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Diurnal and temporal variations of water-soluble dicarboxylic acids and related compounds in aerosols from the northern vicinity of Beijing: Implication for photochemical aging during atmospheric transport

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Abstract:

Aerosol samples were collected in autumn 2007 on day- and nighttime basis in the northern receptor site of Beijing, China. The samples were analyzed for total carbon (TC) and water-soluble dicarboxylic acids (C_2-C_{12}), oxocarboxylic acids (C_2-C_9), glyoxal and methylglyoxal to better understand the photochemical aging of organic aerosols in the vicinity of Beijing. Concentrations of TC are 50% greater in daytime when winds come from Beijing than in nighttime when winds come from the northern forest areas. Most diacids showed higher concentrations in daytime, suggesting that the organics emitted from the urban Beijing and delivered to the northern vicinity in daytime are subjected to photo-oxidation to result in diacids. However, oxalic acid (C_2), which is the most abundant diacid followed by C_3 or C_4, became on average 30% more abundant in nighttime together with azelaic, ω-oxooctanoic and ω-oxononanoic acids, which are specific oxidation products of biogenic unsaturated fatty acids. Methylglyoxal, an oxidation product of isoprene and a precursor of oxalic acid, also became 29% more abundant in nighttime. Based on a positive correlation between C_2 and glyoxylic acid (ωC_2) in nighttime when relative humidity significantly enhanced, we propose a nighttime aqueous phase production of C_2 via the oxidation of ωC_2. We found an increase in the contribution of diacids to TC by 3 folds during consecutive clear days. This study demonstrates that diacids and related compounds are largely produced in the northern vicinity of Beijing via photochemical processing of organic precursors emitted from urban center and forest areas.

Keywords: organic aerosols, dicarboxylic acids, oxalic acid, glyoxylic acid, photochemical aging, aqueous-phase production

1. Introduction

Atmospheric particles have an influence on the global climate system, providing an adverse effect on human health and visibility (Huebert et al., 2003; Kaufman et al., 2002; Menon et al., 2002; Richter et al., 2005). Severe droughts in northern China and enhanced summer floods in southern China may be associated with the anthropogenic atmospheric particles that modify the regional air circulation (Menon et al., 2002). Dicarboxylic acids are ubiquitously present in atmospheric aerosols and they are in general the dominant class of organic components. Oxalic acid (C_2) is usually the dominant organic species in aerosols (Kawamura and Sakaguchi, 1999). Diacids are emitted primarily from combustion of fossil fuels, i.e., motor exhausts and coal burning, and biomass burning (Graham et al., 2002; Kawamura and Kaplan, 1987; Kundu et al., 2010a, b; Narukawa et al., 1999), but more importantly produced by the secondary oxidation of anthropogenic and biogenic volatile organic compounds (VOCs) in the atmosphere (Glasius et al., 2000; Kawamura et al., 2005; Kawamura et al., 1996a; Legrand et al., 2007). Aqueous-phase production of C_2 is also important in aerosol/cloud/fog droplets (Warneck, 2003).

A serious air pollution is common in China due to the huge usage of fossil fuels. One fourth of primary anthropogenic organic aerosols on a global scale are produced in China, ca. 70 % of which are emitted by the burning of coals (Streets et al., 2004). Beijing is located in north China with over 20 million people and 5 million motor vehicles. With several large industrial areas in Beijing, air pollution associated with ambient aerosols is the most serious social problem in the region. To suppress the aerosol concentrations in Beijing, we need to better understand chemical composition of organic aerosols and the chemical processes and photochemical aging during atmospheric transport. In the summer of 2006, a comprehensive field campaign had been performed for observation studies in the city center and also in the southern part of Beijing city (Ho et al., 2010), where dicarboxylic acids significantly contribute to water-soluble organic carbon (WSOC) but wind direction largely controls their concentrations.

However, comprehensive observations of atmospheric aerosol and gaseous components had not been performed in the northern receptor site of Beijing to which urban pollutants are

transported in daytime by southerly winds. In the Beijing city area and its vicinity, southerly wind is dominant in daytime but at night it turns to northerly in summer and autumn. In the northern vicinity of Beijing, an extensive forest park exists and the forest areas expand to further north, we could catch the polluted air masses from Beijing in daytime and the relatively clean air masses from the northern forest areas at night. The air parcels delivered from Beijing should be highly polluted with photochemical processing during the transport. In contrast, the air parcels coming from the north where large forest expands should be less polluted.

Here, we studied aerosol samples collected in the northern vicinity of Beijing in 2007 to investigate the photochemical processing of organic aerosols with an emphasis on polar organic species and total carbon (TC). Here, we report the diurnal and temporal variations of dicarboxylic acids, ω-oxocarboxylic acids, pyruvic acid and α-dicarbonyls in early autumn. Based on the detailed molecular compositions of diacids and related compounds and their contributions to aerosol TC, we discuss photochemical aging of polar organic species during the transport in the atmosphere in day- and nighttime, and chemical processing of organic aerosols during the transport in the vicinity of megacities. We also look at ozone and its correlation with diacids.

2. Experimentals

2.1. Sample collection

We collected atmospheric aerosol samples (TSP) using a high-volume air sampler and pre-combusted quartz fiber filters at Mangshan (40° 16’ N, 116° 17’ E), 40 km north of the center of Beijing, China (Figure 1). The sampling site is located next to the largest national park of natural forest in Beijing Province. No pollution source existed around the sampling site. In the north of Mangshan, there are mountain areas extended further north. In the south of the Mangshan site, urban and industrialized regions are present including Hebei, Tianjin and Beijing Provinces. The elevation of the sampling location is 187 m above sea level.

We collected 3-h daytime (n = 26), 9-h daytime (n = 12), and 15-h nighttime (n = 20) samples as well as four field-blanks during the period of 15 September to 5 October 2007. We

placed each filter in a pre-cleaned glass jar before and after the sampling. The filter samples were frozen at -20°C prior to analysis. Quartz fiber filters may adsorb organic vapors, causing positive artifacts. On the other hand, semi-volatile organics such as α-dicarbonyls collected on the filter may partially evaporate, resulting in negative artifacts. However, such artifacts were not quantified in this study.

Meteorological parameters were obtained at the Mangshan site for wind speed/direction, ambient temperature, and relative humidity (RH). The average daytime temperature was 25°C whereas the RH was 57%. In nighttime, they were 17°C and 78%, respectively. During daytime the wind came from the south and southwest (on average, 205°) whereas during nighttime the wind came from the northeast (on average, 30°) (Table 1). These day/night trends of local surface wind patterns are not always similar with the wind direction obtained by air mass trajectories (500 m above ground level). Typical transport time from downtown Beijing to Mangshan in daytime is approximately 5 hours whereas that from the nearest forest area to the sampling site in nighttime is about 1 hour or more, according to air mass trajectory analysis. Wet precipitation occurred on September 18 and 26, and October 1 and 3 to 5, although the rain of September 3-5 was very light.

We also measured ozone concentrations every one-hour at the site by UV absorption (Model 49C, Thermo Electron Corporation).

2.2. Analytical techniques

2.2.1. Measurements of aerosol masses and total carbon (TC)

The weights of filters were gravimetrically measured prior to and after the sample collection to calculate total aerosol mass concentrations. The measurement of TC was performed using an elemental analyzer (EA; model: NA 1500, Carlo Erba Instruments) with an auto sampler. A small disk (3.14 cm^2) was cut-off from the filter and then placed in a tin cup. The tin cup samples were combusted at 1020°C to oxidize carbonaceous materials with chromium trioxide where the tin cup burns (>1400°C) with pure O_2. The CO_2 produced was measured on gas chromatograph (GC) using a thermal conductivity detector. Based on triplicate

analyses, the uncertainty in TC measurement was confirmed to be 2.5%.

