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Discussions

Diurnal variations of total carbon, dicarboxylic acids, ketoacids and α-dicarbonyls in aerosols in the northern vicinity of Beijing

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Abstract

Aerosol samples (TSP, $n = 58$) were collected on day- and night-time basis at Mangshan in the north of Beijing, China in autumn 2007 to better understand the status of air quality and the influence of urban pollutants in the northern vicinity of Beijing. The samples were analyzed for aerosol mass, total carbon (TC), low molecular weight α, ω-dicarboxylic acids (C_2-C_{12}), ketoacids (ωC_2-ωC_9, pyruvic acid), α-dicarbonyls (glyoxal and methylglyoxal), as well as aromatic (phthalic, iso- and terephthalic) diacids. Aerosol mass and TC concentrations are higher in daytime than in nighttime. TC/aerosol mass ratios in this study are lower than those reported in megacities in East Asia, but higher than those reported in marine aerosols. Molecular distributions of diacids demonstrated that oxalic (C_2) acid was the most abundant species, comprising 38–77 % of total diacids, followed by succinic (C_4) and malonic (C_3) acids. For most compounds, the concentrations were higher in daytime than nighttime, indicating that diacids are produced in daytime by photochemical oxidation of organic precursors emitted from anthropogenic sources in Beijing during the transport to Mangshan area by the northward wind. However, we found that C_2 concentrations are higher in nighttime than in daytime. A positive correlation of C_2 to glyoxylic acid (ωC_2) was obtained at night when relative humidity increased up to 100 %, suggesting that aqueous phase production of C_2 occurs in nighttime via the oxidation of ωC_2. Depletion of C_2 by photolysis of Fe-oxalato complexes might be another reason for the lower concentrations of C_2 in daytime samples. High phthalic acid/C_4 ratios in the aerosol samples suggest that automobile combustion and coal burning products are important sources, which are subjected to photochemical oxidation during the atmospheric transport of urban aerosols from Beijing. In contrast, higher concentrations of methylglyoxal in nighttime than daytime may suggest that isoprene emitted from the northern forest area is oxidized in daytime and then transported to the sampling area at night by northerly winds. This study demonstrates that secondary organic aerosols are significantly produced and aged in the vicinity of Beijing during atmospheric transport.

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1 Introduction

Atmospheric aerosols not only have an impact on human health and visibility, but also affect the global climate system (Kaufman et al., 2002; Menon et al., 2002; Huebert et al., 2003; Richter et al., 2005). Increased summer floods in the south and droughts in the north of China may have been linked to the anthropogenic aerosols that alter the regional atmospheric circulation (Menon et al., 2002). Dicarboxylic acids are ubiquitous and generally the most abundant compound class in atmospheric aerosols. They can be primarily formed from fossil fuel combustion (vehicular exhaust and coal burning) and biomass burning (Kawamura and Kaplan, 1987; Narukawa et al., 1999; Kundu et al., 2010a, b), and secondarily produced by the oxidation of volatile organic compounds (VOCs) in aerosol phase (Kawamura et al., 1996a, 2005). But, dicarboxylic acids are generally considered to be of secondary origin via atmospheric oxidation. Oxalic acid (C_2) usually is the most abundant dicarboxylic acid in the atmosphere (Kawamura and Sakaguchi, 1999). Aqueous phase chemistry in aerosol/cloud/fog droplets is also important in the production of C_2 (Warneck, 2003), and iron(III) catalysed photochemical process serves as a major removal pathway for atmospheric oxalic acid (Zuo and Hoigne, 1992, 1994).

China has been facing serious air pollution problems due to huge usage of fossil fuels. One fourth of global primary anthropogenic organic aerosols are generated in China, approximately 70 % of which originate from coal burning (Streets et al., 2004). Beijing, the capital of China and one of the biggest mega-cities in the world, is located in northern China with a population of over 15.4 million, 4 million automobiles and several huge industrial regions. This megacity has been suffering a persistent problem of air pollution. To control the air quality of Beijing, the chemical processes, atmospheric transport and chemical compositions of aerosols need to be understood. In summer 2006, CAREBEIJING field program was carried out, including intensive observations in the city center and also in the southern part of Beijing city (Ho et al., 2010).

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However, comprehensive observations of atmospheric gaseous and aerosol components had not been performed in the north of Beijing. Over the city area, dominant wind direction is southerly in daytime and northerly in nighttime during August to September. It is thus expected, in north of Beijing where a large forest park exists, that we could sample air that had been transported from Beijing in daytime and from the north in nighttime. The air masses from Beijing may be highly influenced by the pollutants and photochemical processes whereas air masses from forest area may be less affected by the pollutants in nighttime.

In this study, we collected day- and nighttime aerosol samples at Mangshan, 40 km north of Beijing, to better understand the air quality of the northern vicinity of Beijing based on the measurements of water-soluble organic compounds including dicarboxylic acids. We found that the concentrations of oxalic acid increased in nighttime rather than in daytime. Here, we report the molecular compositions of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls and their diurnal variations in early autumn over Mangshan in the north of Beijing in 2007. We will discuss the aqueous phase chemical processing of water-soluble organic species in nighttime during the atmospheric transport, which may be an important process to alter the organic aerosol compositions in the vicinity of megacities.

2 Samples and methods

2.1 Site description and aerosol sampling

Aerosol sampling was carried out at Mangshan site (40°16′ N, 116°17′ E) (Fig. 1). This site is located at 40 km north of Beijing and near the entrance of the biggest forest park of Beijing and vicinity areas. Mountain-surrounded areas are expanded to the north of Mangshan, while populous, urbanized and industrialized areas including Beijing, Tianjin and Hebei Provinces are concentrated in the south of the site. The sampling site of Mangshan is located at an elevation of about 187 m above sea level.

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Three-hour daytime samples ($n = 26$), 9 h daytime samples ($n = 12$), and 15 h nighttime samples ($n = 20$) were collected together with 4 field blanks from 15 September to 5 October 2007 using a high-volume air sampler and pre-combusted quartz fiber filters. Before and after the sampling, filters were stored in a clean glass jar (150 mL) with a Teflon-lined screw cap. The filter samples were stored at −20 °C in a dark freezer room prior to analysis.

Meteorological parameters including temperature, relative humidity, and wind direction were collected at the sampling site. The average temperature and relative humidity at Mangshan were 25 °C and 57 % in daytime and 17 °C and 78 % in nighttime, respectively. The wind from the south-southwest (205°, on average) dominated during daytime and the wind from the northeast (30°, on average) dominated during nighttime (Fig. 2). Wet precipitation occurred on 18 and 26 September, and 1 and 3 to 5 October.

2.2 Analytical methods

2.2.1 Determination of aerosol mass and TC concentrations

The filters were weighed one by one before and after sampling to calculate the amount of aerosol mass. For total carbon (TC) analyses, a small disc (area 3.14 cm^2) was cut off from each filter sample. The disc was placed in a tin cup and shaped into a rounded ball using a pair of flat-tipped tweezers. The samples were introduced into the elemental analyzer (EA; model: NA 1500 NCS, Carlo Erba Instruments) using an auto-sampler, and oxidized in a combustion column packed with chromium trioxide at 1020 °C in which the tin container burns (> 1400 °C) to promote the intensive oxidation of sample materials in an atmosphere of pure oxygen. The combustion products are transferred to a reduction column packed with metallic copper that was maintained at 650 °C. The CO_2 derived during these processes was isolated on a packed GC column and then measured with a thermal conductivity detector. Acetanilide was used as an external standard to determine TC. The analytical error in the determination of TC was 2.5 % based on triplicate analyses.

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2.2.2 Determination of organic acids and dicarbonyls

Detailed procedures for the analysis of dicarboxylic acids and related compounds are described in Kawamura and Ikushima (1993) and Kawamura (1993). Briefly, aliquots of the filter samples were extracted with Milli Q water for the isolation of dicarboxylic acids and related compounds under ultrasonication. The extracts were concentrated using a rotary evaporator and then derivatized to dibutyl esters and acetals with 14 % borontrifluoride (BF_3) in *n*-butanol at 100 °C. The derived dibutyl esters and dibutoxy acetals were determined using a capillary gas chromatograph (GC) (Hewlett-Packard, HP6890) equipped with a split/splitless injector, fused silica capillary column (HP-5, 25 m × 0.2 mm i.d. × 0.5 µm film thickness) and an FID detector. For the peak identification and quantification, authentic diacid dibutyl esters were used as external standards. Recoveries of diacid standards spiked to quartz filter were more than 70 %. Replicate analyses of the samples showed that the analytical errors in the determination of organic species was on average < 10 %. Levels of field blanks were below 10 % of actual samples. The data reported here were all corrected against the field blanks.

