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Size distributions and formation of ionic species in atmospheric particulate pollutants in Beijing, China: 2—dicarboxylic acids

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Abstract

Sparse data on the size distributions of ionic species, especially organic ions, in atmospheric particles are available in the literature. To study the size distributions and the formation of atmospheric ionic species, 14 sets of measurements of the concentrations of the gases and size-segregated atmospheric particles were made in Beijing in the summer of 2001 and the spring of 2002. Significant differences of the size distribution characteristics and the formation mechanism of the ions in these two periods were found. Using the size distributions of SO_4^{2-}, K^+ and Ca^{2+} as references, the size distributions of oxalic, malonic and succinic acids were examined to investigate the formation of these acids in the atmospheric particles in Beijing. In the summer, oxalate was present mostly in the fine mode with an MMAD of $0.7 \pm 0.1\,\mu m$, coincident with the droplet mode of sulfate. The formation of fine mode oxalate, like sulfate, was attributed to in-cloud processes. Malonate was also present mostly in the fine mode with an MMAD of $0.8 \pm 0.2\,\mu m$ and its formation was also attributed to in-cloud processes. The MMAD of fine mode malonate sometimes shifted to values larger than that of sulfate, which can be explained by a minor evaporation of malonate during water evaporation from cloud droplets. The size distribution and the formation of succinate are similar to those of oxalate. In the spring, oxalate sometimes dominated in the fine mode, where oxalate was highly correlated with sulfate ($r = 0.86$) and had an MMAD ($0.45 \pm 0.05\,\mu m$) similar to sulfate, but it sometimes dominated in the coarse mode, in association with Ca^{2+}. The fine mode oxalate was attributed to heterogeneous formation but the coarse mode oxalate was probably related to biological formation.

Keywords: Particle size; In-cloud processes; Biological processes; Oxalate; Malonate; Succinate

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1. Introduction

Dicarboxylic acids in atmospheric particles potentially play an important role as cloud condensation nuclei (CCN) in the global atmosphere (Cruz and Pandis, 1997; Facchini et al., 1999; Kerminen, 2001). They can reduce the surface tension and the hygroscopic property of CCN and can thus affect cloud formation and the earth's radiation balance (Facchini et al., 1999). Kerminen (2001) suggested that organics are more important than sulfate in the initial growth of very small particles (<40–50 nm in diameter) because organics can reduce surface tension, but sulfate becomes more important when the particles reach the sizes of the smallest CCN corresponding to high cloud supersaturations. Although the concentrations of dicarboxylic acids

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are smaller than the concentration of sulfate in atmospheric particles (Kawamura and Ikushima, 1993, Röhrl and Lammel, 2001; Kerminen et al., 2000; Yao et al., 2002a), they are important in the growth of very small particles to larger particles that can be activated to cloud droplets.

The knowledge of the size distributions of dicarboxylic acids in atmospheric particles are essential to a better understanding of their potential contributions to CCN. The size distribution data also provide evidence for an examination of the routes of the formation of atmospheric particles (Kerminen et al., 2000; Blando and Turpin, 2000; Yao et al., 2002a). In general, the condensation mode at 0.2±0.1 μm is attributed to gas-particle condensation and the droplet mode at 0.7±0.2 μm is attributed to in-cloud processes including cloud droplet activation, physical transferring and chemical transformation in cloud droplets and evaporation of cloud droplets. Nevertheless, in very clean environments, the smallest cloud-processed particles can fall into the condensation mode. So far, most studies on low molecular weight dicarboxylic acids and their salts have focused on their chemical characterization and their formation in total suspended particulates (TSP) (Kawamura and Kaplan, 1987; Kawamura et al., 1996; Limbeck et al., 2001; Röhrl and Lammel, 2001). In the literature, only a few papers have focused on the size distributions of dicarboxylic acids (Kerminen et al., 2000; Yao et al., 2002a).