2.2.2. Measurements of dicarboxylic acids, oxoacids and α-dicarbonyls

Details of analytical protocols are described elsewhere for the determination of diacids, oxoacids and a-dicarbonyls (Kawamura, 1993; Kawamura and Ikushima, 1993). In brief, we extracted the filter aliquots with Milli Q water to isolate organic acids and related compounds under ultrasonication. After the concentration using a rotary evaporator under vacuum, the extracts were reacted with 14% borontrifluoride (BF_3) in n-butanol at 100°C to derive dibutyl esters and dibutoxy acetals. The ester and acetal derivatives were measured with a capillary GC-FID (HP6890) installed with a split/splitless injector and capillary column (Kawamura and Ikushima, 1993). Authentic diacid dibutyl esters were used as external standards for the peak identification and quantification. Identifications of the organic compounds were confirmed by GC/MS analyses. We performed a recovery text of diacid standards, which showed that the recoveries are better than 70%, and relative standard deviations (RSD) of diacids are 10-15%. Duplicate analyses of real samples showed that the analytical uncertainties for major organic species are less than 10%. A few organic species (e.g., oxalic, phthalic, and glyoxylic acids) were detected in the field blanks, but the blank levels are less than 10% of real samples. The concentrations reported in this study are blank-corrected.

3. Results and discussion

3.1. Concentrations of TSP mass and total carbon

During the field campaign, we found enhanced aerosol mass concentrations in daytime (see Figure 2a), with daytime mean of 270 μg m^{-3} (range, 48 - 603 μg m^{-3}) and nighttime mean of 150 μg m^{-3} (29 - 270 μg m^{-3}) at Mangshan site. The greater values in daytime should be caused by the transport of polluted air parcels northward from the Beijing areas, where pollutants are seriously emitted from fossil fuel combustions. Pollutants emitted from the Beijing regions are likely delivered to the northern vicinity in daytime by southerly wind (Table 1). The daytime increase of aerosol mass may also be associated with photochemical production

of atmospheric particles via photochemical oxidation of various gaseous precursors during the atmospheric transport from the urban regions. It is noteworthy that in nighttime wind direction shifted to northerly and hence the relatively clean air parcels were transported from the northern forest to the sampling site.

Ranges of daytime TC concentrations were 6 - 51 μg m^{-3} (av. 25±13 μg m^{-3}) whereas those of nighttime concentrations were 4 - 34 μg m^{-3} (av. 17±10 μg m^{-3}). They are in general greater in daytime than nighttime (Figure 2b), being consistent with aerosol mass. TC account for on average 9±2% (range: 3% to 14%) of aerosol mass in daytime and 11±3% (4% to 17%) in nighttime (Figure 2c). Generally, TC concentrations and their proportions in aerosol mass should be controlled by emission strengths, photochemical processing and/or dilution by inorganic species. TC values and their proportions to aerosol masses in Mangshan are smaller than those (49 μg m^{-3}, 17%) reported from Beijing (Sekine et al., 1992) and those (24 μg m^{-3}, 21%) from Tokyo (Kawamura and Yasui, 2005), but are significantly greater than those (0.38 μg m^{-3}, 0.75%) reported in the remote marine aerosols from the Pacific (Kawamura and Sakaguchi, 1999), in which sea-salts are abundant.

3.2. Molecular distributions and temporal variations of dicarboxylic acids, oxoacids and α-dicarbonyls

A homologous series of α,ω-dicarboxylic acids (C_2-C_{12}) and ω-oxocarboxylic acids (ωC_2-ωC_9), as well as pyruvic acid (Pyr), α-dicarbonyls (glyoxal and methylglyoxal) and aromatic (phthalic, iso-/terephthalic) dicarboxylic acids, were detected in the samples. Table 2 summarizes their concentrations for day- and nighttime.

Concentration ranges of total dicarboxylic acids were 120 - 2400 ng m^{-3} (av. 1000±700 ngm^{-3}) in daytime whereas those of nighttime were 110 - 3100 ng m^{-3} (1200±800 ng m^{-3}). These concentration levels are higher than those (range 90–1370 ng m^{-3}, av. 480 ng m^{-3}) reported in urban Tokyo, Japan (Kawamura and Ikushima, 1993). However, they are equivalent to or slightly higher than the concentrations (320-1900 ng m^{-3}, av. 900 ng m^{-3} in winter, and 210-2200 ng m^{-3}, av. 890 ng m^{-3} in summer) reported in 14 cities from China (Ho et al., 2007). They are similar with the concentrations (300-2100 ng m^{-3}) reported from Nanjing, China (Wang et al., 2002).

Interestingly, abundances of diacids in Mangshan are greater than Beijing (290 - 1440 ng m^{-3}, av. 760 ng m^{-3}) (Ho et al., 2007). Higher concentrations of diacids were found in nighttime than in daytime, which is in contrast to the concentrations of TSP mass and TC. We will discuss this point later in more detail. However, the levels of diacids are significantly smaller than those (220 - 6100 μg m^{-3}) from Mount Tai in North China during the agricultural burning of wheat straw wastes in May to June (Kawamura et al., 2013).

Figure 3a presents averaged molecular distributions of dicarboxylic acids and related compounds in the Mangshan aerosols for day- and nighttime. Oxalic acid (C_2) is found as the dominant diacid followed by malonic (C_3) or succinic (C_4) acid. We also found that C_2 is more abundant in nighttime (800±600 ng m^{-3}) than daytime (600±400 ng m^{-3}). In contrast, the concentrations of C_3 and C_4 were lower in nighttime (89 ng m^{-3} and 107 ng m^{-3}, respectively) than in daytime (123 ng m^{-3} and 115 ng m^{-3}, respectively). C_2 can be produced by the combustion of fossil fuels (Kawamura and Kaplan, 1987) and forest fires (Narukawa et al., 1999), but more importantly produced by the photochemical oxidation of VOCs and other precursors in aerosols during long-range transport (Carlton et al., 2007; Carlton et al., 2006; Kawamura et al., 1996a; Kawamura et al., 1996b; Warneck, 2003, 2005). We also found greater levels of azelaic (C_9) acid (28 ng m^{-3}) at night than mid-day (24 ng m^{-3}). C_9 is a specific oxidation product of unsaturated fatty acids (Kawamura and Gagosian, 1987; Stephanou and Stratigakis, 1993; Yokouchi and Ambe, 1986).

Phthalic acid (Ph) was found as the fourth most abundant diacid. This feature is in contrast to the Beijing aerosols where Ph is the 2nd most abundant diacid species following oxalic acid (Ho et al., 2010). Ph is more abundant in daytime (67±6 ng m^{-3}) than at night (42±4 ng m^{-3}). Concentrations of Ph are much higher than those (av. 29 ng m^{-3}) from urban Tokyo in summer (Kawamura and Yasui, 2005). However, they are lower than those (90 ng m^{-3}) from Chinese cities (Ho et al., 2007). Although Ph is directly emitted from fossil fuel combustion (Kawamura and Kaplan, 1987), secondary formation via atmospheric oxidation of aromatic hydrocarbons such as naphthalene may be more important (Ho et al., 2010; Kawamura and Ikushima, 1993). These results indicate that the aerosols from Mangshan are not so seriously polluted as the aerosols from Beijing and other urban sites in China probably due to the dilution by addition of

other diacids from biogenic sources in the forest areas.

Concentrations of total oxocarboxylic acids ranged from 23 to 340 ng m^{-3} (av. 131 ng m^{-3}) in daytime and from 13 to 230 ng m^{-3} (av. 98 ng m^{-3}) in nighttime. Although most oxoacids are more abundant in daytime, ωC_8 and ωC_9 acids that are produced by the oxidation of unsaturated fatty acids (Kawamura and Gagosian, 1987) are more abundant in nighttime, being consistent with azelaic (C_9) acid that showed higher concentrations in nighttime. Glyoxylic acid (ωC_2) is the dominant oxoacid followed by Pyr and 4-oxobutanoic acid (ωC_4). They have been considered as intermediate oxidation products of cyclic olefins (Hatakeyama et al., 1987) to produce dicarboxylic acids in the atmosphere (Kawamura and Ikushima, 1993; Kawamura et al., 1996a). Higher concentrations of oxocarboxylic acids, except for ωC_8 and ωC_9, in daytime might suggest more emissions of their precursors from anthropogenic sources. The concentrations of total oxoacids are equivalent to those from Gosan site (av. 53 ng m^{-3}) in Jeju Island in the East China Sea (Kawamura et al., 2004) and slightly more abundant than those from urban sites in China (45 ng m^{-3}) (Ho et al., 2007).