3 Results and discussion

3.1 Total aerosol mass concentrations

Throughout the 3-weeks observation of aerosols at Mangshan site, we found enhanced concentrations of total aerosol masses in daytime, as shown in Fig. 3a. The daytime concentrations ranged from 47.8 to 603 µg m^{-3} with an average of 267 µg m^{-3}. While in nighttime, the concentrations ranged from 29.4 to 270 µg m^{-3} with an average of 146 µg m^{-3}. The higher concentrations in daytime are probably associated with the northward transport of polluted air mass from the Beijing area, where many industries exist and emissions from the city of Beijing are serious as well as automobile exhaust emissions. Pollutants emitted from the combustion of fossil fuels in the urban

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and industrial regions are possibly transported to Mangshan site by the northeasterly wind in daytime, causing the higher concentrations of aerosol masses in daytime. The enhanced concentrations of aerosol masses in daytime may also be caused by photochemical production of organic and inorganic aerosols via gas-to-particle conversion. Meanwhile, wind direction shifts northerly at night thus the air masses originate from the forest areas in the north of Beijing.

3.2 Total carbon

The concentrations of total carbon (TC) in bulk aerosol are shown in Fig. 3b. We found that TC is generally higher in daytime than nighttime. The concentrations of TC ranged from 5.8 to 51.3 $\mu g\,m^{-3}$ with an average of 24.9 $\mu g\,m^{-3}$ in daytime and from 3.5 to 34.5 $\mu g\,m^{-3}$ with an average of 16.9 $\mu g\,m^{-3}$ in nighttime. The proportions of TC in bulk aerosol masses are shown in Fig. 3c. TC comprised 9 % of bulk aerosol mass in daytime and 11 % in nighttime. Usually, the concentrations of TC and their proportion in bulk aerosol mass are higher in the source regions, and lower in the region which is far from the source. In this study, the TC values are lower than those observed in Beijing (49 $\mu g\,m^{-3}$, 17 %, Sekine et al., 1992) and those observed in Tokyo (24 $\mu g\,m^{-3}$, 21 %, Kawamura and Yasui, 2005), but are higher than those reported in marine aerosols from the Pacific (0.38 $\mu g\,m^{-3}$, 0.75 %, Kawamura and Sakaguchi, 1999). These comparisons suggest that the Mangshan aerosols are not seriously influenced by the emission sources in Beijing.

3.3 Molecular compositions of dicarboxylic acids, ketoacids, and α-dicarbonyls

A homologous series of α, ω-dicarboxylic acids (C_2-C_{12}), ketocarboxylic acids (ωC_2-ωC_4, ωC_7-ωC_9, and pyruvic acid), α-dicarbonyls (glyoxal and methylglyoxal) and aromatic (phthalic, iso-/tere-phthalic) dicarboxylic acids were detected in the samples. Ta-

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ble 1 presents concentrations of 32 water-soluble organic species in the Mangshan aerosols for daytime and nighttime.

The concentrations of total dicarboxylic acids ranged from 122 to 2380 ng m^{-3} with an average of 1090 ng m^{-3} in daytime and from 105 to 3050 µg m^{-3} with an average of 1210 ng m^{-3} in nighttime. These values are higher than those (90–1370 ng m^{-3}, av. 480 ng m^{-3}) reported in urban Tokyo, Japan (Kawamura and Ikushima, 1993), but are close to those reported in 14 Chinese cities (319 to 1940 ng m^{-3}, av. 904 ng m^{-3} in winter, and 211 to 2160 ng m^{-3}, av. 892 ng m^{-3} in summer) (Ho et al., 2007), and are also close to those (300 to 2100 ng m^{-3}) reported in Nanjing, China (Wang et al., 2002). Interestingly, the concentrations in Mangshan are higher than those (290–1440 ng m^{-3}, av. 760 ng m^{-3}) reported in Beijing (Ho et al., 2010). Further, we found higher concentrations of diacids in nighttime than in daytime, being in contrast to total aerosol masses and TC, which showed higher concentrations in daytime. This point will be discussed in more details in terms of chemical processes of organic aerosols. However, the concentrations of diacids are significantly lower than those (220–6070 µg m^{-3}) reported from Mt. Tai in the North China Plain during field burning season of agricultural wastes (wheat straws) in early summer (Kawamura et al., 2013), although their concentrations became equivalent to the values in Mangshan after the end of field burning in the North China Plain.

Oxalic acid (C_2) was found as the most abundant diacid, followed by malonic (C_3) or succinic (C_4) acid. C_2 can be primarily generated by fossil fuel combustion (Kawamura and Kaplan, 1987) and biomass burning (Narukawa et al., 1999) and secondarily formed by the oxidation of volatile organic compounds (VOCs) and other organic precursors in gas phase and/or aerosol phase (Kawamura et al., 1996a, b, 2005). Aqueous phase chemistry in aerosol/cloud/fog droplets is also important in the production of C_2 (Warneck, 2003, 2005; Miyazaki et al., 2009). The average concentration of C_2 was 607 ng m^{-3} in daytime and 806 ng m^{-3} in nighttime. The concentration of C_4 was 115 ng m^{-3} in daytime and 107 ng m^{-3} in nighttime, whereas that of C_3 was 123 ng m^{-3} in daytime and 88.5 ng m^{-3} in nighttime. Phthalic acid (Ph) was found as the fourth

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most abundant diacid. Ph is directly emitted from combustion sources (Kawamura and Kaplan, 1987) and secondarily formed by atmospheric degradation of aromatic hydrocarbons such as naphthalene (Kawamura and Ikushima, 1993; Ho et al., 2010). Interestingly, Ph was reported as the second most abundant diacid following oxalic acid in the urban aerosols from Beijing (Ho et al., 2010). This result suggests that the Mangshan aerosols are less polluted than the Beijing aerosols. The average concentration of Ph was 66.7 ng m^{-3} in day samples and 42.4 ng m^{-3} in night samples, which are significantly higher than those (av. 29 ng m^{-3}) reported in urban Tokyo in summer (Kawamura and Yasui, 2005), but lower than those (av. 90 ng m^{-3}) reported in Chinese cities (Ho et al., 2007).

Concentrations of total ketocarboxylic acids ranged from 23 to 340 ng m^{-3} with an average of 131 ng m^{-3} in daytime and from 13 to 230 ng m^{-3} with an average of 98 ng m^{-3} in nighttime. They have been considered as intermediates in the oxidation of monocarboxylic acids and other precursors in the atmosphere, resulting in dicarboxylic acids (Kawamura and Ikushima, 1993; Kawamura et al., 1996a). In this study, glyoxylic acid (ωC_2) was found as the most abundant ketocarboxylic acid, followed by pyruvic acid (Pyr) and 4-oxobutanoic acid (ωC_4). The concentrations of ketocarboxylic acids are similar to those (av. 53 ng m^{-3}) reported at Gosan site in Jeju Island, South Korea (Kawamura et al., 2004) and slightly higher than those reported at urban sites in China (45 ng m^{-3}) (Ho et al., 2007). These comparisons suggest that the organic aerosols were more aged in Mangshan than in Chinese urban sites due to photochemical processing during the atmospheric transport.

α–Dicarbonyls showed concentrations ranging from 5.3 to 271 ng m^{-3} (average 51.5 ng m^{-3}) in daytime and from 3.5 to 289 ng m^{-3} (average 59.8 ng m^{-3}) in nighttime. Glyoxal (Gly) and methylglyoxal (MeGly) are gas-phase oxidation products of numerous VOCs such as benzene, toluene, xylene (Volkamer et al., 2001), ethylene (Ervens et al., 2004), isoprene (Zimmermann et al., 1996) and terpene (Fick et al., 2004). These α-dicarbonyls could act as precursors of secondary organic aerosols via heterogeneous processes (Kroll et al., 2005; Liggio et al., 2005). The concentrations of

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α-dicarbonyls in the Mangshan samples were several times higher than those reported in Chinese cities (0 to 64 ng m^{-3}, average 12 ng m^{-3}) (Ho et al., 2007). This result also supports that organic aerosols are photochemically more altered in the vicinity of megacity like Mangshan than in Chinese urban sites during the atmospheric transport.