Beijing is the capital and one of the major cities in China. A year-long study was conducted to study the chemical characterization of PM2.5 in Beijing in 1999–2000 by Yao et al. (2002b). They found that oxalate correlated well with sulfate in PM2.5, but it correlated poorly with nitrate, organic carbon and carbon monoxide. The total mass concentration of oxalate, malonate and succinate accounted for only 0.5% of the organic carbon. Moreover, the aerosol acidity in Beijing was low because of the high concentration of NH_3 (Zhou et al., 1998). For example, Zhou et al. (1998) reported that the aerosol acidity was only 0.6, 6.4, 4.6 and 1.5 nmol m^{-3} in the spring, summer, fall and winter of 1995, respectively. Low aerosol acidity reduces the possibility of dicarboxylic acids evaporating from the particulate phase during cloud droplet evaporation, which can complicate the size distributions of these acids (Yao et al., 2002b). In Beijing, clouds are often present in the summer, although clouds are rare in the winter and spring because of the dry weather (http://www.bjmb.gov.cn/bj.htm). Hence, it is interesting to investigate the seasonal dependence of the size distributions and the formation mechanisms of dicarboxylic acids in Beijing. The formation of particulate sulfate is well understood (John et al., 1990; Hering and Friedlander, 1982; Meng and Seinfeld, 1994). Size distributions of some metal elements are also valuable in tracing the sources of particles (Pakkanen et al., 2001). In this study, by utilizing the size distributions of SO_4^{2-}, K^+ and Ca^{2+} as references, the formation of these dicarboxylic acids in Beijing is examined.

2. Experimental method

Two sampling studies were carried out in Beijing in the summer of 2001 and the spring of 2002, and a total of 14 sets of samples were collected. Detailed information on these samplings is available in Yao et al. (2003). In the summer, samples were collected by an eight-stage MOUDI (Model 100, MSP) and a Harvard honeycomb PM2.5 sampler (R&P, USA). In the spring, a 10-stage MOUDI and the PM2.5 sampler were used. The ionic concentrations of the aqueous extracts were determined by ion chromatography (Dionex LC20) with an electrochemical detector (ED 40). The detection limits in μg/ml were 0.01 for oxalate, 0.02 for malonate and succinate, 0.004 for SO_4^{2-}, 0.01 for NO_3^- and 0.004 for Cl^- in the aqueous extracts. Uncertainties were ±15% for oxalate and ±20% for malonate and succinate. Uncertainties were ±5% for SO_4^{2-}, Cl^- and NO_3^-.

3. The size distributions and formation of the dicarboxylic acids in the summer

3.1. The size distribution and formation of oxalate

The size distributions of oxalate, malonate and succinate in the summer are shown in Fig. 1(a–c). In this study, fine and coarse particles are defined as particles smaller and larger than 1.8 μm, respectively. Oxalate was dominant in the fine mode with a mass median aerodynamic diameter (MMAD) of 0.7±0.1 μm. Several atmospheric processes have been proposed to explain the observation of oxalate in the fine mode. These include in-cloud processes (Blando and Turpin, 2000; Yao et al., 2002a), gas phase photochemical reactions of hydrocarbons with oxidants followed by gas-particle condensation (Kawamura et al., 1993, Kalberer et al., 2001), and heterogeneous reactions (Kerminen et al., 1999). Potential sources of oxalate can also include direct emissions from vehicle exhausts (Kawamura and Kaplan, 1987), biogenic activity (Kawamura and Kaplan, 1987) and biomass burning (Narukawa et al., 1999; Yamasoe et al., 2000). In this paper, the plausibility of these various processes and sources are examined.