Concentrations of α-dicarbonyls ranged from 5 - 270 ng m^{-3} (av. 51 ± 57 ng m^{-3}) during mid-day and from 3.5 - 271 ng m^{-3} (av. 60±70 ng m^{-3}) at night. Glyoxal (Gly) and methylglyoxal (MeGly) are produced by gaseous-phase oxidation from various VOCs including ethylene (Ervens et al., 2004), and toluene, benzene, xylene (Volkamer et al., 2001) as well as terpenes (Fick et al., 2004) and isoprene (Zimmermann and Poppe, 1996). Interestingly, Gly showed higher concentrations in daytime whereas MeGly is more abundant in nighttime (Table 2). Gly may be associated with pollution sources whereas MeGly may be involved with biogenic sources such as isoprene. These α-dicarbonyls may serve as the precursors to produce secondary organic aerosols through heterogeneous reactions (Kroll et al., 2005; Liggio et al., 2005). Interestingly, levels of α-dicarbonyls in the Mangshan samples (3.5 to 271 ng m^{-3}, av. 54±61 ng m^{-3}) are several times higher than those (0 to 64 ng m^{-3}, 12 ng m^{-3}) from megacities in China including Beijing (Ho et al., 2007). This result emphasizes that α-dicarbonyls are vigorously produced in the vicinity of Chinese megacity and organic aerosols are photochemically more aged than urban aerosols during the transport in the atmosphere.

Figure 3b presents the variations in the abundances of total dicarboxylic acids, oxoacids

and α-dicarbonyls in the Mangshan aerosols. We found significant fluctuations in the concentrations of diacids and related compounds with maxima during September 16, 22, 26 and October 3 and minima during the late evening of September 17, evening of September 26, and mid-day of October 1. The minima were observed when rain events occurred. Weak wet precipitation continued from October 3 to 5 during which the levels of water-soluble organic species decreased gradually (Figure 3b). Wet precipitation (washout effect) should have scavenged diacids and related compounds from the atmosphere. α-Dicarbonyls seem to be more significantly scavenged during the wet precipitation (Figure 3b). The atmospheric aerosols enriched with low molecular weight diacids and α-dicarbonyls together with sulfate may act as cloud condensation nuclei during the wet precipitation (Kumar et al., 2003; Leaitch et al., 1996; Yu, 2000).

After the end of rainfall, concentrations of diacids and related compounds stayed low for one or two days, but they initiated to build-up. For example, their abundances showed gradual increase in the following clear days from September 19 - 22 (Figure 3b) due to the photochemical production during the transport from urban areas to the sampling site. Organic acids and α-dicarbonyls continue to accumulate in the aerosols before the next rainfall starts to scavenge the particles on 26 September. Similar increases of diacids and related compounds were observed from 28 September to 2 October until the next rain came. The duration of this cycle (increase and decrease of the concentrations) was approximately 5-9 days in the Mangshan site during the campaign.

Principal Component Analysis (PCA) is a useful approach to verify the sources of aerosols (Hopke, 1985). It has been successfully used for a series of dicarboxylic acids and other atmospheric trace species (Fu et al., 2008; Kawamura and Sakaguchi, 1999b; Wolff and Korsog, 1985). The data sets of diacids and related compounds for daytime (n = 38) and nighttime (n = 20) aerosol samples from Mangshan were subjected to PCA analysis based on their correlation matrix, followed by the varimax rotation of the eigenvectors (Table 3). Three components were extracted for daytime samples and 4 components were for nighttime samples by the scree tests. Although there were no outstanding features detected among the different components, small diacids (C_2-C_6) as well as oxoacids (Pyr, ωC_2-ωC_9) generally showed higher

correlations with component 1 in both day (variance, 31%) and night (32%) samples. This result may demonstrate that Mangshan aerosols origin from mixed sources in both daytime and nighttime, and the organic species in aerosols are largely produced by photochemical oxidation of various anthropogenic and biogenic organic precursors (Kawamura et al., 1996a, 1996b).

3.3. Diurnal variations of dicarboxylic acids, oxocarboxylic acids and a-dicarbonyls

Most organic species showed higher concentrations in daytime than nighttime (Figure 3a). However, oxalic (C_2), azelaic (C_9), undecanedioic (C_{11}), dodecanedioic (C_{12}), 8-oxooctanoic (ωC_8) and 9-oxononanoic (ωC_9) acids showed higher concentrations in nighttime as well as maleic (M) and fumaric (F) acids and methylglyoxal (MeGly). Although all the species are largely produced by photochemical oxidation of organic precursors in daytime, additional source(s) and processes for the above-mentioned species may be present in nighttime. During daytime, wind blew from the south (Beijing) to the north (sampling site) (Table 1) and thus anthropogenic organics emitted from Beijing may be transported to the Mangshan site. The direction of wind changed at night from the south to north. Hence, the daytime aerosols originated from Beijing and delivered to the north likely came back at night to the site of Mangshan by north winds with an addition of biogenic emissions from the forest areas, north of Beijing. Interestingly, specific oxidation products of biogenic unsaturated fatty acids (i.e., C_9, ωC_8, and ωC_9) (Kawamura and Gagosian, 1987) became more abundant in nighttime (Table 2, Figure 3a). The relative abundances of Ph in total diacids clearly increased in daytime (Figure S2a). This result indicates that anthropogenic contributions are more serious during daytime.

Malonic acid (C_3) can be formed by the photochemical breakdown of succinic acid (C_4) and thus C_3/C_4 ratio has been used as an indicator of enhanced photochemical aging of organic aerosols (Aggarwal and Kawamura, 2008; Kawamura and Ikushima, 1993). Lower C_3/C_4 ratios (0.2 – 0.4, av. 0.3) have been reported in vehicular exhaust in comparison to those (0.6 – 2.9, av. 1.6) of atmospheric particles (Kawamura and Kaplan, 1987) because C_3 is thermally more unstable compared to C_4 during high-temperature combustion (Kawamura and Ikushima, 1993). In this study, C_3/C_4 ratios became higher in daytime (0.7 to 3.8, av. 1.2±0.6) than in nighttime (0.5 to 1.8, av. 1.0±0.4). These ratios from Mangshan are much greater than that (0.6) from

summer aerosols in northern Chinese cities (Ho et al., 2007). These comparisons suggest that a secondary formation of diacids and the subsequent aging occur more frequently in the vicinity of Beijing than urban site. Very high C_3/C_4 ratios (2.6-3.7) were obtained on 17 to 18 September after the end of rainfall (Figure S2b). This result suggests that C_3 is vigorously produced under a strong solar radiation by photochemical oxidation of C_4 (Kawamura et al., 1996a).

C_6 diacid is formed by the ozone oxidation of cyclohexene (Grosjean et al., 1978; Hatakeyama et al., 1987). On the other hand, C_9 is produced by the oxidation of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987; Stephanou and Stratigakis, 1993). Thus C_6/C_9 ratio has been utilized as a tracer to estimate the anthropogenic v.s. biogenic contributions to organic aerosols (Kawamura and Yasui, 2005). In the present study, C_6/C_9 ratios present greater values during daytime (0.5-2.0, av. 0.9±0.4) than nighttime (0.2-1.2, av. 0.6±0.2) (see Figure S2c). These results suggest that anthropogenic source is more important in daytime than in nighttime whereas biogenic organic compounds more contribute in nighttime to the Mangshan organic aerosols.

C_{11}-C_{12} dicarboxylic acids are produced by the oxidation of unsaturated fatty acids (Kawamura and Gagosian, 1987) although ω-oxidation of monocarboxylic acids could produce corresponding α,ω-dicarboxylic acids. Interestingly, their abundances are higher in nighttime than daytime within the same date; average nighttime/daytime concentration ratios of C_9, C_{11} and C_{12} were 1.2, 1.7 and 2.3, respectively. The present results again demonstrate an importance of biogenic unsaturated fatty acids as sources of water-soluble organic aerosols via the oxidation at nighttime. Because vaccenic acid ($C_{18:1}\omega_7$), a positional isomer of oleic acid, is derived from bacterial cell membrane (Kawamura and Gagosian, 1987), the predominance of undecanedioic acid (C_{11}) in the range of C_{10}-C_{12} diacids in nighttime (Table 2) suggests that bacterial lipids are more contributed to the aerosols and oxidized at night. Bacterial growth may be possible in wetted aerosols at night under the high RH.