Figure 4 shows temporal changes in the concentrations of water-soluble diacids, ketoacids and α-dicarbonyls during the campaign. Interestingly, lower concentrations of diacids were obtained when rain events occurred in the night of 17 September, evening of 26 September, and daytime of 1 October. Weak rain lasted from 4 to 5 October when the concentrations gradually decreased (Fig. 4). The drastic decrease in the concentrations of diacids and related compounds indicates that wet scavenging of aerosols (washout effect) controls the concentrations of water-soluble organic species. The atmospheric particles containing water-soluble organic acids and related compounds as well as sulfate may have acted as cloud condensation nuclei (CCN) during the precipitation events (Leaitch et al., 1996; Yu et al., 2000; Pradeep Kumar et al., 2003). After the rainfall ended, their concentrations stayed low for 1–2 days before the aerosols started to built up again. The concentrations gradually increased in the subsequent sunny days due to the transport of aerosols from the urban and other areas and photochemical formation of water-soluble organics in the atmosphere. High loadings of diacids and related compounds were maintained before the next rainfall came. The period of this cycle was approximately 9 days.

3.4 Diurnal variations of dicarboxylic acids, ketoacids, and α-dicarbonyls

Most organic species, except for oxalic (C_2), azelaic (C_9), 8-oxooctanoic (ωC_8) and 9-oxononanoic (ωC_9) acids, were more abundant in daytime than nighttime, indicating that they are produced by photochemical oxidation of organic precursors emitted from anthropogenic sources in Beijing, and are transported from urban Beijing to Mangshan area by the northward wind in daytime. Phthalic acid (Ph) clearly showed higher concentrations relative to total diacids in daytime than nighttime (Fig. 5a), suggesting that anthropogenic sources are more important in daytime than nighttime. Because the wind blew from the south to the north in daytime, the organic precursors emitted from motor vehicles and fossil fuel combustion may be transported to the Mangshan site from the urban and industrial regions. The wind direction shifted from southerly to northerly at night, thus it is likely that the aerosols, which are emitted in Beijing and transported to the north in daytime, should come back to Mangshan with the northerly wind in nighttime with additional contribution from natural sources in the forest areas located in the north of Beijing.

Succinic acid (C_4) can be a precursor of malonic acid (C_3) by the photochemical breakdown in the atmosphere. The C_3/C_4 ratio can be used as an indicator of enhanced photochemical aging of organic aerosols (Kawamura and Ikushima, 1993). Lower C_3/C_4 ratios (0.25–0.44, av. 0.35) were reported in vehicular exhaust (Kawamura and Kaplan, 1987) compared to those of atmospheric aerosols (0.56–2.9, av. 1.6) because C_3 is thermally less stable than C_4 in the high temperature combustion process (Kawamura and Ikushima, 1993). Further, malonic acid is probably more produced in the air by photochemical process (Kawamura and Ikushima, 1993). In this study, C_3/C_4 ratios were 1.22 in daytime samples and 0.97 in nighttime samples (Fig. 5b), which are higher than those reported in northern Chinese cities in summer (0.61) (Ho et al., 2007). Higher C_3/C_4 ratios in Mangshan aerosols suggest that secondary formation and transformation of diacids are more important in daytime than nighttime under the strong sunlight conditions. However, the C_3/C_4 ratios in Mangshan aerosols are significantly lower than those (0.7–10.8, av. 5.4) reported in the remote marine atmosphere (Kawamura and Sakaguchi, 1999), where photochemical processing is commonly more extensive.

C_6 acid is produced by the atmospheric oxidation of anthropogenic cyclohexene (Grosjean et al., 1978; Hatakeyama et al., 1987), whereas C_9 is from biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987). Thus C_6/C_9 ratio can be used as an indicator to evaluate the relative contributions from anthropogenic and biogenic sources to organic aerosols (Kawamura and Yasui, 2005). In this study, C_6/C_9 ratios show higher values in daytime (av. 0.93) than in nighttime (av. 0.61) (Figure 5c). The

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C_6/C_9 ratios of less than unity for both day- and nighttime samples support that biogenic organic compounds are an important source of organic aerosols in Mangshan especially in nighttime. C_9 and C_{11}-C_{12} diacids are oxidation products of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987). Interestingly, their concentrations are higher in nighttime than daytime within the same date; nighttime/daytime concentration ratios of C_9, C_{11} and C_{12} are on average 1.2, 1.7 and 2.3, respectively. These results emphasize the important contribution of biogenic unsaturated fatty acids to organic aerosols in nighttime. Because vaccenic acid ($C_{18:1}\omega_7$) is of bacterial origin (Kawamura and Gagosian, 1987), the predominance of its oxidation product, i.e., undecanedioic acid (C_{11}), in nighttime suggests that bacterial lipids are more oxidized at night probably in aqueous phase.

3.5 Formation mechanism of oxalic acid (C_2) in nighttime

We found that concentrations of C_2 are higher in nighttime than daytime with its nighttime to daytime concentration ratio of 1.3 on average. A similar result has been reported in the New Delhi aerosol samples where average nighttime concentration of oxalic acid is almost twice as high as the daytime concentration (Miyazaki et al., 2009). Because C_2 can be produced by the oxidations of longer-chain diacids (Kawamura et al., 1996b), C_2/total diacid ratio can be used to evaluate the aging of organic aerosols (Kawamura and Sakaguchi, 1999). With the progress of aerosol aging, the ratio should become higher. Interestingly, the C_2/total diacids ratios show peaks in nighttime (Fig. 5d), indicating that the nighttime aerosols were more aged with a production of oxalic acid. It is likely that anthropogenic aerosols, which are emitted from the urban and industrial regions, can travel to the north in daytime by the southerly wind and return to the sampling site in nighttime by the northerly wind. During the atmospheric transport, the aerosols are subjected to photochemical aging to result in an increase in C_2/total diacid ratios.

Because the relative humidity was quite high in nighttime (up to 100 %, 78 % on average), we suppose that C_2 was produced in aqueous phase in nighttime. Biogenic and

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anthropogenic VOCs can react with oxidants to produce MeGly and Gly in gas phase in both day- and nighttime. In daytime, important oxidants are OH radical (Fan and Zhang, 2004) and O_3 (Kamens et al., 1982) whereas the main oxidant in nighttime is NO_3, which only react with biogenic VOCs such as isoprene and monoterpenes emitted from the forest area (Warneke et al., 2004). Hence, biogenic VOCs may act as important source in nighttime. As illustrated in Fig. 6, MeGly and Gly that are produced in gas phase can be dissolved in aqueous phase and hydrated to form $CH_3COCH(OH)_2$ and $(OH)_2CHCH(OH)_2$, respectively. Hydrated MeGly is further oxidized to result in pyruvic acid, acetic acid, hydrated glyoxylic acid (ωC_2), and finally oxalic acid. Similarly, hydrated Gly can be oxidized to ωC_2, and finally to oxalic acid (Lim et al., 2005; Sorooshian et al., 2007). Aqueous phase reactions are mainly initiated by NO_3 in nighttime (Herrmann et al., 2000), as well as H_2O_2 (in the presence of H_2SO_4) (Claeys et al., 2004). However, the mechanisms of aqueous phase reactions in nighttime are not fully understood at present.

Although C_2 is more abundant in nighttime, the concentrations of ωC_2 become lower in nighttime than daytime (see Fig. 7). This result is consistent with the higher ratio of C_2/total diacids in nighttime (Fig. 5d). Thus, it is likely that C_2 is partly produced via the oxidation of ωC_2, which is derived from methylglyoxal and glyoxal. These α-dicarbonyls may be produced by the oxidation of biogenic VOCs emitted from the northern forest in daytime, then transported southward to the Mangshan site in nighttime and react with NO_3 and other oxidants in gaseous phase to result in ωC_2 and then C_2 in aqueous phase. As shown in Fig. 8, the slope of regression line between C_2 and C_3 in nighttime is twice greater than that in daytime, suggesting that C_2 is more produced from C_3 in nighttime than in daytime. Similar trend was found for the slope for the combination of C_2 and C_4, although the difference between day- and nighttime is smaller. These results may suggest that both anthropogenic and biogenic sources contribute to the production of C_2 probably via aqueous phase reactions at night. In contrast, C_2 is primarily produced in daytime from anthropogenic sources, e.g. automobile exhaust

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and coal burning in the urban areas, and is secondarily produced by the photochemical oxidation of anthropogenic and biogenic precursors during the atmospheric transport.

