate in the droplet mode was almost completely neutralized since the cation-to-anion equivalent ratio was generally close to unity for the droplet mode particles as shown in Fig. 1(i). NH_4^+, much more abundant than K^+, Ca^{2+}, Na^+ and Mg^{2+} in the particles at 0.54–1.0 μm (Fig. 1(d)–(h)), played a major role in neutralizing sulfate.

The coarse particles were alkaline because the cation-to-anion equivalent ratio was larger than unity, as shown in Fig. 1(i) (Kerminen et al., 2001). Because the concentration of Ca^{2+} was about an order magnitude larger than the sum of the concentrations of K^+, Na^+ and Mg^{2+} in Fig. 1(f)–(h), the coarse mode sulfate was mostly associated with Ca^{2+} and was completely neutralized. Sulfate sometimes peaked at the same particle size of Ca^{2+} but sometimes shifted to a small particle size, which can be explained by the kinetic limitations in the heterogeneous reactions of SO_2 with crustal aerosols and/or the larger surface area in smaller coarse particles. The reaction of H_2SO_4(g) with crustal aerosols is of minor importance in the formation of coarse mode sulfate because the concentration of H_2SO_4(g) is usually very low, even in polluted environments (Weber et al., 1995).

In Fig. 1(a), the concentration of sulfate at 0.54–1.0 μm dramatically decreases compared with a much smaller decrease in the concentration of SO_2 in the 1 and 2 August samples. Because sulfate dominates in the droplet mode at 0.54–1.0 μm, in-cloud processes are therefore a major path to form sulfate. Moreover, the sulfate equivalent concentration is three to four times the sum of the concentrations of K^+, Na^+, Ca^{2+} and Mg^{2+} in this size range. Sulfate associated with these metal ions via heterogeneous reactions therefore cannot account for the droplet mode sulfate. The smaller concentration of droplet mode sulfate can be explained by a lower rate of sulfate formation and/or a lower vertical flux of in-cloud formed sulfate aerosols from aloft to the ground level on those 2 days. Fig. 2(b) indicates that a decrease in O_3 concentration on those 2 days was not found (O_3 data from http://www.bjepd.gov.cn). Low-clouds were present on 1 and 2 August and the percentage of low-cloud coverage was higher than that on 30 July, when the highest sulfate concentration at 0.54–1.0 μm was observed (Fig. 2(a)). Hence, the formation rate of sulfate on 1 and 2 August is not expected to be particularly lower than the rest of the sampling period. From 31 July to 3 August, the prevailing wind was from the northeast (not shown) and the average wind speed varied slightly from 1.9 to 1.4 m/s as shown in Fig. 2(b). These observations suggest that sulfate from long-distance transport, if it existed, was uniform during this period. A lower vertical flux of sulfate aerosols formed in clouds may explain the disproportionate decrease of sulfate concentration on 1 and 2 August, although the vertical meteorological data were not available.

3.2. The size distribution of nitrate

As shown in Fig. 1(b), a major fraction of nitrate appeared in the fine mode on 28–31 July and 3 August, but it appeared in the coarse mode on 1–2 August. The