Relative abundances of oxalic acid in total diacids ranged from <40% to >75%. An increased C_2/total diacid ratio has been reported in the marine aerosols from the Pacific during the long-range atmospheric transport (Kawamura and Sakaguchi, 1999a) and used as a proxy of

photochemical aging of organic aerosols (Kawamura and Yasui, 2005). Interestingly, the ratios of C_2/total diacids are generally higher in nighttime than daytime (Figure S2d), probably due to the preferential production of oxalic acid in nighttime via the oxidation of its precursors in the aerosol particles. Further, the ratios in daytime showed an increase from 18 to 24 September and 27 September to 1 October when clear sky condition continued after the end of rain. Photochemical aging of organic aerosols probably result in the increase of C_2/total diacid ratios. During these periods, oxalic acid should have accumulated in aerosols due to the photochemical production via the oxidation of various precursors.

3.4. Enhanced contributions of diacids, oxoacids and α-dicarbonyls to aerosol TC

Figure 4 presents temporal variations in the contributions of total diacids and oxalic acid to aerosol total carbon (TC). Total diacid-C/TC ratios ranged from 0.4% to 3.6% (av. 1.8±0.7%) in daytime and from 0.9% to 9.7% (av. 3.0±2.1%) in nighttime. Interestingly, total diacid-C/TC ratios are generally higher in nighttime than in daytime (see black circles for nighttime in Figure 4). Oxalic acid-C/TC (%) ranged from 0.1% to 1.2% (av. 0.7±0.3%) in daytime and from 0.3% to 4.3% (av. 1.2±0.9%) in nighttime. The average ratio in nighttime is almost twice higher than that of nighttime, suggesting that oxalic acid is more produced in nighttime. This point will be discussed in more detail in section 3.6. Although TC includes elemental carbon (EC), averaged EC/TC ratio was 0.16 (Taketani et al., 2008, unpublished result), suggesting that the above ratios may not be seriously affected by the variation of EC.

Contributions of total diacids and oxalic acid to aerosol TC increased after the rainfall ended on 17 September, from which a clear sky condition continued until 24 September (Figures 3b and 5). Total diacid-C/TC and oxalic acid-C/TC ratios also increased gradually by 3 fold from 26 September to 1 October before another rain came. These results suggest that polar diacids are more enriched in organic aerosols during the back and forth movement of air parcels between Beijing and northern forest areas due to photochemical aging of organic aerosols. However, aging of organic aerosols was reset by wet precipitation, although photochemical aging again initiated under the fine conditions after the end of rain. Enhanced contributions of diacids to TC were detected at nighttime (18h-9h) during 3-5 October (Figure 4) when light rain

or cloud condition continued (Figure 3b). Being different from other sampling periods, the 6-day backward air mass trajectories in nighttime did not reach the remote regions but hovered over Beijing and its vicinities with the southerly winds that bring the urban pollutants to the sampling site (see Figure S1 for air mass trajectories). These meteorological situations may cause the higher oxalic acid-C/TC ratios. Alternatively, coarse particles that contained high abundance of TC might be preferentially scavenged from the atmosphere during light rain, causing higher oxalic acid-C/TC ratios in the fine particles.

The contributions of total diacids to TC in Mangshan aerosols (0.4-9.6%, av. 2.2±1.4%) are equivalent to those (1.2-6.6%, av. 2.4%) reported for the Mt. Tai aerosols in North China during biomass burning of agriculture residue (wheat straw) in late May to early June (Kawamura et al., 2013). These values are significantly higher than those (0.2-1.8%, av. 1.0%) reported in the urban Tokyo aerosols (Kawamura and Ikushima, 1993) and those (0.3-2.1%, av. 0.9%) reported in the marine aerosols from the Arctic Ocean in summer (Kawamura et al., 2012). However, they are lower than those (1.5-7.0%, av. 4.0%) reported in the Arctic (Alert) aerosols from February to June including a polar sunrise season (Kawamura et al., 2010) and are significantly lower than those (1.1-15.8%, av. 8.8%) reported in the remote marine aerosols collected from the North to Central Pacific including tropics (Kawamura and Sakaguchi, 1999a). We found that photochemical aging of organic aerosols and the reset by wet precipitation significantly control the contributions of diacids to TC.

3.5. Relations of diacids with ozone

During the campaign, O_3 concentrations ranged from 12 to 148 ppbv in daytime and from 10 to 70 ppbv in nighttime. Although very high levels of ozone were found in daytime, the levels stayed sometimes high even at night. Temporal variations of ozone for daytime and nighttime, respectively, together with total diacid concentrations are represented in supplementary Figure S3. Interestingly, a fairly good correlation was obtained between ozone and total diacid concentrations for both day- and nighttime with the correlation coefficient (r^2) of 0.23 and 0.25, respectively. These results suggest that diacids are secondarily produced in the atmosphere via the oxidation of various organic precursors. It is also important to note that the

highest ozone concentration was recorded at 12h-15h of 22 September when dicarboxylic acids peaked, suggesting that ozone and other oxidants may be involved with the production of diacids.

Oxalic acid showed a good correlation with ozone in daytime (r^2=0.30), but no correlation (0.06) was found in nighttime. Interestingly, malonic acid strongly correlated with ozone (0.59) in daytime, but no correlation (0.03) was found in nighttime. Succinic acid showed a weak correlation in daytime (0.19), but there is no correlation (0.01) in nighttime. Other organic species did not show any correlations with ozone, except for phthalic acid (0.21) and glyoxylic acid (0.41) in daytime. These results support that oxalic, malonic, and succinic acids as well as phthalic and glyoxylic acids are produced by the photochemical oxidation of organic precursors, or these acids are produced together with ozone in daytime. The low correlation coefficients of ozone and oxalic and other diacids in nighttime may suggest that the nighttime chemistry of diacids is mainly initiated with NO_3 radical and other oxidizing agents such as H_2O_2 (Claeys et al., 2004; Herrmann et al., 2000).

3.6. Possible production of oxalic acid in nighttime

Concentrations of C_2 are greater at night than mid-day with its average night-to-day concentration ratio of 1.3. The aerosol study from New Delhi reported the similar result; the average night-to-day ratio is ca. 2 (Miyazaki et al., 2009). Although lower levels of the nighttime boundary layer may enhance the diacid concentrations, we detected a preferential increase of C_2 in nighttime whereas other diacids such as C_3 and C_4 did not show any increase as stated before. Because C_2 could be formed by the oxidation of higher molecular weight diacids (Kawamura et al., 1996b), ratios of C_2/total diacids can be used as a proxy of photochemical aging of organic aerosols (Kawamura and Sakaguchi, 1999~~a~~). The ratios should become higher with the progress of photochemical aging of organic aerosols. The higher ratios of C_2/total diacids in nighttime indicate that organic aerosols are more enriched with oxalic acid by chemical processing at night.

Some laboratory studies demonstrated that aqueous phase reactions to produce C_2 could be mainly initiated in nighttime by NO_3 (Herrmann et al., 2000) and H_2O_2 (in the presence of

H_2SO_4) (Claeys et al., 2004), although NO_3 reactions are usually slow. Because the nighttime RH increased significantly (up to 100%, on average 78%), C_2 could be produced in aqueous phase in nighttime. Biogenic and anthropogenic VOCs can react with oxidants to produce methylglyoxal (MeGly) and glyoxal (Gly) in gas phase. During mid-day, OH radicals are important oxidants (Fan and Zhang, 2004) as well as O_3 (Kamens et al., 1982). In contrast, the nighttime oxidant is mainly NO_3, which attacks biogenic (such as monoterpenes and isoprene) and anthropogenic VOCs (Warneke et al., 2004). Thus, VOCs and their oxidation products may serve as precursors in nighttime. MeGly and Gly are produced in gas phase and can be hydrated in aqueous phase to result in $CH_3COCH(OH)_2$ and $(OH)_2CHCH(OH)_2$, respectively. The hydrated MeGly is further reacted with oxidants, resulting in Pyr, acetic acid, hydrated ωC_2, and finally C_2. Similarly, hydrated Gly can be converted to ωC_2, and then C_2 (Lim et al., 2005; Sorooshian et al., 2007).