Further, the higher concentrations of C_9 diacid, ωC_8 and ωC_9, which are produced by the oxidation of biogenic unsaturated fatty acids (Yokouchi and Ambe, 1986; Kawamura and Gagosian, 1987), also indicate that biogenic emissions in daytime are important source for the production of these C_8 and C_9 species in nighttime. Photochemical breakdown of C_9, ωC_8 and ωC_9 may produce low molecular weight dicarboxylic acids including C_4, C_3, and C_2 as illustrated in Fig. 9. However, detailed mechanisms for the production of C_2-C_4 diacids need to be further explored. Although oxalic acid is known as a by-product of fossil fuel combustion, its omnipresence in the remote atmospheres, coupled with its estimated lifetime of six to eight days, suggest either a background primary source or mechanism for the formation from natural precursors (Crahan et al., 2004; Myriokefalitakis et al., 2011).

Figure 10 compares the concentrations of total diacids and oxalic acid in Mangshan aerosols with those reported from various locations in East Asia. The concentrations of total diacids and C_2 are much higher in the aerosols from Mangshan than those from Tokyo (Kawamura and Ikushima, 1993), Gosan (Kundu et al., 2010a) and Chinese cities (Ho et al., 2007), indicating that the Mangshan aerosols are significantly polluted and/or photochemically aged. However, they are lower than those reported for Mt. Tai aerosols that are significantly influenced by field burning of agriculture wastes as stated above (Kawamura et al., 2013). Because Mangshan is located in the north of Beijing (Fig. 1), this site is heavily influenced by the transport of pollutants emitted from Beijing and the subsequent photochemical processing. Interestingly, the concentrations obtained in Mangshan are higher than those reported in the center of Beijing and the south of Beijing (Ho et al., 2010). The primary aerosols and organic precursors are transported from Beijing to Mangshan in daytime and are subjected to photochemical processing during the atmospheric transport.

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3.6 Loss process of oxalic acid (C_2) in daytime

Various loss processes also control the concentrations of C_2 and its fractions in total diacids. These loss processes may be another important reason to lower the concentrations of C_2 in daytime than in nighttime. It was reported that C_2 can be decomposed by photolysis of iron (III)/iron (II)-oxalato complexes to result in CO_2, which is an important sink of C_2 in the aqueous phase in the atmosphere (Zuo and Hoigne, 1992, 1994; Ervens et al., 2003; Pavuluri and Kawamura, 2012). This process largely depends on light intensity, pH, and concentrations of iron, and the photolysis of iron-oxalato complexes is more effective in OH radical-enriched environment (Zuo and Hoigne, 1992). This loss process is considered to be much more effective than the oxidation of C_2 by OH (Zuo and Hoigne, 1992, 1994). Therefore, it is likely that during daytime, oxalic acid is in part destroyed by the photolysis of Fe-oxalato complexes in atmospheric aerosols.

In summary, C_2 in Mangshan aerosols can be produced by the nighttime aqueous phase oxidation during the return transport of the polluted air masses, but it can be removed by iron(III) catalysed photochemical decomposition process in atmospheric waters during daytime.

4 Summary and conclusions

Distributions of low molecular weight dicarboxylic acids and related compounds were studied in the aerosol samples collected from Mangshan in the north of Beijing, China. Oxalic (C_2) acid was detected as the most abundant diacid (daytime: 607 ng m^{-3}; nighttime: 806 ng m^{-3}, on average), followed by succinic (C_4) (daytime: 115 ng m^{-3}; nighttime: 107 ng m^{-3}) or malonic (C_3) acid (daytime: 123 ng m^{-3}; nighttime: 88.5 ng m^{-3}). We found phthalic acid (Ph) is the fourth most abundant diacid with higher concentrations in daytime (66.7 ng m^{-3}) than nighttime (42.4 ng m^{-3}), being different from the urban aerosols from Beijing in which Ph is the second dominant diacid. Higher abundance of phthalic acid in daytime can be explained by the photochemical oxidation

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of anthropogenic organic precursors, which are emitted from Beijing and its industrial regions, and then transported to Mangshan area by the southerly wind in daytime.

We discovered higher concentrations of oxalic acid in nighttime aerosols throughout the campaign. In nighttime, anthropogenic aerosols, which are emitted from the urban Beijing area and transported to the north in daytime, move back to the south (Mangshan) by the northerly wind. During the atmospheric transport in nighttime when ambient temperature decreases and relative humidity increases (up to 100 %). C_2 is likely to be produced in nighttime by the aqueous phase oxidation of C_3 and C_4 as well as glyoxal and methylglyoxal, the latter are oxidation products of biogenic and anthropogenic hydrocarbons. Diurnal variations of C_2 suggest that oxalic acid may be in part removed by photolysis of Fe-oxalato complexes in atmospheric waters in daytime. This study also demonstrates that water-soluble organic aerosols are built up by the atmospheric transport (back and forth daily) of air masses in the vicinities of megacity Beijing until the low-pressure system dominates over the region and the wet precipitation starts to scavenge the aerosol particles from the atmosphere.

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References

Claeys, M., Wang, W., Ion, A. C., Kourtchev, I., Gelencsér, A., and Maenhaut, W.: Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide, Atmos. Environ. 38, 4093–4098, 2004.

Crahan, K. K., Hegg, D., Covert, D. S., and Jonsson, H.: An exploration of aqueous oxalic acid production in the coastal marine atmosphere, Atmos. Environ., 38, 3757–3764, 2004.

Ervens, B., George, C., Williams, J.E., Buxton, G.V., Salmon, G.A., Bydder, M., Wilkinson, F., Dentener, F., Mirabel, P., Wolke, R., and Herrmann, H.: CAPRAM 2.4 (MODAC mechanism):

An extended and condensed tropospheric aqueous phase mechanism and its application, J. Geophys. Res., 108, 4426, doi:10.1029/2002JD002202, D14, 2003.
Ervens, B., Feingold, G., Frost, G. J., and Kreidenweis, S. M.: A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, J. Geophys. Res., 109, D15205, doi:10.1029/2003JD004387, 2004.
Fan, J. W. and Zhang, R. Y.: Atmospheric oxidation mechanism of isoprene, Environ. Chem. 1, 140–149, doi:10.1071/EN04045, 2004.
Fick, J., Nilsson, C., and Andersson, B.: Formation of oxidation products in a ventilation system, Atmos. Environ., 38, 5895–5899, 2004.
Grosjean, D., Van Cauwenberghe, K., Schmid, J. P., Kelley, P. E., and Pitts Jr., J. N.: Identification of C_3-C_{10} aliphatic dicarboxylic acids in airborne particulate matter, Environ. Sci. Technol., 12, 313–317, 1978.
Hatakeyama, S., Ohno, M., Weng, J., Takagi, H., and Akimoto, H.: Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air, Environ. Sci. Technol. 21, 52–57, 1987.
Herrmann, H., Ervens, B., Jacobi, H. W., Wolke, R., Nowacki, P., and Zellner, R.: CAPRAM 2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry, J. Atmos. Chem., 36, 231–284, 2000.
Ho, K. F., Cao, J. J., Lee, S. C., Kawamura, K., Zhang, R., Chow, J. J. C., and Watson, J. G.: Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban atmosphere of China, J. Geophys. Res., 112, D22S27, doi:10.1029/2006JD008011, 2007.
Ho, K. F., Lee, S. C., Kawamura, K., Tachibana, E., Cheng, Y., Zhu, T., and Ho, S. H. S.: Dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls, fatty acids and benzoic acid in urban aerosols collected during 2006 campaign of air quality research in Beijing (CAREBeijing-2006), J. Geophys. Res., 115, D19312, doi:10.1029/2009JD013304, 2010.
Huebert, B. J., Bates, T., Russell, P. B., Shi, G., Kim, Y. J., Kawamura, K., Carmichael, G., and Nakajima, T: An overview of ACE-Asia: Strategies for quantifying the relationships between Asian aerosols and their climatic impacts, J. Geophys. Res., 108, 8633, doi:10.1029/2003JD003550, 2003.
Kamens, R. M., Gery, M. W., Jeffries, H. E., Jackson, M., and Cole, E. I.: Ozone–isoprene reactions: Product formation and aerosol potential, Int. J. Chem. Kinet., 14, 955–975, doi:10.1002/kin.550140902, 1998.