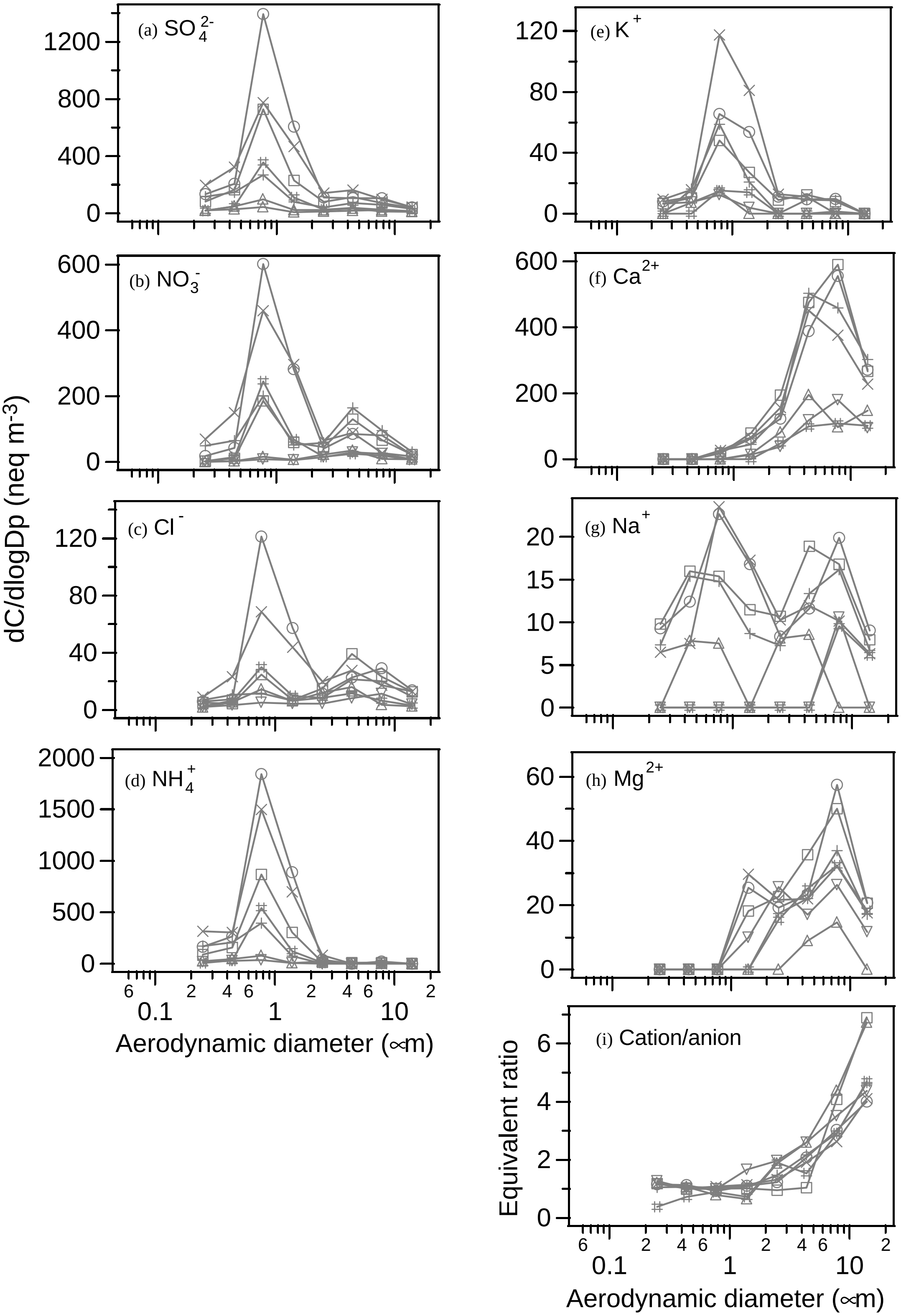

Fig. 1. The size distributions of inorganic ionic species in the summer: (+) 28 July, (×) 29 July, (○) 30 July, (□) 31 July, (△) 1 August, (▽) 2 August, (♯) 3 August.