Once oxalic acid is formed, it can stay longer in aerosols because all the carbons in oxalic acid are already oxidized and there is no hydrogen atom to be subtracted by OH radicals. At Mangshan site, C_2 should be more produced than other diacids because C_2 precursors (e.g., Gly, ωC_2) are more abundant than $\geqq C_3$ precursors such as ωC_3 and ωC_4 (Table 2). In fact, when C_2 became more abundant in nighttime, ωC_2 became less abundant in nighttime (Figure 3a). We found a good positive correlation between C_2 and ωC_2 in both daytime (R^2=0.76) and nighttime (R^2= 0.68), although the slope of the regression line is greater in nighttime. Hence, the ratios of C_2/total diacids could be enhanced in nighttime. These results suggest that C_2 is partly produced via the oxidation of ωC_2, which may be derived from MeGly and Gly (Ervens and Volkamer, 2010). Oxidation of biogenic VOCs (e.g., isoprene) emitted from the forest areas in the north during daytime produces α-dicarbonyls, which may be transported to the Mangshan site in nighttime, and finally oxidized to ωC_2 and then C_2 in aqueous phase as discussed above.

We also found that C_2 and C_3 positively correlate in day (R^2=0.81) and night (R^2=0.68), although the slope of regression line is twice greater in nighttime than daytime. These results suggest that the production of C_2 from C_3 is more significant in nighttime than in mid-day. Although we obtained similar difference in the regression line for C_2 and C_4, the difference is

smaller between mid-day (R^2=0.88) and night (R^2=0.60). We consider that secondary formation of C_2 is probably caused by the liquid-phase oxidation of C_2 precursors (e.g., ωC_2) that are derived from biogenic sources at night. In daytime, C_2 is primarily produced by fossil fuel combustion (i.e., coal burning and motor exhaust) in urban regions, and formed secondarily by the photochemical processing of anthropogenic organic compounds during the transport. Although there is a clear split between day and nighttime samples for higher concentrations of diacids (>500 ng m^{-3}), most points at lower concentrations seem to exist on the same line (Figure 5a-c), which are mostly associated with wet precipitation and then scavenging from the atmosphere (Figure 3b).

Further, C_9 diacid and ωC_8 and ωC_9 oxoacids, which are specific oxidation products of biogenic unsaturated fatty acids as stated earlier (Kawamura and Gagosian, 1987; Yokouchi and Ambe, 1986), presented greater abundances at night than mid-day. The present result indicates that unsaturated fatty acids are important precursors to result in the production of these C_8 and C_9 species via liquid-phase reactions at night. Photochemical breakdown of C_9, ωC_8 and ωC_9 may produce small dicarboxylic acids including C_4, C_3, and C_2, as illustrated in Figure 6. Although oxalic acid is known to produce via fossil-fuel combustion, its relatively high abundance in the remote atmosphere, coupled with the estimated lifetime of 6-8 days, may demonstrate either a background presence or secondary production from anthropogenic and natural precursors (Graham et al., 2002; Myriokefalitakis et al., 2011).

3.7. Potential photolysis of oxalic acid in daytime

Previous studies reported that Fe(III)-oxalato complexes exist in the atmosphere, which can photo-decompose in aqueous phase serving as a sink of oxalic, glyoxylic and pyruvic acids in the atmosphere (Ervens et al., 2003; Pavuluri and Kawamura, 2012; Zuo and Hoigne, 1992, 1994). Those organic acids can act as ligands to coordinate with iron, forming organic acid-iron complexes. Thus, they have a significant effect on the speciation and reactivity of Fe(III) in atmospheric water (Zuo and Zhan, 2005). Fe(III) in the atmosphere is commonly emitted from both natural and anthropogenic sources (Zhu et al., 1993). Iron should be abundantly present in continental aerosols although we did not measure Fe(III) in this study. This loss mechanism is

strongly dependent on solar radiation, pH, and abundances of iron (Zuo and Hoigne, 1992). Oxalate is more effectively destructed by photolysis of the complexes than the destruction by hydroxyl radicals (Zuo and Hoigne, 1992, 1994).

Typical transport time from urban Beijing to Mangshan is approximately 5 hours for daytime samples as stated above, whereas that from the forest area is 1 hour (or more) for nighttime samples because the sampling site is adjacent to the main forest area. The time scale for photolysis of Fe-oxalato complex in aqueous phase is approximately 60 minutes (Zuo and Zhan, 2005), which means that such reaction can be sufficiently carried out during the atmospheric transport. Hence, oxalic acid is likely destroyed in daytime via the photo-decomposition of Fe-oxalato complexes in aerosols. We consider that C_2 can be generated by the oxidation of precursors in aerosol waters in nighttime during the transport of the polluted air parcels from the north to Mangshan. However, it can be in part decomposed during mid-day by iron(III)-catalyzed photolysis in wetted aerosols. Malonic acid could also decompose in the presence of Fe (III), but the decomposition rate of its Fe-complex is ca. 20 times lower than that of oxalic acid (Faust and Zepp, 1993).

3.8. Comparison of Mangshan diacid concentrations with other geographical sites

We compare the atmospheric abundances of total dicarboxylic acids as well as oxalic acid in aerosols from the Mangshan site with those from various sites in East Asia and other parts of the world (Figure 7). In East Asia, atmospheric aerosols are often influenced by long-range transport of pollutants from various regions during monsoon season. The abundances of total dicarboxylic acids and C_2 are much greater in the samples from Mangshan than those from Gosan, Tokyo and Chinese cities. These comparisons demonstrate that that the aerosols from Mangshan are significantly enriched with diacids possibly due to the photochemical production during atmospheric transport. But, their concentrations are smaller than those from the summit of Mt. Tai, which are heavilly affected by agriculture-waste burning as described above. Since the sampling site of Mangshan locates at the northern vicinity of Beijing (see Figure 1), it is significantly affected by the atmospheric transport of pollutants from Beijing as well as biogenic VOCs emitted from forest areas.

We found that concentrations of diacids in Mangshan are ca. 20-30% higher than those from the Beijing urban center (Ho et al., 2010). Our finding demonstrates that organic precursors are photochemically processed in the vicinity of megacities during the atmospheric transport, producing water-soluble organic acids that are important components of organic aerosols in China. Photochemical processing of organic aerosols and their precursors during the transport may be more important for the production of atmospheric particles in the vicinities of megacities rather than urban centers in China. Finally, concentrations of diacids in Asian aerosols are much higher than those from remote marine, arctic and Antarctic regions as expected (Figure 7).

4. Conclusions

Molecular distributions of dicarboxylic acids in the aerosol samples from the northern vicinity of Beijing, China were characterized by the predominance of oxalic (C_2) acid followed by succinic (C_4) or malonic (C_3) acid. Phthalic acid (Ph) was found as the fourth most abundant diacid with higher concentrations in daytime than nighttime, being in contrast to urban Beijing where Ph was the second dominant diacid following C_2. Ph is probably more produced in daytime due to the atmospheric oxidation of aromatic hydrocarbons such as naphthalenes, which should be emitted from anthropogenic sources in Beijing and transported in daytime to northern vicinities by south wind.

We found greater abundances of C_2 and zelaic (C_9) acid at night as well as ωC_8 and ωC_9 oxoacids that are specifically produced by the oxidation of unsaturated fatty acids. We propose that an aqueous phase production of C_2 and C_9 may be important in nighttime (RH often reached to 100%) during the transport of the mixed (both biogenic and anthropogenic) air masses from the forest area to the Mangshan site by the southward winds. It is also possible that C_2 could partly be photolyzed in daytime via the decomposition of iron(III)-oxalate complex in atmospheric waters.

We also discovered that contributions of diacids to TC are 70% higher in nighttime than daytime and that they gradually increased by three times in the northern vicinity of Beijing for

consecutive 3-5 clear days after the rainfall due to the photochemical aging of organic aerosols during the atmospheric transport. Further, diacids and related compounds in Mangshan (vicinity) were found to be more abundant than in megacity Beijing, indicating that photochemical production and processing (aging) of water-soluble organic acids and related compounds are more significant in the northern vicinity of Beijing rather than the urban center.

Finally, the present observation study provides an atmospheric contemporary reference for the current studies of the heavily polluted air conditions in Beijing where an extremely high loading of $PM_{2.5}$ causes a serious haze in winter. The outcome of this research opened a special angle to examine the causes of the high loading of $PM_{2.5}$ in Beijing. It may be associated with high abundances of water-soluble organic aerosols that are photochemically produced and accumulated in the atmosphere of Beijing and its vicinity during the day/night transport (back and forth of air masses).

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Table 1. Fractions of local wind directions at Mangshan site, north of Beijing.