Since sulfate has a droplet mode with an MMAD of 0.7±0.1 μm and is attributable to in-cloud processes (see Fig. 1a in Yao et al., 2003), the mode of oxalate peaking at 0.7±0.1 μm was also possibly a droplet mode formed by in-cloud processes. Moreover, in the 0.54–1.0 μm

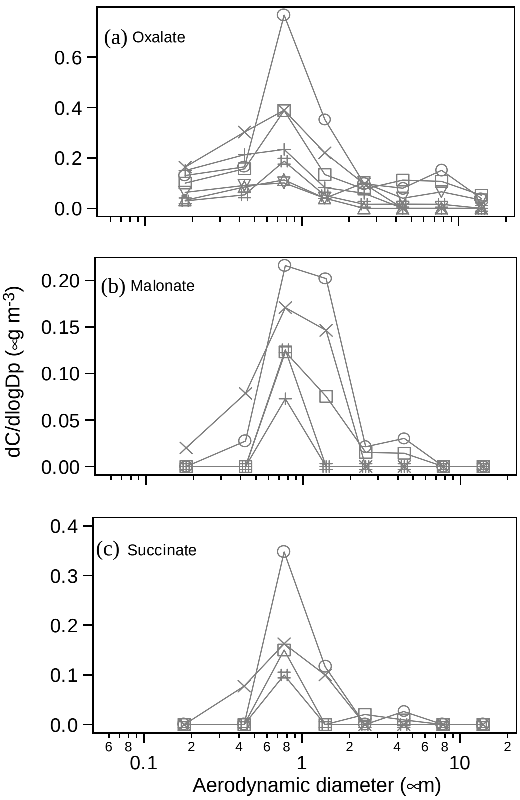

Fig. 1. The size distributions of oxalate, malonate and succinate in the summer: (+) 28 July, (×) 29 July, (○) 30 July, (□) 31 July, (△) 1 August, (▽) 2 August, (♯) 3 August.

particles, oxalate was highly correlated with sulfate with a correlation coefficient of 0.99 but the correlation coefficient of oxalate with NO_3^-, NH_4^+, K^+, Ca^{2+} and Na^+ was only 0.92, 0.77, 0.58, 0.58 and 0.75, respectively. This strongly suggests that oxalate and sulfate originated from similar atmospheric processes. Oxalate condensation on the particles would form a condensation mode of oxalate of 0.2±0.1 μm (Yao et al., 2002a), which cannot be verified because particles below 0.18 μm were not collected using the eight-stage MOUDI. Nevertheless, we can evaluate the possibility of the gas-particle condensation of oxalic acid and the growth of the condensation mode oxalate to form oxalate at 0.7 μm.

The gas phase photochemical formation of oxalic acid is initiated by the reaction of organics with photochemical oxidants, such as OH free radicals and O_3 (Kawamura et al., 1996; Kalberer et al., 2001). In general, the reaction of organics with OH free radicals is much faster than that with O_3 (Finlayson-Pitts and Pitts Jr., 1986). Since OH free radicals principally exist in the daytime (Yang et al., 2002) and the time scale of the gas-particle condensation at 0.2 μm is only a few seconds (Seinfeld and Pandis, 1998), photochemical formation of oxalic acid is possible in the daytime. Most of the vapor condenses onto existing particles immediately because of the low vapor pressure of oxalic acid (Saxena and Hildemann, 1996). However, gas-particle condensation alone would lead to the highest concentration of oxalate found in 0.18–0.32 μm particles, followed by the 0.32–0.54 and 0.54–1.0 μm particles, which are discordant with our measurements. It is also possible that the condensation mode oxalate-containing particles were activated and became the droplet mode particles after cloud processing.