Table 1
Summary of gas and SO_4^{2-} concentrations

Date	HCl^a (ppb)	HNO_3	SO_2	NH_3	SO_4^{2-b} (neq m^{-3})	[HCl] [NH_3] (ppb^2)	[HNO_3] [NH_3]	[SO_4^{2-}]/[SO_2] (mol/mol)
28 July	0.35	0.52	2.1	20.4	60.4	7.2	10.6	0.4
29 July	0.50	0.20	1.4	42.2	152.1	21.2	8.4	1.3
30 July	0.44	0.53	1.3	26.4	316.7	11.7	13.9	3.0
31 July	0.29	0.55	1.6	25.1	164.6	7.2	13.8	1.3
1 August	0.18	0.36	1.0	16.8	22.9	3.0	6.1	0.3
2 August	0.25	0.15	0.7	20.8	10.4	5.1	3.1	0.2
3 August	0.26	0.13	0.4	18.6	81.3	4.8	2.4	2.5
8 March	—	0.41	19.0	8.8	52.1	—	3.6	0.03
9 March	—	0.36	18.2	8.4	68.8	—	3.0	0.05
10 March	—	0.15	4.0	4.6	20.8	—	0.7	0.06
11 March	—	1.02	23.5	8.1	52.1	—	8.3	0.03
12 March	—	0.72	15.9	8.3	31.3	—	6.0	0.02
13 March	—	0.66	23.0	11.1	37.5	—	7.3	0.02
14 March	—	0.20	18.0	13.2	60.4	—	2.7	0.04

[a] In the spring samples, chloride was not estimated because of interference with a large nitrite peak.
[b] The SO_4^{2-} concentration at 0.54–1.0 μm in the summer and SO_4^{2-} concentration at 0.32–0.54 μm in the spring (neq m^{-3}).

total nitrate concentrations in the particles on 28–31 July and 3 August were much higher than those on 1 and 2 August. The MMAD of the fine mode nitrate was 0.7 ± 0.1 μm, similar to that of the droplet mode sulfate. The MMAD of the coarse mode nitrate was 6.0 ± 1.5 μm, similar to that of the coarse mode Ca^{2+}. At 0.54–1.0 μm, nitrate correlated well with sulfate with a correlation coefficient of 0.92, but at 3.2–5.6 μm, nitrate correlated well with Ca^{2+} with a correlation coefficient of 0.91.

The mode distributions of nitrate are governed by the thermodynamic equilibrium of $HNO_3(g) + NH_3(g) \leftrightarrows NH_4NO_3(s, aq)$, which is affected by the RH, temperature and the concentrations of $(NH_4)_2SO_4$, $HNO_3(g)$ and $NH_3(g)$ (John et al., 1990). When the thermodynamic equilibrium favors the formation of $NH_4NO_3(s, aq)$, nitrate will dominate in the fine mode. On the other hand, if the formation of $NH_4NO_3(s, aq)$ is not favored, the reactions of HNO_3 with $CaCO_3$ or NaCl in the coarse mode become important (Pakkanen et al., 1996; Zhuang et al., 1999). John et al. (1990) found that nitrate was dominant in the fine mode and that fine mode particles were almost completely neutralized in the samples taken from Rubidoux, California, because of the abundance of ammonia. In contrast, coarse mode nitrate was dominant in the samples taken from Long Beach, California, where the $NH_3(g)$ concentration was low and the fine mode aerosols were not completely neutralized. To examine the possibility of the formation of NH_4NO_3 (s, aq), the required [HNO_3] [NH_3] product to form NH_4NO_3 (s, aq) in the fine mode was estimated by SCAPE2 (Simulation Composition of Atmospheric Particles at Equilibrium, Meng et al., 1995). On 28 and 29 July, the maximum hourly average RH was 80% and 91% and the corresponding temperature at these RH was 20.3°C and 21.6°C, respectively. The required product of [HNO_3][NH_3] to form nitrate in the droplet mode was 3.4 and 0.9 ppb^2 on 28 and 29 July, respectively, which was only about 1/3 and 1/9 of the measured products (24 h average) listed in Table 1. Therefore, NH_4NO_3(s, aq) was likely to exist, at least during the period with a high RH. On 2 August, the required product at the hourly average maximum RH (66%) and the corresponding temperature at this RH was 51.3 ppb^2, which was much higher than the measured product (3.1 ppb^2). Nitrate was not expected in the fine mode on that day.