Wind Directions	Daytime (%)	Nighttime (%)
Northeast	23.45	99.56
Southeast	6.21	0.44
Southwest	69.66	0
Northwest	0.69	0

Table 2. Concentrations of dicarboxylic acids, oxocarboxylic 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	2.9	72.4	34.2	21.7	3.5	78.3	27.8	19.9
Adipic, C_6	1.4	44.1	19.7	13.2	1.2	45.7	15.2	11.6
Pimeric, C_7	N.D.	21.1	6.2	4.8	0.3	15.9	6.2	4.2
Suberic, C_8	N.D.	24.3	1.2	3.9	N.D.	2.2	0.5	0.5
Azelaic, C_9	1.1	74.4	24.0	17.7	1.8	64.1	27.8	17.8
Sebaric, C_{10}	N.D.	5.8	2.6	1.6	0.3	5.0	1.9	1.2
Undecanedioic, C_{11}	N.D.	5.3	1.6	1.6	0.1	7.7	2.8	2.2
Dodecanedioic, C_{12}	N.D.	1.6	0.6	0.6	0.1	5.6	1.3	1.6
Methylmalonic, iC_4	0.2	11.5	6.2	2.9	1.3	6.8	3.9	2.0
Methylsuccinic, iC_5	1.4	37.8	14.2	8.7	1.2	26.7	12.8	8.2
2-Methylglutaric, iC_6	0.3	8.6	2.4	2.0	0.2	19.5	3.0	4.1
Maleic, M	0.4	84.3	15.3	24.1	0.1	135	18.7	29.4
Fumaric, F	1.3	16.4	7.2	4.1	1.4	19.0	8.6	5.3
Methylmaleic, mM	1.3	26.0	9.1	6.1	0.8	25.7	9.3	7.3
Malic, hC4	N.D.	11.9	3.3	3.0	0.1	9.3	1.3	1.9
Phthalic, Ph	7.0	218	66.7	5.6	5.0	203	42.4	4.4
Isophthalic, iPh	0.4	18.0	8.1	7.6	0.8	15.3	6.9	6.5
Terephthalic, tPh	0.6	29.8	9.9	44.2	0.3	21.5	10.3	43.0
Ketomalonic, kC_3	0.4	6.5	2.6	1.6	0.4	5.3	1.7	1.2
4-Ketopimelic, kC_7	N.D.	16.2	6.1	4.6	0.5	10.3	4.1	3.0
Total diacids	122	2384	1088	671	105	3056	1208	829
Oxocarboxylic acids (ng m^{-3})								
Pyruvic	2.0	73.8	24.7	18.1	1.5	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	2.6	47.0	19.1	13.8	1.8	17.6	7.8	4.1
4-Oxobutanoic, ωC_4	2.4	35.0	17.3	9.8	0.9	23.2	10.5	6.5
7-Oxoheptanoic, ωC_7	0.5	14.0	5.8	3.3	1.0	13.2	5.5	3.4
8-Oxooctanoic, ωC_8	0.4	14.1	5.9	3.8	0.7	18.1	7.5	4.7
9-Oxononanoic, ωC_9	N.D.	11.6	3.9	3.2	0.1	15.4	5.5	4.4
Total oxoacids	23.0	340	159	95	12.7	232	97.9	64.8
α-Dicarbonyls (ng m^{-3})								
Glyoxal, Gly	3.1	35.3	14.9	8.8	2.6	33.8	12.6	7.9
Methylglyoxal, MeGly	1.0	242	36.6	50.7	1.0	255	47.2	66.3
Total dicarbonyls	5.3	271	51.5	56.9	3.6	289	59.8	70.1
Bulk analyses								
Aerosol mass (μg m^{-3})	47.8	603	267	129	29.4	270	146	78.6
Total carbon (TC) (μg m^{-3})	5.8	51.3	24.9	13.4	3.5	34.5	16.9	9.5

N.D. = Not Detected; Detection limit is ca. 0.1 ng m^{-3}.

Note: All the numerical data in this table, except integers, show one decimal place.

Table 3. Results of principal component analysis of organic compounds in daytime/nighttime Mangshan aerosols.

	Daytime (n=38)			Nighttime (n=20)			
Compounds	Component 1	Component 2	Component 3	Component 1	Component 2	Component 3	Component 4
Dicarboxylic acids							
Oxalic, C_2	0.68	0.59	0.36	0.42	0.49	0.30	0.60
Malonic, C_3	0.74	0.35	0.48	0.63	0.60	0.30	0.33
Succinic, C_4	0.55	0.64	0.45	0.79	0.46	0.28	0.10
Glutaric, C_5	0.70	0.56	0.36	0.83	0.47	0.21	0.11
Adipic, C_6	0.75	0.53	0.22	0.60	0.75	0.18	0.11
Pimeric, C_7	0.58	0.75	-0.02	0.33	0.88	0.22	0.11
Suberic, C_8	-0.01	0.02	0.03	0.26	0.13	0.82	0.30
Azelaic, C_9	0.52	0.69	0.14	0.39	0.81	0.17	0.18
Sebaric, C_{10}	0.27	0.27	0.69	0.30	0.19	0.29	0.80
Undecanedioic, C_{11}	0.40	0.64	0.35	-0.03	0.91	0.22	0.08
Dodecanedioic, C_{12}	0.64	0.41	0.34	0.86	0.25	-0.05	0.07
Methylmalonic, iC_4	0.83	0.16	0.26	0.64	0.53	0.16	0.35
Methylsuccinic, iC_5	0.44	0.64	0.59	0.62	0.58	0.20	0.21
2-Methylglutaric, iC_6	0.13	0.87	0.16	0.18	0.17	0.93	0.09
Maleic, M	0.17	0.23	0.80	0.09	0.11	0.04	0.90
Fumaric, F	0.55	0.43	0.60	0.57	0.62	0.27	0.24
Methylmaleic, mM	0.36	0.78	0.41	0.68	0.45	0.42	0.06
Malic, hC4	0.40	0.11	0.57	0.03	0.13	0.96	0.06
Phthalic, Ph	0.64	0.39	0.60	0.67	0.43	0.46	0.27
Isophthalic, iPh	0.40	0.72	0.44	0.40	0.71	0.16	0.48
Terephthalic, tPh	0.44	0.49	0.59	0.92	-0.03	0.15	0.13
Ketomalonic, kC_3	0.80	0.34	0.17	0.48	0.43	0.73	0.05
4-Ketopimelic, kC_7	0.86	0.11	0.38	0.72	0.42	0.28	0.39
Oxocarboxylic acids							
Pyruvic, Pyr	0.52	0.32	0.21	0.83	0.13	0.25	0.20
Glyoxylic, ωC_2	0.53	0.39	0.68	0.40	0.38	0.31	0.33
3-Oxopropanoic, ωC_3	0.58	0.11	0.71	0.55	0.36	0.61	0.26
4-Oxobutanoic, ωC_4	0.72	0.33	0.55	0.71	0.49	0.33	0.05
7-Oxoheptanoic, ωC_7	0.63	0.33	0.39	0.77	0.28	0.35	0.35
8-Oxooctanoic, ωC_8	0.73	0.26	0.50	0.43	0.79	0.25	0.13
9-Oxononanoic, ωC_9	0.55	0.76	0.08	0.74	0.48	0.28	0.15
α-Dicarbonyls							
Glyoxal, Gly	0.43	0.58	0.58	0.47	0.34	0.67	0.08
Methylglyoxal, MeGly	-0.04	0.79	0.28	0.03	0.23	0.00	-0.02
Variance (%)	31.4	26.0	20.7	32.5	24.6	17.3	10.0

Data sets of the 16 samples were subjected to PCA analysis with SPSS software (version 16.0).
Because of sharp drops in eigenvalue for factor 4 in daytime samples and factor 5 in nighttime samples, those results are not given here.

Figure captions

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

Figure 2. 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.