Kaufman, Y. J., Tanre, D., and Boucher, O.: A satellite view of aerosols in the climate system, Nature, 419, 215–223, 2002.
Kawamura, K.: Identification of C_2-$C_{/0}$ ω-oxocarboxylic acids, pyruvic acid, and C_2-C_3 α-dicarbonyls in wet precipitation and aerosol samples by capillary GC and GC/MS, Anal. Chem., 65, 3505–3511, 1993.
Kawamura, K. and Gagosian, R. B.: Implication of ω-oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids, Nature, 325, 330–332, 1987.
Kawamura, K. and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, Environ. Sci. Technol., 27, 2227–2235, 1993.
Kawamura, K. and Kaplan, I. R.: Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air, Environ. Sci. Technol., 21, 105–110, 1987.
Kawamura, K. and Sakaguchi, F.: Molecular distribution of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, J. Geophys. Res., 104, 3501–3509, 1999.
Kawamura, K. and Yasui, O.: Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, Atmos. Environ., 39, 1945–1960, 2005.
Kawamura, K., Kasukabe, H., and Barrie, L. A.: Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: one year of observations, Atmos. Environ., 95, 1709–1722, 1996a.
Kawamura, K., Seméré, R., Imai, Y., Fujii, Y., and Hayashi, M.: Water soluble dicarboxylic acids and related compounds in Antarctic aerosols, J. Geophys. Res., 101, 18721–18728, doi:10.1029/96JD01541, 1996b.
Kawamura, K., Kobayashi, M., Tsubonuma, N., Mochida, M., Watanabe, T., and Lee, M.: Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition. Geochemical Investigation in Earth and Space Science: A Tribute to Issac R. Kaplan, edited by: Hill, R. J., Leventhal, J., Aizenshtat, Z., Baedecker, M. J., Glaypool, G., Eganhouse, R., Goldhaber, M., and Peters, K., 243–265, Elsevier, 2004.
Kawamura, K., Imai, Y., and Barrie, L. A.: Photochemical production and loss of organic acids in high Arctic aerosols during long-range transport and polar sunrise ozone depletion events, Atmos. Environ., 39, 599–614, 2005.

Kawamura, K., Tachibana, E., Okuzawa, K., Aggarwal, S. G., Kanaya, Y., and Wang, Z. F.: High abundances of water-soluble dicarboxylic acids, ketocarboxylic acids and a-dicarbonyls in the mountain aerosols over the North China Plain during wheat burning season, Atmos. Chem. Phys. Discuss., 13, 3695–3734, doi:10.5194/acpd-13-3695-2013, 2013.

Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, J. Geophys. Res., 110, D23207, doi:10.1029/2005JD006004, 2005.

Kundu, S., Kawamura, K., and Lee, M.: Seasonal variations of diacids, ketoacids, and α-dicarbonyls in aerosols at Gosan, Jeju Island, South Korea: Implications for sources, formation, and degradation during long-range transport, J. Geophys. Res., 115, D19307, doi:10.1029/2010JD013973, 2010a.

Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: Molecular distributions of dicarboxylic acids, ketocarboxylic acids and a-dicarbonyls in biomass burning aerosols: implications for photochemical production and degradation in smoke layers, Atmos. Chem. Phys., 10, 2209–2225, doi:10.5194/acp-10-2209-2010, 2010b.

Leaitch, W. R., Li, S.-M., Liu, P. S. K., Banic, C.M., Macdonald, A. M., Isaac, G. A., Couture, M. D., and Strapp, J. W.: Relationships among CCN, aerosol size distribution and ion chemistry from airborne measurements over the bay of fundy in August–September, 1995, Nucleation and Atmospheric Aerosols 1996, edited by: Kulmala, M. and Wagner, P. E., 840–843, Elsevier, 1996.

Liggio, J., Li, S. M., and McLaren, R.: Reactive uptake of glyoxal by particulate matter, J. Geophys. Res., 110, D10304, doi:10.1029/2004JD005113, 2005.

Lim, H. J., Carlton, A. G., and Turpin, B. J.: Isoprene forms secondary organic aerosol through cloud processing: Model simulations, Environ. Sci. Technol., 39, 4441–4446, 2005.

Menon, S., Hansen, J., Nazarenko, L., and Luo, Y.: Climate effects of black carbon aerosols in China, Science, 297, 2250–2253, 2002.

Miyazaki, Y., Aggarwal, S. G., Singh, K., Gupta, P. K., and Kawamura, K.: Dicarboxylic acids and water-soluble organic carbon in aerosols in New Delhi, India, in winter: Characteristics and formation processes, J. Geophys. Res., 114, D19206, doi:10.1029/2009JD011790, 2009.

Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K., Segers, A., and Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D modeling study, Atmos. Chem. Phys., 11, 5761–5782, doi:10.5194/acp-11-5761-2011, 2011.

Narukawa, M., Kawamura, K., Takeuchi, N., and Nakajima, T.: Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, Geophys. Res. Lett., 26, 3101–3104, 1999.
Pavuluri, C. M. and Kawamura, K.: Evidence for 13-carbon enrichment in oxalic acid via iron catalyzed photolysis in aqueous phase, Geophys. Res. Lett., 39, L03802, doi:10.1029/2011GL050398, 2012.
Pradeep Kumar, P., Broekhuizen, K., and Abbatt, J. P. D.: Organic acids as cloud condensation nuclei: Laboratory studies of highly soluble and insoluble species, Atmos. Chem. Phys., 3, 509–520, doi:10.5194/acp-3-509-2003, 2003.
Richter, A., Burrows, J., Nub, H., Granier, C., and Niemeier, U: Increase in tropospheric nitrogen dioxide over China observed from space, Nature, 437, 129–132, 2005.
Saxena, P. and Hildemann, L.: Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, J. Atmos. Chem., 24, 57–109, 1996.
Sekine, Y., Hashimoto, Y., Nakamura, T., Chen, Z., and Mitsuzawa, S.: Characterization of atmospheric aerosols components at Beijing, China, J. Jpn Soc. Air Pollut., 27, 237–245, 1992.
Sorooshian, A., Ng, N. L., Chan, A. W. H., Feingold, G., Flagan, R. C., and Seinfeld, J. H.: Particulate organic acids and overall water-soluble aerosol composition measurements from the 2006 Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), J. Geophys. Res., 112, D13201, doi:10.1029/2007JD008537, 2007.
Streets, D. G., Bond, T. C., Lee, T., and Jang, C.: On the future of carbonaceous aerosol emissions, J. Geophys. Res., 109, D24212, doi:10.1029/2004JD004902, 2004.
Volkamer, R., Platt, U., and Wirtz, K.: Primary and secondary glyoxal formation from aromatics: Experimental evidence for the bicycloalkyl-radical pathway from benzene, toluene, and p-xylene, J. Phys. Chem. A, 105, 7865–7874, 2001.
Wang, G. H., Niu, S. L., Liu, C., and Wang, L. S.: Identification of dicarboxylic acids and aldehyde of PM_{10} and $PM_{2.5}$ aerosols in Nanjing, China, Atmos. Environ. 36, 1941-1950, 2002.
Warneck, P.: In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, Atmos. Environ., 37, 2423–2427, 2003.
Warneck, P.: Multi-phase chemistry of C_2 and C_3 organic compounds in the marine atmosphere, J. Atmos. Chem., 51, 119–159, 2005.

Warneke, C., de Gouw, J. A., Goldan, P. D., Kuster, W. C., Williams, E. J., Lerner, B. M., Jakoubek, R., Brown, S. S., Stark, H., Aldener, M., Ravishankara, A. R., Roberts, J. M., Marchewka, M., Bertman, S., Sueper, D. T., McKeen, S. A., Meagher, J. F., and Fehsenfeld, F. C.: Comparison of daytime and nighttime oxidation of biogenic and anthropogenic VOCs along the New England coast in summer during New England Air Quality Study 2002, J. Geophys. Res., 109, D10309, doi:10.1029/2003JD004424, 2004.
Yokouchi, Y. and Ambe, Y.: Characterization of polar organics in airborne particulate matter, Atmos. Environ., 20, 1727–1734, 1986.
Yu, S. C.: Role of organic acids (formic, acetic, pyruvic and oxalic) in the formation of cloud condensation nuclei (CCN): A review, Atmos. Res., 53, 185–217, 2000.
Zimmermann, J. and Poppe, D.: A supplement for the RADM2 chemical mechanism: The photooxidation of isoprene, Atmos. Environ., 30, 1255–1269, 1996.
Zuo, Y. and Hoigne, J.: Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron (III)-oxalato complexes, Environ. Sci. Technol., 26, 1014, doi:10.1021/es00029a022, 1992.
Zuo, Y. and Hoigne, J.: Photochemical decomposition of oxalic, glyoxalic and pyruvic acid catalysed by iron in atmospheric waters, Atmos. Environ., 28, 1231–1239, 1994.