On 1 and 2 August, the minor fine mode of nitrate may be associated with metal ions such as K^+ because K^+, which also generally peaked at 0.54–1.0 μm, had an equivalent concentration about 50% larger than that of nitrate. However, the equivalent concentration of K^+ in the fine particles was much smaller than that of Ca^{2+} in the coarse particles. Nitrate was therefore predominantly partitioned in the coarse particles on those 2 days. On the other days, the equivalent concentration of K^+ was only 6–29% of that of fine mode nitrate and hence the nitrate associated with K^+ cannot account for the total fine mode nitrate. The dominant fine mode of nitrate was believed to originate from the current flux of NH_3 and HNO_3 onto sulfate particles and/or from in-cloud processes, but the individual contributions of these two processes to fine mode nitrate are not known.

The measured products of [HNO_3][NH_3] were much smaller than the equilibrium constants to form NH_4NO_3 in the daytime as shown in Fig. 2(a). Daytime formation of NH_4NO_3 is not expected. Although the diurnal

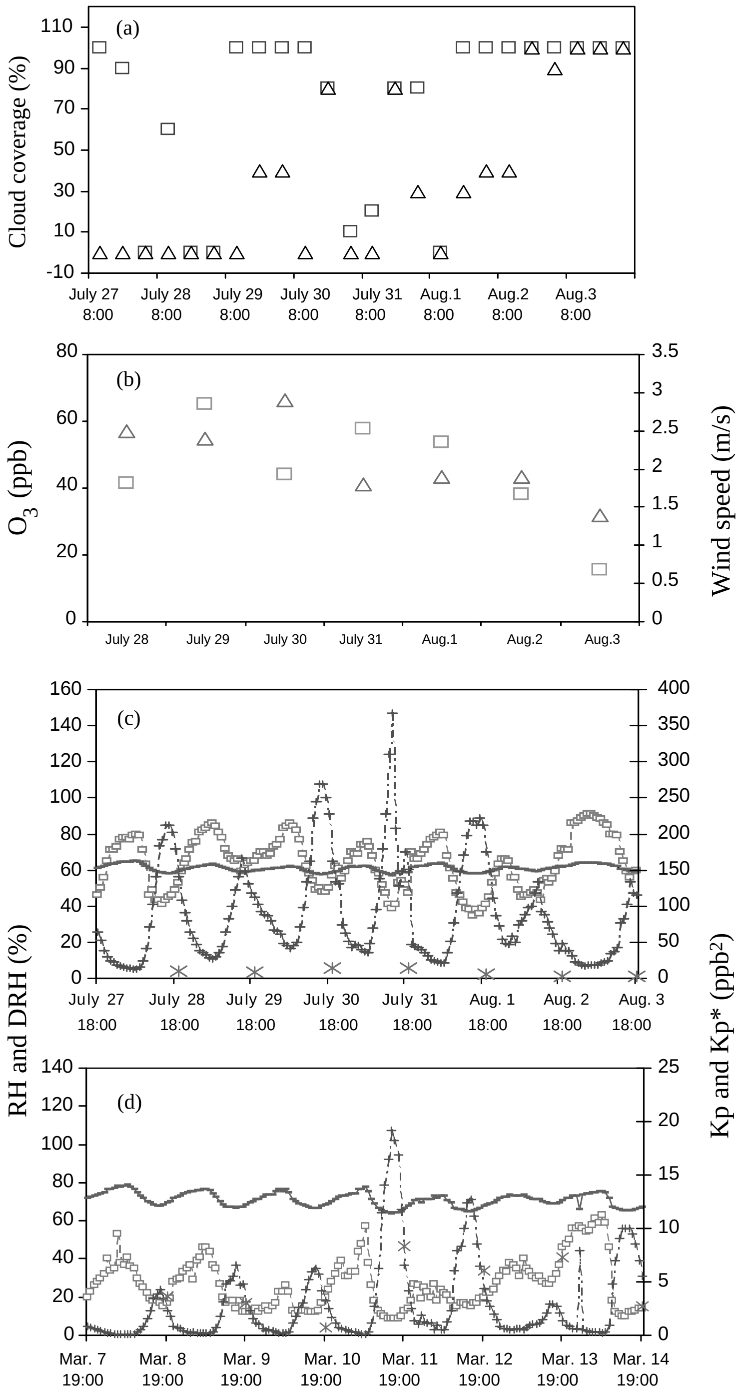

Fig. 2. The meteorological conditions during the sampling periods: (a) (□) total cloud, (△) low-cloud; (b) (□) O_3 concentration, (△) wind speed; (c) (□) RH, (−−) DRH, (+) Kp, the required product to form NH_4NO_3 (the effects of RH and sulfate aerosols were not considered), (×) Kp*, the measured product of [HNO_3] [NH_3]; (d) (□) RH, (−−) DRH, (+) Kp, the required product to form NH_4NO_3 (the effects of RH and sulfate aerosols were not considered), (×) Kp*, the measured product of [HNO_3] [NH_3].

variation of the size distribution of nitrate was not measured, nighttime formation of fine mode nitrate was expected due to higher RH and lower temperatures at night. NO_3 free radicals are the principal precursors of HNO_3 at night. However, the nitrate formed at night evaporated into the gas phase in the daytime.

The coarse mode nitrate generally peaked at 3.2–5.6 μm and was highly correlated with Ca^{2+}, which suggests that the nitrate possibly originated from the reactions of HNO_3 with $CaCO_3$ (Pakkanen et al., 1996). In the coarse mode, the concentrations of NH_4^+, K^+, Na^+ and Mg^{2+} were too low to account for the observed concentration of nitrate, as shown in Fig. 1(b) and (d)–(h). Significant amounts of nitrate formed on soil-derived particles have also been observed and have been attributed to the reaction of HNO_3 with $CaCO_3$ (Pakkanen et al., 1996; Zhuang et al., 1999). In the coarse mode, nitrate sometimes peaked at the same particle size of Ca^{2+} and sometimes shifted slightly to a size smaller than the Ca^{2+} peak. The shift of the nitrate peak was probably due to mass transfer limitations and/or the larger surface area of the smaller particles.

3.3. The size distribution of chloride