The role of hygroscopic growth of the condensation mode of pure oxalic acid or the mixture of oxalic acid, sulfate and nitrate into the droplet mode was investigated. The deliquescence relative humidity of pure oxalic acid is very high (97% at 25°C) (Peng et al., 2001). In the daytime, the ambient relative humidity was generally lower than 60% (Yao et al., 2002c, Fig. 2a), indicating that the particles were dry. Hygroscopic growth of the condensation mode of oxalic acid could not occur even at night because the maximum relative humidity during the sampling periods was only 91%. Hence, condensation mode particles could not grow into droplet mode particles, leaving oxalate in the condensation mode. It is possible that oxalate coexists with sulfate and nitrate to form an internal mixture in the condensation mode. However, the hygroscopic growth of the condensation mode cannot form the droplet mode of sulfate at 0.7 μm (Meng and Seinfeld, 1994). Similarly, heterogeneous formation of oxalate cannot account for the fine mode oxalate because it would lead to a concentration at 0.18–0.32 μm higher than that at 0.54–1.0 μm. Although organic carbon was not measured in this study, Yao et al. (2002b) found that oxalate was poorly correlated with organic carbon ($r<0.1$) in PM2.5 in Beijing. Therefore, non-cloud heterogeneous reactions of particulate organic carbon were not a major process for the formation of oxalate. Nevertheless, it is possible that condensation mode oxalate-containing particles were

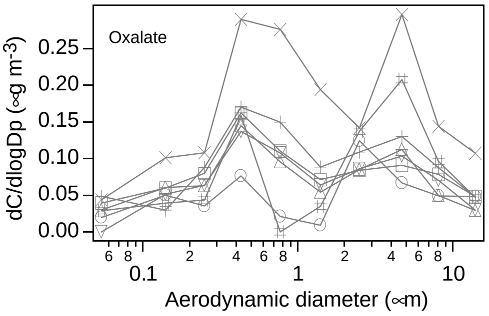

Fig. 2. The size distributions of oxalate in the spring: (+) 8 March, (×) 9 March, (○) 10 March, (□) 11 March, (△) 12 March, (▽) 13 March, (♯) 14 March.

activated and became droplet mode particles after cloud processing.

Primary emissions of oxalic acid from biomass burning have also been proposed (Narukawa et al., 1999). K^+ is a typical element associated with biomass burning (Yamasoe et al., 2000). However, at 0.54–1.0 μm, the correlation of oxalate with K^+ was poor ($r = 0.58$). Moreover, on 29 and 30 July, and 3 August, the MMAD of the fine mode oxalate was 0.7 μm but the corresponding MMAD of the fine mode K^+ (Yao et al., 2003) were 1.0, 1.0 and 1.3 μm on those days. Therefore, primary biomass burning was not a major source of the fine mode oxalate. Kawamura and Kaplan (1987) estimated that the mass ratio of malonate to succinate of primary vehicle exhaust is about 0.3–0.5. The mass concentration of particles from primary vehicle exhaust is also expected to peak at below 0.4 μm under dry conditions (Ondov and Wexler, 1998). In this study, we found that the mass ratio of malonate to succinate ranged from 0.7 to 1.6 and there was no peak below 0.4 μm. Hence, primary vehicle exhaust was also not a major source for the fine mode oxalate.

Potential biogenic sources of oxalate are plants and microorganisms. Plant leaves do not emit oxalic acid into the atmosphere directly. However, plant leaves can emit fatty acids, which may be broken down to form oxalic acid in the atmosphere as secondary pollutants (Kawamura et al., 1996). Biogenic processes can also generate oxalic acid in the soil and the roots of plants (Jones, 1998). The role of biological aerosols (bacteria, yeasts and molds) in the formation of fine mode oxalate is unknown.

In the coarse mode, the concentration of oxalate was significantly smaller than that in the fine mode. Coarse mode oxalate may originate from soil particles since oxalic acid is ubiquitously present in the soil. Oxalate is a by-product of the hydrolysis of oxaloacetate from citric acid and glyoxylate through the metabolic processes of fungi in the soil (Dutton and Evans, 1996; Gadd, 1999). Oxalate can also be destroyed by soil organisms (Granstein et al., 1977), leading to a wide variation in the concentration of oxalic acid in the soil. The reactions of oxalic acid with $CaCO_3$ and organic carbon with OH-free radicals in the coarse particles have been studied, but they are not a major route for the formation of coarse mode oxalate in the spring, as is discussed later. Since the Na^+ concentrations in the coarse mode are much smaller than those of Ca^{2+}, the role of sea salt in the formation of oxalate is negligible at this site, although it may be important in marine and coastal environments.