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Table 1. Concentrations of dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls and bulk parameters in aerosol samples from Mangshan, China.

	Daytime ($n = 38$)				Nighttime ($n = 20$)			
Component	Min.	Max.	Ave.	S.D.	Min.	Max.	Ave.	S.D.
Dicarboxylic acids (ng m^{-3})								
Oxalic, C_2	53.2	1300	607	398	57.6	1879	806	604
Malonic, C_3	29.3	233	123	67.9	16.6	169	88.5	47.6
Succinic, C_4	11.0	270	115	72.0	11.1	286	107	72
Glutaric, C_5	2.91	72.4	34.2	21.7	3.46	78.3	27.8	19.9
Adipic, C_6	1.40	44.1	19.7	13.2	1.18	45.7	15.2	11.6
Pimelic, C_7	N.D.	21.1	6.16	4.81	0.32	15.9	6.15	4.20
Suberic, C_8	N.D.	24.3	1.23	3.92	N.D.	2.19	0.53	0.48
Azelaic, C_9	1.05	74.4	24.0	17.7	1.82	64.1	27.8	17.8
Sebaric, C_{10}	N.D.	5.82	2.56	1.62	0.29	5.04	1.91	1.23
Undecanedioic, C_{11}	N.D.	5.27	1.62	1.56	0.14	7.66	2.80	2.22
Dodecanedioic, C_{12}	N.D.	1.64	0.58	0.56	0.11	5.63	1.35	1.57
Methylmalonic, iC_4	0.22	11.5	6.22	2.89	1.30	6.78	3.90	2.00
Methylsuccinic, iC_5	1.36	37.8	14.2	8.74	1.21	26.7	12.8	8.2
2-Methylglutaric, iC_6	0.34	8.57	2.40	1.97	0.20	19.5	2.96	4.13
Maleic, M	0.37	84.3	15.3	24.1	0.14	135	18.7	29.4
Fumaric, F	1.28	16.4	7.23	4.06	1.37	19.0	8.61	5.30
Methylmaleic, mM	1.33	26.0	9.07	6.11	0.84	25.7	9.29	7.28
Malic, hC4	N.D.	11.9	3.25	2.98	0.09	9.28	1.32	1.94
Phthalic, Ph	7.01	218	66.7	5.55	5.00	203	42.4	4.44
Isophthalic, iPh	0.44	18.0	8.06	7.61	0.76	15.3	6.88	6.49
Terephthalic, tPh	0.60	29.8	9.90	44.2	0.32	21.5	10.3	43.0
Ketomalonic, kC_3	0.41	6.52	2.60	1.62	0.37	5.26	1.73	1.16
4-Ketopimelic, kC_7	N.D.	16.2	6.06	4.60	0.54	10.3	4.13	3.03
Total diacids	122	2384	1088	671	105	3056	1208	829
Ketocarboxylic acids (ng m^{-3})								
Pyruvic	2.04	73.8	24.7	18.1	1.52	67.0	21.0	18.8
Glyoxylic, ωC_2	11.8	195	82.1	54.0	10.1	121	58.6	32.4
3-Oxopropanoic, ωC_3	2.62	47.0	19.1	13.8	1.82	17.6	7.80	4.05
4-Oxobutanoic, ωC_4	2.39	35.0	17.3	9.76	0.86	23.2	10.5	6.48
7-Oxoheptanoic, ωC_7	0.50	14.0	5.76	3.26	0.96	13.2	5.52	3.40
8-Oxooctanoic, ωC_8	0.36	14.1	5.95	3.84	0.69	18.1	7.45	4.72
9-Oxononanoic, ωC_9	N.D.	11.6	3.90	3.18	0.09	15.4	5.51	4.39
Total ketoacids	23.0	340	159	95	12.7	232	97.9	64.8
α-Dicarbonyls (ng m^{-3})								
Glyoxal, Gly	3.15	35.3	14.9	8.82	2.59	33.8	12.6	7.93
Methylglyoxal, Megly	1.01	242	36.6	50.7	0.96	255	47.2	66.3
Total dicarbonyls	5.27	271	51.5	56.9	3.55	289	59.8	70.1
Bulk parameters (µg m^{-3})								
Aerosol mass	47.8	603	267	129	29.4	270	146	78.6
Total carbon	5.79	51.3	24.9	13.4	3.51	34.5	16.9	9.51

N.D. = Not Detected.

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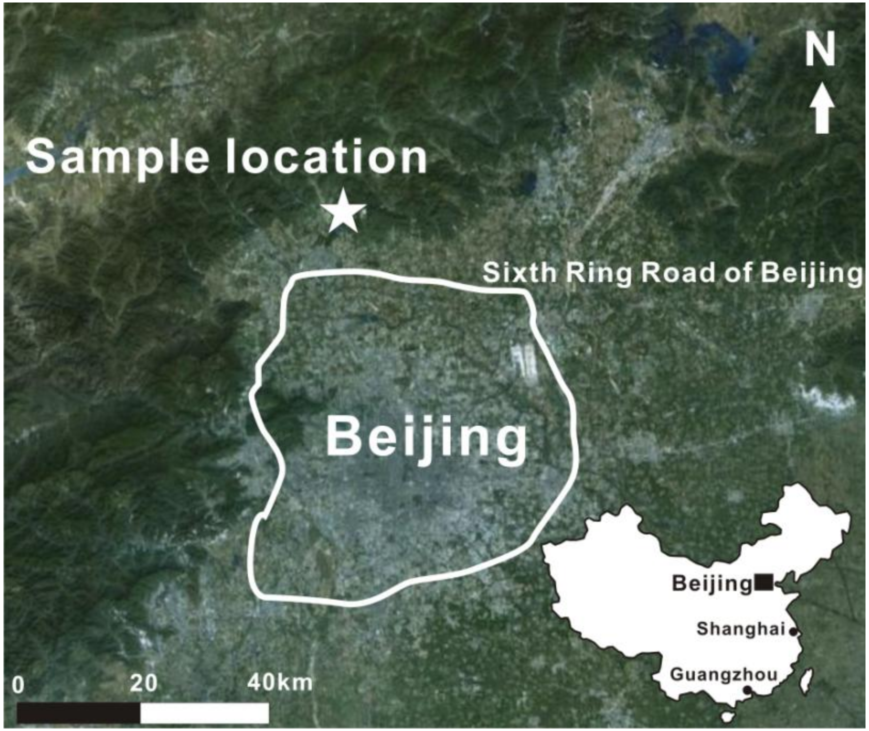

Fig. 1. A map of Beijing and its vicinity with the sampling site at Mangshan (white star).

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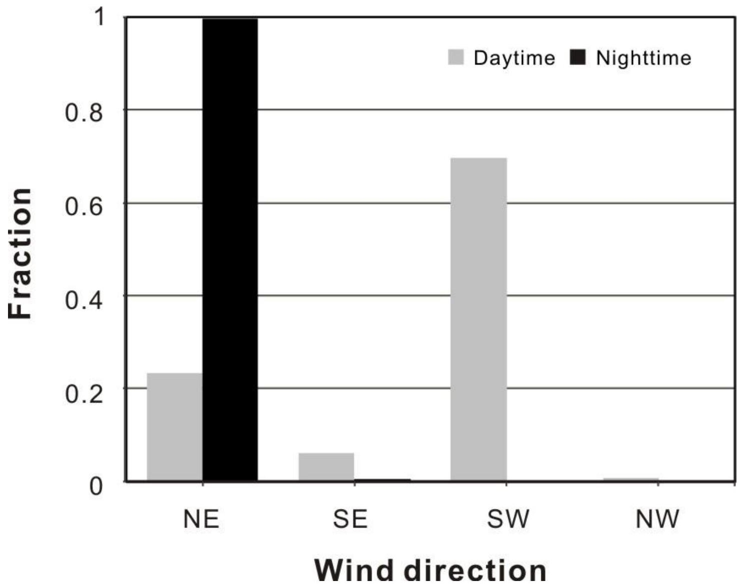

Fig. 2. Fractions of 4 local wind directions in daytime and nighttime, respectively. Winds blew mainly from southwest to northeast in daytime and the winds blew dominantly from northeast to southwest in nighttime.