With size distribution characteristics similar to those of nitrate, chloride has mechanisms to partition into different modes of particles similar to those of nitrate. The major fraction of chloride in the droplet mode was possibly formed from the flux of HCl and NH_3 onto pre-existing sulfate particles, from multi-step cloud processes, or from primary sources associated with K^+. However, under the dry conditions on 2 August, chloride was associated with the metal ions such as K^+ because NH_4Cl was not formed. As shown in Fig. 1(c), the major fraction of chloride was present in the coarse mode on 28 and 31 July and 1–2 August. There are more cases when chloride peaked than when nitrate peaked in the coarse mode because chloride is more volatile than nitrate. In the coarse mode, similar to sulfate and nitrate, chloride sometimes peaked at the same particle size as Ca^{2+}, but sometimes it shifted slightly to the smaller particles.

4. The size distributions of sulfate, nitrate and chloride in the spring

4.1. The size distribution of sulfate

The size distributions of sulfate, nitrate and chloride in the spring are shown in Fig. 3(a)–(c). In the spring, the MMAD of sulfate in the fine mode appeared at 0.45 ± 0.05 μm, a decrease by 0.25 μm when compared to that in the summer. Since the equivalent ratio in the fine particles was generally close to unity as shown in Fig. 3(i), sulfate was completely neutralized. In the spring, data shown in Fig. 2(d), the ambient RH was much smaller than the deliquescence relative humidity (DRH, the equilibrium RH at which solid particles become aqueous droplets) of NH_4NO_3, indicating that the particles were dry. Hence, the oxidation of SO_2 and the subsequent hygroscopic growth could have occurred only in air plumes near high-temperature combustion sources. The humid air plume became dry very fast in the atmosphere, leading to the termination of the heterogeneous oxidation of SO_2 and the hygroscopic growth. This explanation is corroborated by the much lower mole ratio of sulfate in the particles at 0.32–0.54 μm to SO_2 in the spring than in the summer, as listed in Table 1. Since the rate of in-cloud oxidation of SO_2 can reach 100%/h (Meng and Seinfeld, 1994), the low sulfate-to-SO_2 mole ratio in the spring suggested that the fine mode sulfate did not originate from in-cloud processes. Moreover, low-clouds were not observed in the daytime (not shown) during the whole sampling period. Although information on the low-cloud coverage (%) at night is not available, low clouds were not expected because of the low relative humidity (generally lower than 60% at night). The sulfate formed was then neutralized by NH_4^+ because NH_4^+ was the major cation in the fine particles as shown in Fig. 3(d). In the coarse particles, sulfate was associated with the oxidation of SO_2 on dry crustal particles because both SO_4^{2-} and Ca^{2+} peaked at 3.2–5.6 μm. Since the prevailing wind direction was from northwest during the entire sampling period (not shown), the mountains to the northwest have eliminated the possibility of long-range transport of sulfate.