3.2. *The size distributions and formation of malonate and succinate*

The size distributions of malonate and succinate are shown in Fig. 1(b) and (c). Malonate has the major fraction in the fine mode with an MMAD of 0.8±0.2 μm. On 29 and 30 July, the MMAD of the fine mode malonate was 1.0 μm, coincident with the corresponding MMAD of fine mode K^+ (Yao et al., 2003, Fig. 1e). However, on 3 August, the MMADs of malonate and K^+ were 0.7 and 1.3 μm, respectively. Although malonate associated with K^+ can explain the fine mode of malonate on 29 and 30 July, it cannot explain that on 3 August. Like the formation of oxalate, in-cloud processes can form droplet mode malonate (Yao et al., 2002a). Compared to the MMAD of the droplet mode sulfate at 0.7 μm, the MMAD of malonate shifted to 1.0 μm on 29 and 30 July. This shift can be explained by the minor evaporation of malonate during cloud droplet evaporation to form aerosols. Similar shifts of oxalate in the droplet mode have been reported in Hong Kong where the major peak of malonate almost completely shifted into coarse particles (Yao et al., 2002a). Pakkanen and Hillamo (2002) also observed that the major peak of malonate shifted to the coarse mode in Helsinki but without a similar shift of oxalate. We believe that the difference in the observed size distributions among these three studies is due to the different acidity of the aerosols, which affects the extent of the evaporation of semi-volatile species such as nitrate and the organic acids. Since the acidity of the aerosols was not available in these studies, we used the size distribution of nitrate as an indicator for a qualitative comparison of the aerosol acidity.

While there was only a coarse mode nitrate peak in Hong Kong (Yao et al., 2002a), there was both a major nitrate peak in the coarse mode and a minor peak in the fine mode and a major peak of nitrate in the fine mode in Helsinki (Pakkanen and Hillamo, 2002) and only a minor peak in the coarse mode in Beijing (this study). The high concentration of nitrate in the fine mode is a manifestation of high ambient concentrations of NH_3 and low aerosol acidity. High acidity would favor the evaporation of nitric acid from the fine mode particles and lead to a coarse mode of nitrate in the abundance of crustal or sea-salt aerosols. On the basis of the nitrate size distributions, we infer that the acidity of the aerosols in Beijing is likely the lowest among the three studies. The low acidity of the aerosols leads to a minor evaporation of malonate and a negligible evaporation of oxalate during cloud droplet evaporation, which was observed in this study and by Pakkanen and Hillamo (2002). In their hygroscopic measurements using an electrodynamic balance, Peng et al. (2001) observed the evaporation of malonic acid but did not observe similar evaporation of oxalic acid. It is possible that oxalic acid is less volatile than malonic acid in the concentrated solutions used in the single particle study or in the aerosols containing ammonium salts because of hydrogen bonding. In fact, ammonium oxalate is not volatile

(Peng and Chan, 2001). The condensation of malonic acid on sulfate particles cannot explain this shift because it would result in malonate having the same MMAD of sulfate or shifting to a small particle size. Succinate was principally present in the fine mode with an MMAD at 0.7 μm, as shown in Fig. 1(c). The fine mode succinate possibly originated from in-cloud processes, like oxalate and malonate.

4. The size distributions and formation of dicarboxylic acids in the spring

The size distributions of oxalate in the spring are shown in Fig. 2. Malonate and succinate concentrations were below the detection limits during this season. The major fraction of oxalate sometimes appeared in the fine mode and sometimes appeared in the coarse mode. The fine mode oxalate has the same MMAD of 0.45 ± 0.05 μm as sulfate (Yao et al., 2003). The correlation coefficient between sulfate and oxalate was 0.86. These observations suggest that oxalate and sulfate originated from a similar process, that is, from heterogeneous reactions in the air plume from high-temperature sources (Yao et al., 2003). A small condensation mode was sometimes present with an MMAD of 0.1 μm due to gas-particle condensation. Since the ambient relative humidity was very low (daily average %RH = 20–37%) in the spring, the hygroscopic growth of the gas-particle condensation mode to the larger fine mode was negligible. The MMAD of K^+ was 0.8 ± 0.1 μm, which was much larger than the MMAD of oxalate. On March 14, an elevated K^+ concentration peaked at 0.54–1.0 μm, but the corresponding oxalate concentration at this size was below detection limits. Therefore, primary biomass burning was not a likely major source of fine mode oxalate. Since the concentrations of malonate and succinate were below detection limits, the contribution of primary vehicle exhaust toward oxalic acid cannot be evaluated.