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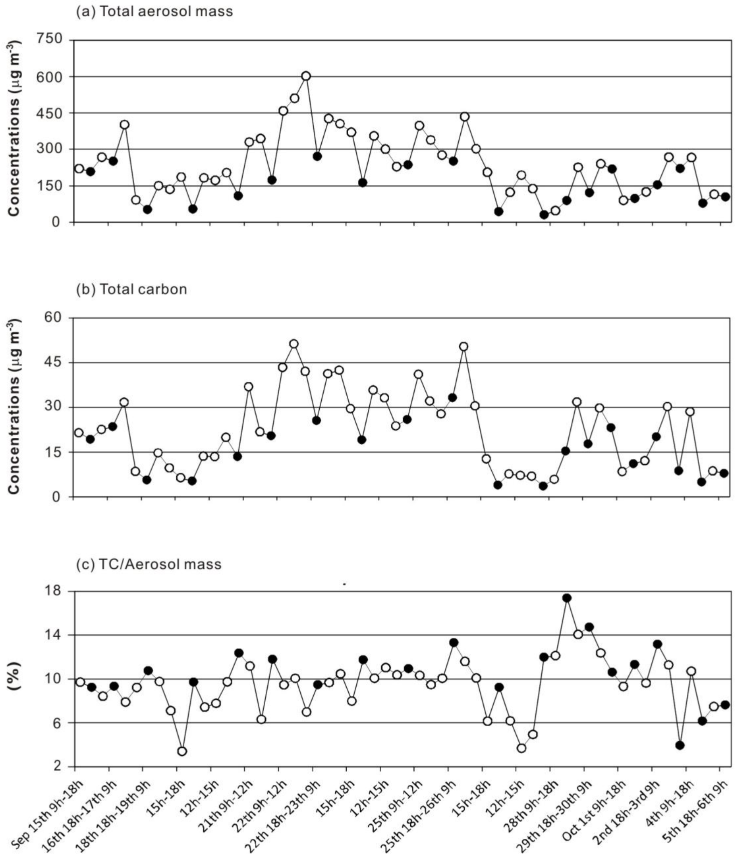

Fig. 3. Temporal variations of **(a)** total aerosol masses (µg m^{-3}), **(b)** total carbon concentrations (µg m^{-3}) and **(c)** proportion of TC in bulk aerosols in Mangshan TSP samples. The hollow circle represents daytime sample and the solid circle represents nighttime sample.

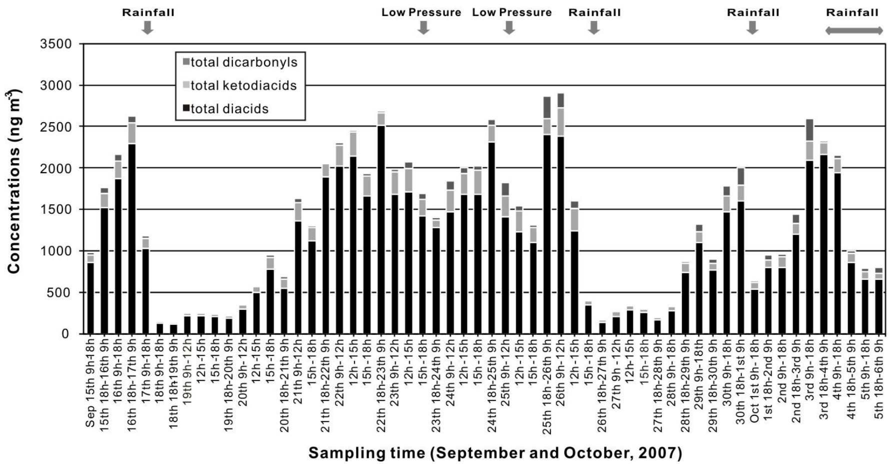

Fig. 4. Changes in the concentrations (ng m^{-3}) of total water-soluble dicarboxylic acids, keto-carboxylic acids and α-dicarbonyls in the ambient aerosols from Mangshan.

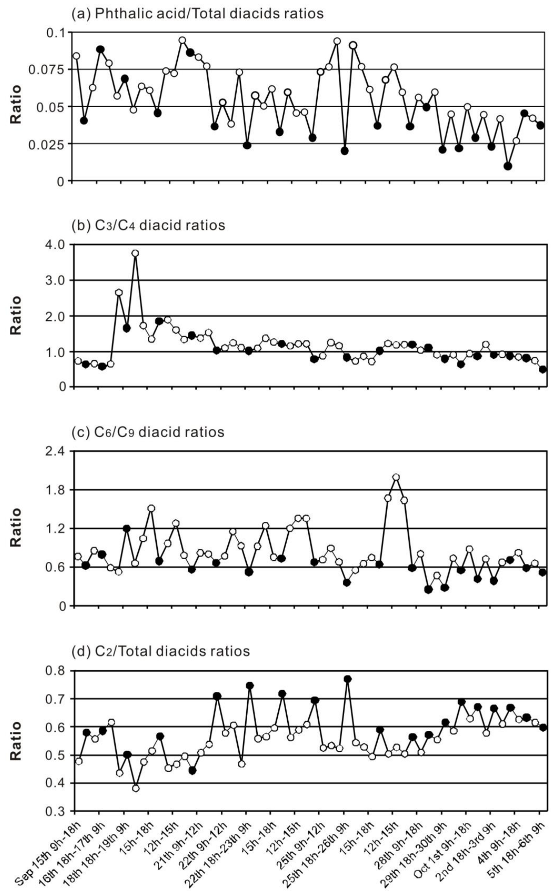

Fig. 5. Temporal variations of **(a)** Ph/total diacids ratios, **(b)** C_3/C_4 diacid ratios, **(c)** C_6/C_9 diacid ratios and **(d)** C_2/total diacids ratios in Mangshan aerosols. The hollow circle represents daytime sample and the solid circle represents nighttime sample.

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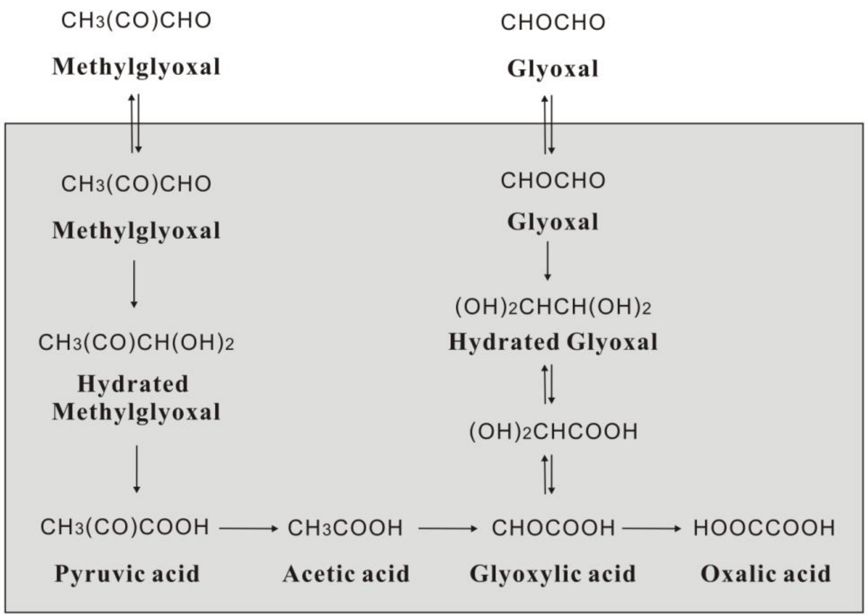

Fig. 6. Multiphase mechanisms for the production of small organic acids (shaded area means aerosol aqueous phase whereas non-shaded area means gas phase).