4.2. Size distributions of nitrate and chloride

As shown in Fig. 3(b), the major fraction of nitrate was present in the fine mode with an MMAD of 0.5 ± 0.2 μm. As shown in Fig. 2(d), the product required to form NH_4NO_3 was smaller than the measured product and the particles were dry during the sampling periods. Nitrate in the fine mode is attributed to the concurrent flux of NH_3 and HNO_3 onto dry sulfate aerosols. On 13 and 14 March, the MMAD of nitrate in the fine mode shifted to 0.7 ± 0.1 μm, larger than the MMAD of sulfate at 0.5 μm. Since K^+ peaked at 0.54–1.0 μm on these 2 days, as shown in Fig. 3(e), nitrate at 0.54–1.0 μm was partially associated with K^+ although most of the sulfate and nitrate was still associated with NH_4^+. In the coarse mode, nitrate originated from the reaction of HNO_3 with $CaCO_3$ (Zhuang et al., 1999) because nitrate and Ca^{2+} had a similar MMAD and the concentrations of Na^+ and Mg^{2+} were much smaller than those of Ca^{2+}. As shown in Fig. 3(c), the major fraction of chloride was present in the fine mode with an MMAD of 0.45 ± 0.05 μm, which was close to that of sulfate. Like sulfate, chloride formation in the fine mode possibly occurred in the air plume from high-temperature combustion sources because HCl principally originated from coal-burning in Beijing (Yao et al., 2002a). Coarse mode chloride was attributed to the reactions of HCl with $CaCO_3$.