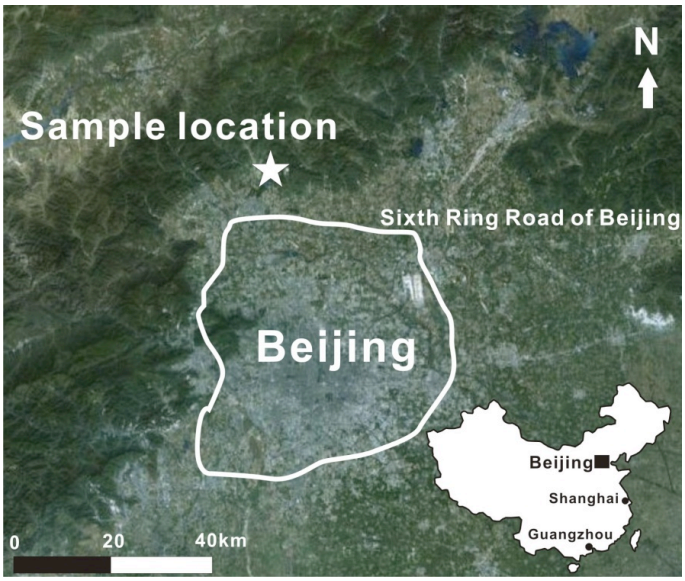
Figure 3. (a) Averaged molecular distributions of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in the day and nighttime aerosols from Mangshan. (b)Temporal variationsin the concentrations (ng m^{-3}) of water-soluble dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in the ambient aerosols from Mangshan.

Figure 4. Temporal variations in the contributions of total dicarboxylic acids and oxalic acid to aerosol total carbon (TC) in the ambient aerosols from Mangshan.

Figure 5. Correlation plots for the concentrations of (a) oxalic acid (C_2) and glyoxylic acid (ωC_2), (b) oxalic acid (C_2) and malonic acid (C_3), and (c) oxalic acid (C_2) and succinic acid (C_4) in Mangshan aerosols for daytime and nighttime.

Figure 6. 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).

Figure 7. Comparisons of the Manshan data with the results from previous studies in East Asia (1: Kawamura et al., 1996b; 2: Kawamura et al., 2010; 3: Kawamura et al., 2012; 4: Kawamura and Sakaguchi, 1999; 5: Kawamura and Ikushima, 1993; 6: Kundu et al., 2010a; 7: Ho et al., 2007; 8: Ho et al., 2010; 9: Kawamura et al., 2013).



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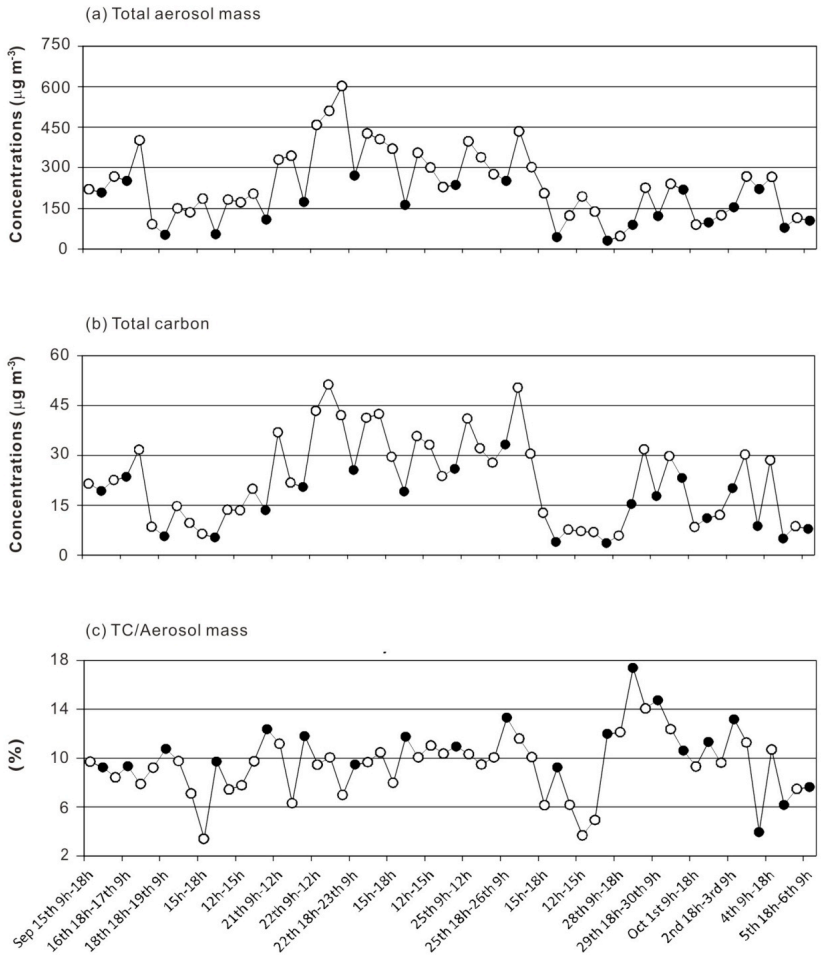

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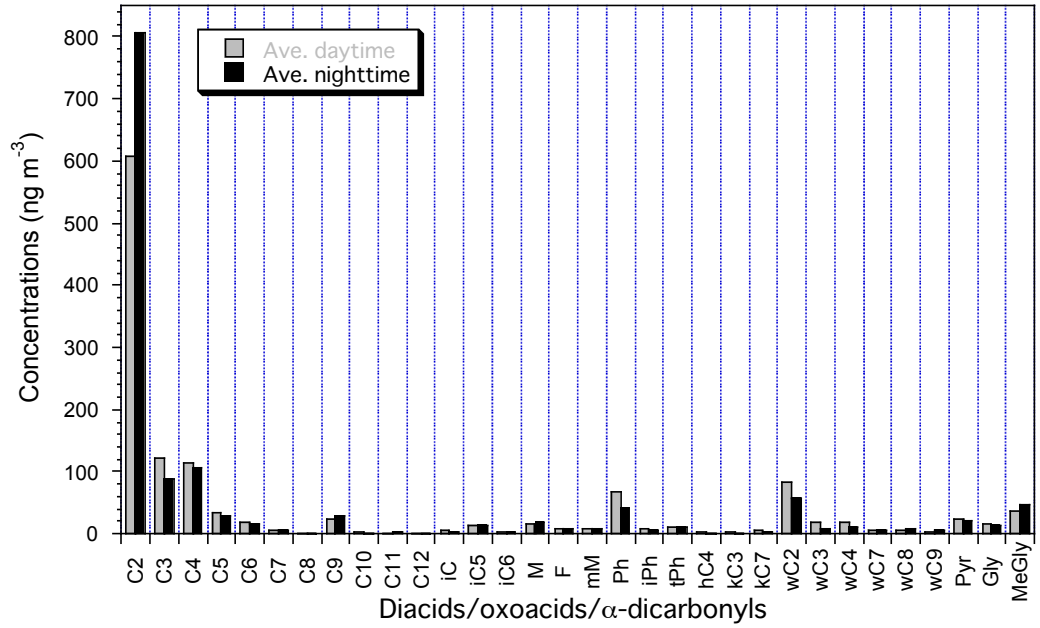
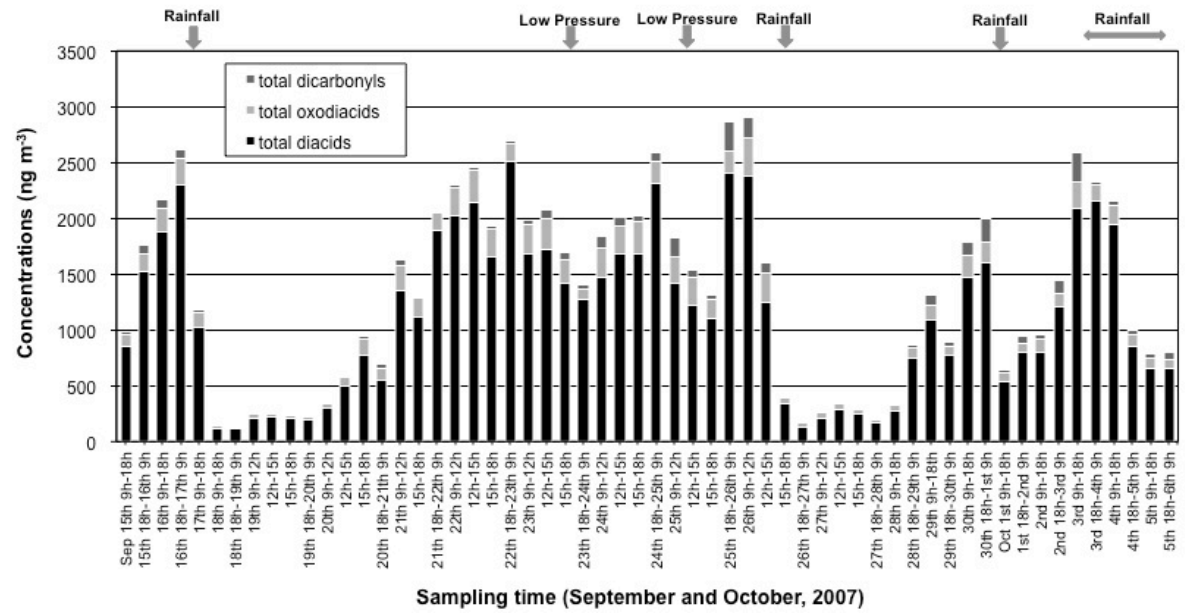
(a)