The size distribution of coarse mode oxalate was generally similar to that of Ca^{2+} and the correlation coefficient of oxalate with Ca^{2+} in the 3.2–5.6 μm particles was 0.86. Since the fine particles in Beijing were likely neutralized as discussed earlier and in Yao et al. (2003) and the equivalent concentration of Ca^{2+} was several times that of oxalate even in the condensation mode, the reaction of oxalic acid with $CaCO_3$ would favor the formation of a condensation mode over a coarse mode of oxalate. For example, the concentration of Ca^{2+} was 11 and 125 neq m^{-3} at 0.54–1.0 and 3.2–5.6 μm, respectively, on 14 March. If the particles are assumed to be spherical, the ratio of the total surface area of the $CaCO_3$ particles at 0.54–1.0 μm to that at 3.2–5.6 μm was 0.67. However, the time scale for gas-to-particle transformation to 3.2–5.6 μm particles is more than one order of magnitude of that to 0.54–1.0 μm particles (Seinfeld and Pandis, 1998), leading to a smaller amount of oxalate in the coarse mode. This predicted trend is not in agreement with the experimental measurements and hence the reactions of oxalic acid with $CaCO_3$ cannot account for the coarse mode oxalate. The high correlation between oxalate and Ca^{2+} in the coarse mode leads to the possibility of their origins from soil particles, in which oxalate can be produced by metabolic processes from fungi. Oxalic acid is commonly produced in large quantities by many different soil fungal species (Dutton and Evans, 1996). In the metabolic processes of fungi, succinic acid and malonic acid are not the precursors of oxalic acid (Dutton and Evans, 1996; Fuzzi et al., 1997; Gadd, 1999). Hence, biological formation of oxalic acid is a plausible explanation of the absence of malonate and succinate in the spring, although the coarse mode oxalate concentration in the spring sometimes was higher than that in the summer when malonate and succinate were detected.

5. Conclusion

Like the measurements of the inorganic ions presented in the first part of this study (Yao et al., 2003), a significant difference in the abundance and the size distribution characteristics of the dicarboxylic acids, especially oxalate, was observed in the summer and in the spring. Oxalate had the major fraction in the fine mode in the summer but it sometimes had the major fraction in the fine mode and sometimes in the coarse mode in the spring. In the fine mode, the MMAD of oxalate in the summer was at 0.7 ± 0.1 μm, which was 0.25 μm larger than that in the spring (0.45 ± 0.05 μm). Oxalate was well correlated with sulfate, with a correlation coefficient of 0.99 in the summer and 0.86 in the spring, and it had an MMAD similar to sulfate. Similar to sulfate, the formation of oxalate in the fine mode was attributed to in-cloud processes in the summer and non-cloud heterogeneous reactions in the spring. Oxalate in the coarse mode may be due to biological processes. Biological production of oxalic acids should be further investigated.

In the summer, malonate also had a major fraction in the fine mode with an MMAD of 0.8 ± 0.2 μm. In some cases, the droplet mode of malonate shifted to a size larger than the corresponding droplet mode of sulfate, which can be explained by a partial evaporation of malonate during water evaporation from cloud droplets. The fine mode of malonate was also attributed to in-cloud processes. Since the size distribution of succinate was similar to that of oxalate, the mechanism of the formation of fine mode succinate was probably similar to that of oxalate.

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