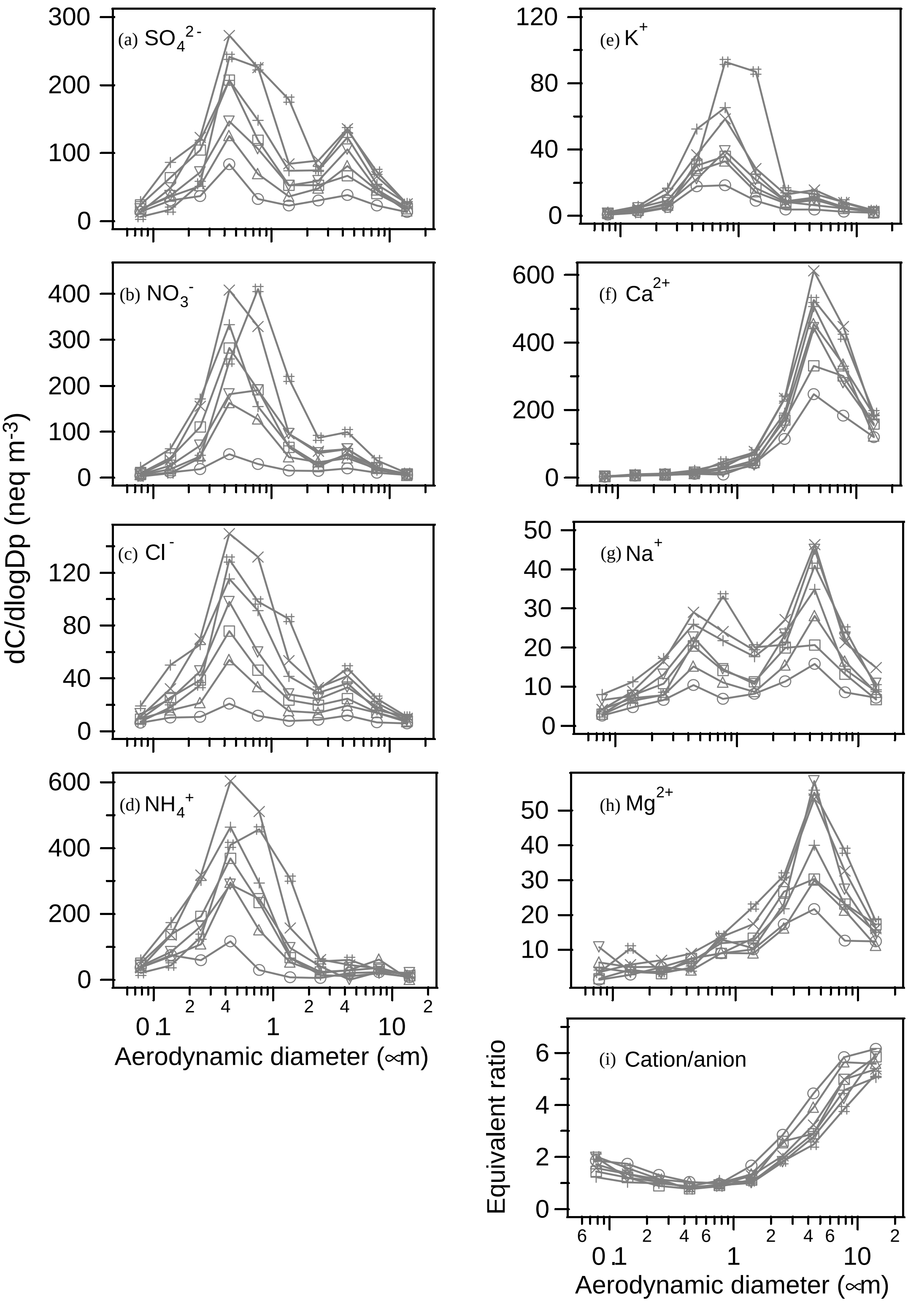

Fig. 3. The size distributions of inorganic ionic species in the spring. (+) 8 March, (×) 9 March, (○) 10 March, (□) 11 March, (△) 12 March, (▽) 13 March, (♯) 14 March.

5. Conclusion

A significant difference in the size distributions of ionic species in the particulate pollutants collected in the summer of 2001 and the spring of 2002 in Beijing was observed. The measurements of inorganic ions are presented in this paper while those of the organic ions are discussed in a companion paper. Different dominant mechanisms of the formation of sulfate, nitrate and chloride are found in the summer and in the spring. In the summer, because of the high RH, sulfate was dominantly present in the droplet mode with an MMAD of $0.7 \pm 0.1\,\mu m$ and was most likely formed by in-cloud processes. When nitrate dominantly existed in the fine mode (MMAD at $0.7 \pm 0.1\,\mu m$), it originated from the concurrent flux of NH_3 and HNO_3 into pre-existing sulfate aerosol particles and/or from multi-step in-cloud processes at night. However, NH_4NO_3 was not expected in the daytime due to the low RH. When nitrate dominantly existed in the coarse mode, it was associated with the reaction of HNO_3 with $CaCO_3$. Similar size distribution characteristics and formation mechanisms of chloride were concluded. In the spring, because of the lower RH, sulfate was also dominantly present in the fine mode with an MMAD at $0.45 \pm 0.05\,\mu m$. Sulfate was ascribed to heterogeneous formation in air plumes near emissions sources. Nitrate and chloride were mainly found in the fine mode with size distribution characteristics very similar to those of sulfate. They were formed by the deposition onto existing fine mode sulfate particles. Overall, much more efficient sulfate formation by cloud processing has led to a higher sulfate concentration in the summer than in the spring, although the SO_2 concentration follows a reverse trend in Beijing.

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