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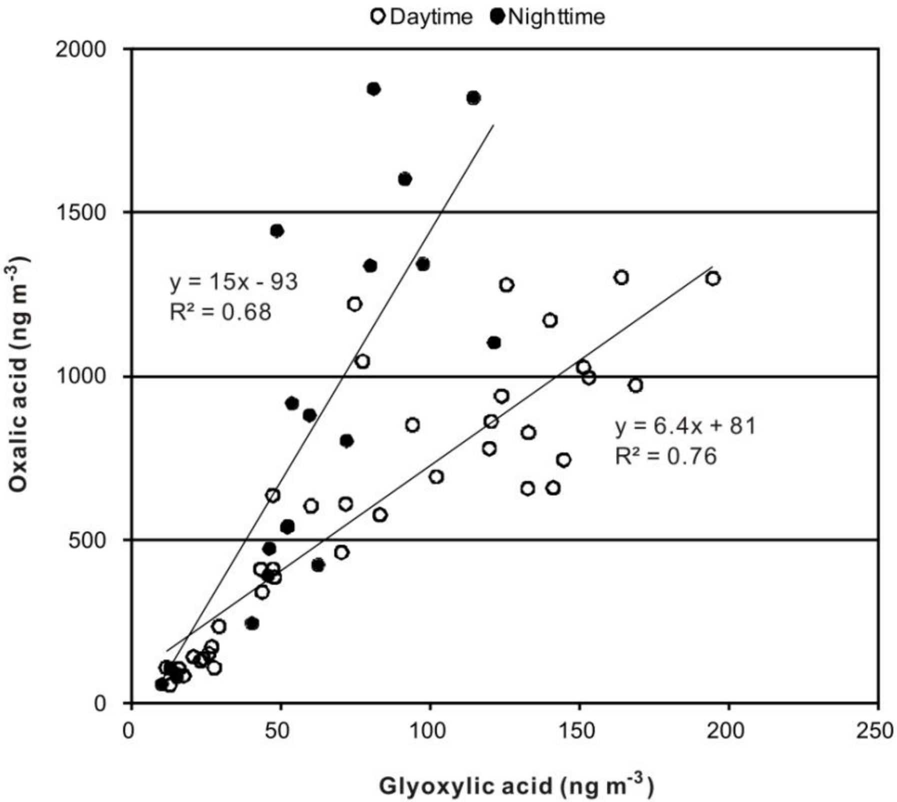

Fig. 7. Correlation plots for the concentrations of oxalic acid (C_2) and glyoxylic acid (ωC_2) in Mangshan aerosols for daytime and nighttime.

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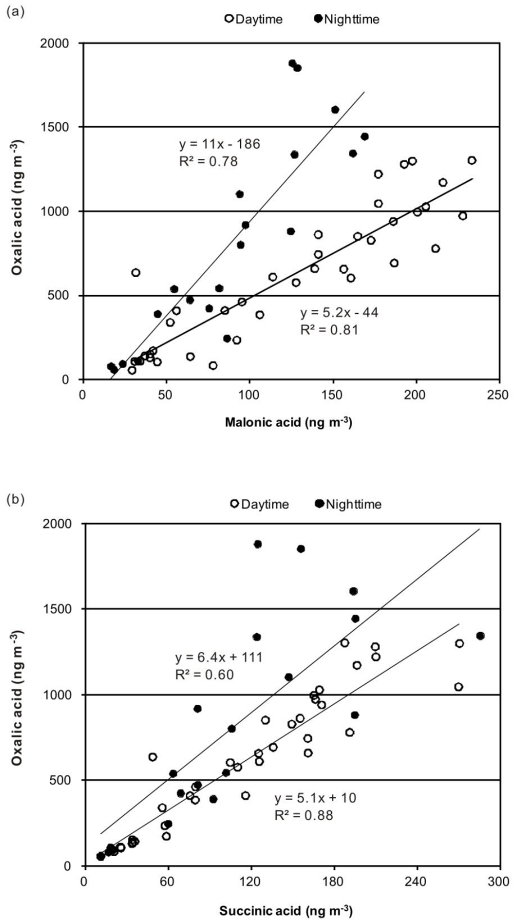

Fig. 8. Correlation plots for the concentrations of **(a)** oxalic acid (C_2) and malonic acid (C_3) and **(b)** oxalic acid (C_2) and succinic acid (C_4) in Mangshan aerosols for daytime and nighttime.

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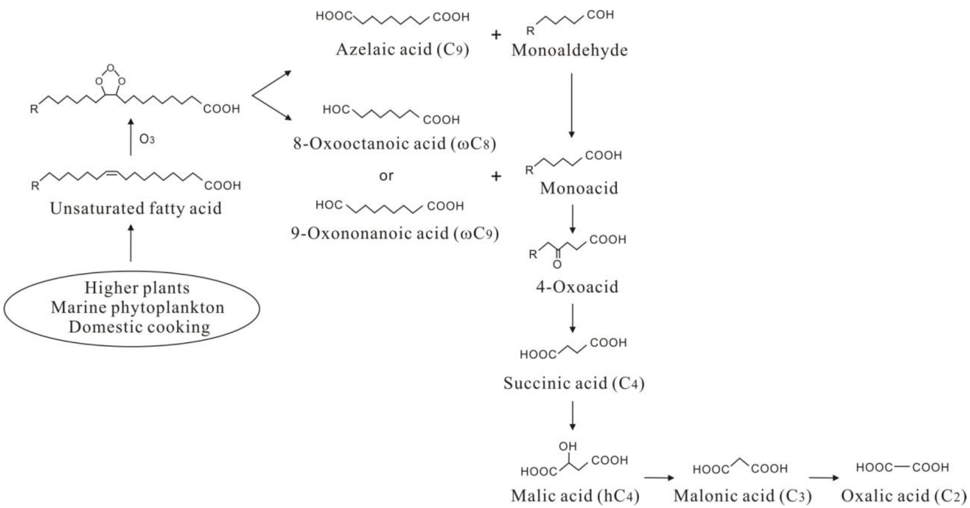

Fig. 9. Photochemical formation mechanisms of ωC_8, ωC_9 and C_9, as well as C_4, C_3 and C_2 from biogenic unsaturated fatty acids emitted from higher plants, marine phytoplankton and domestic cooking. Modified from Kawamura et al. (1996a, 1996b) and Kawamura and Sakaguchi (1999).

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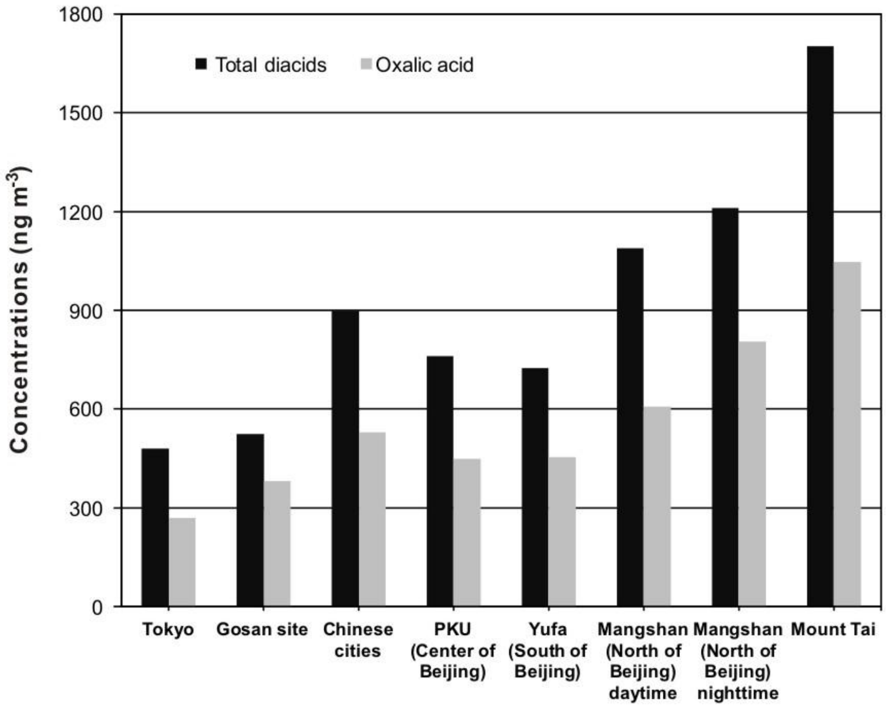

Fig. 10. Comparisons of the Manshan data with the results from previous studies in East Asia (Kawamura and Ikushima, 1993; Ho et al., 2007; Kundu et al., 2010a; Ho et al., 2010; Kawamura et al., 2013).

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