(b)



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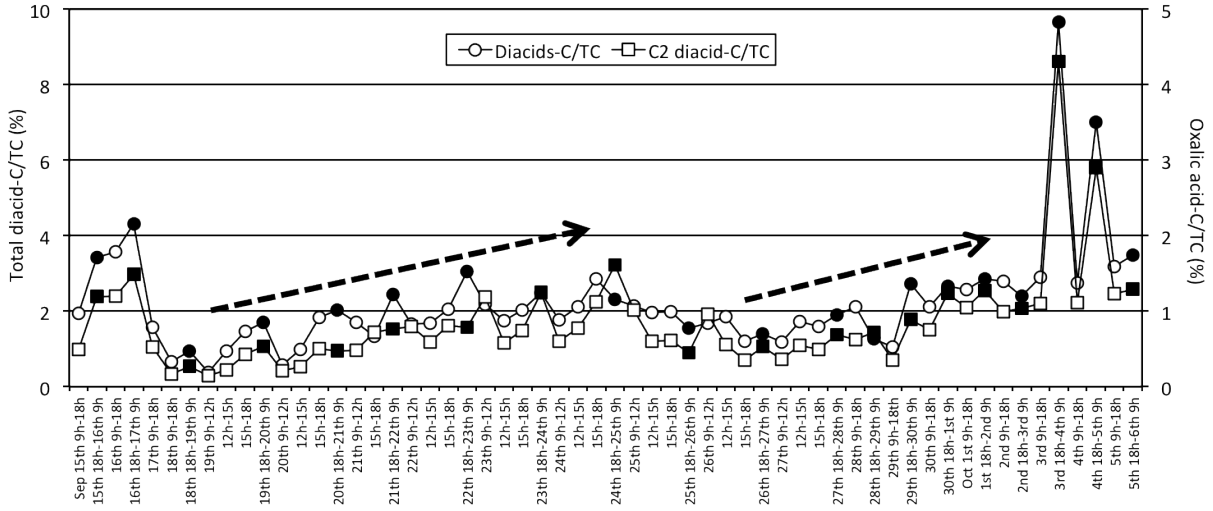

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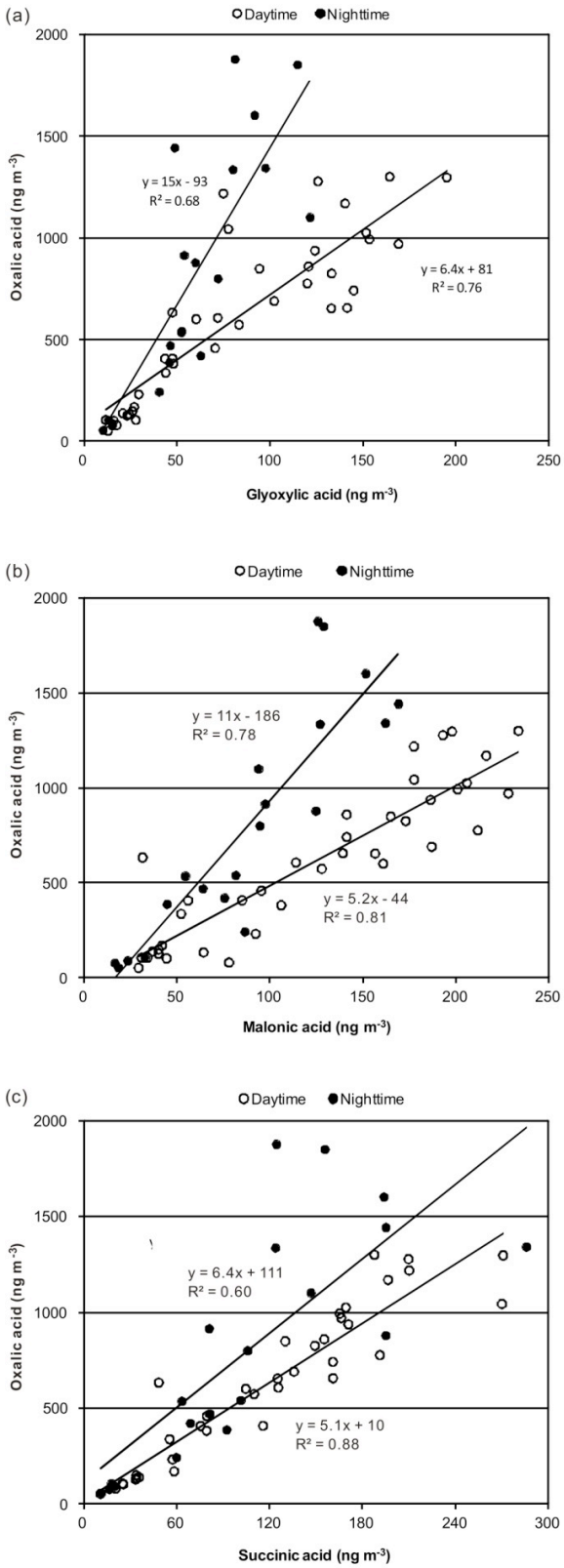

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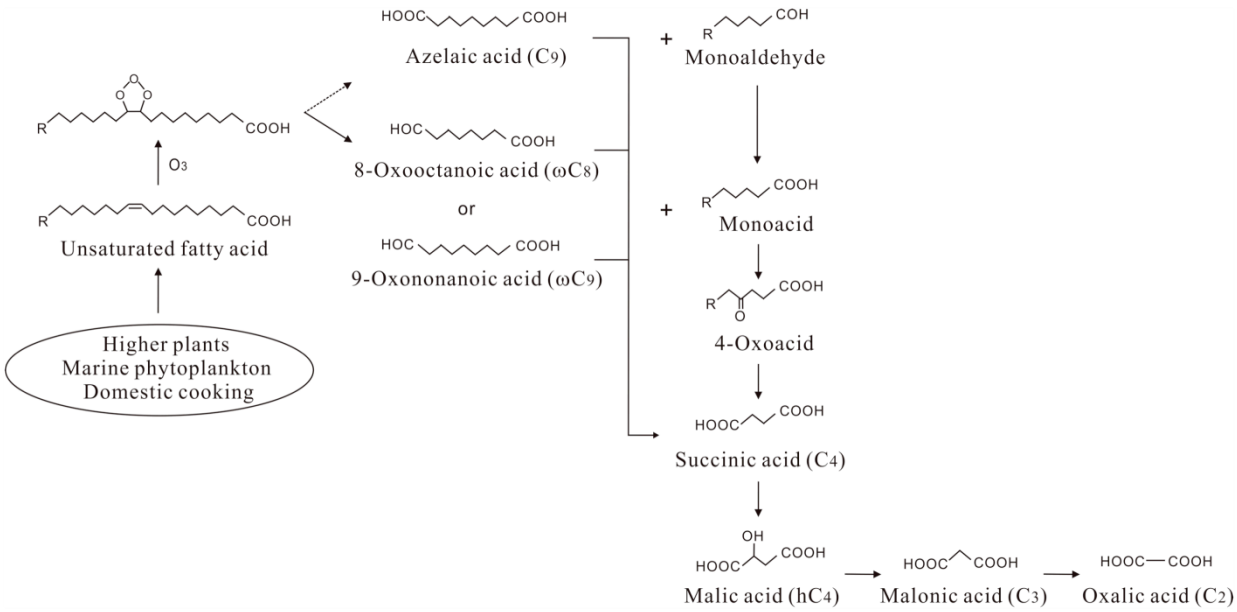

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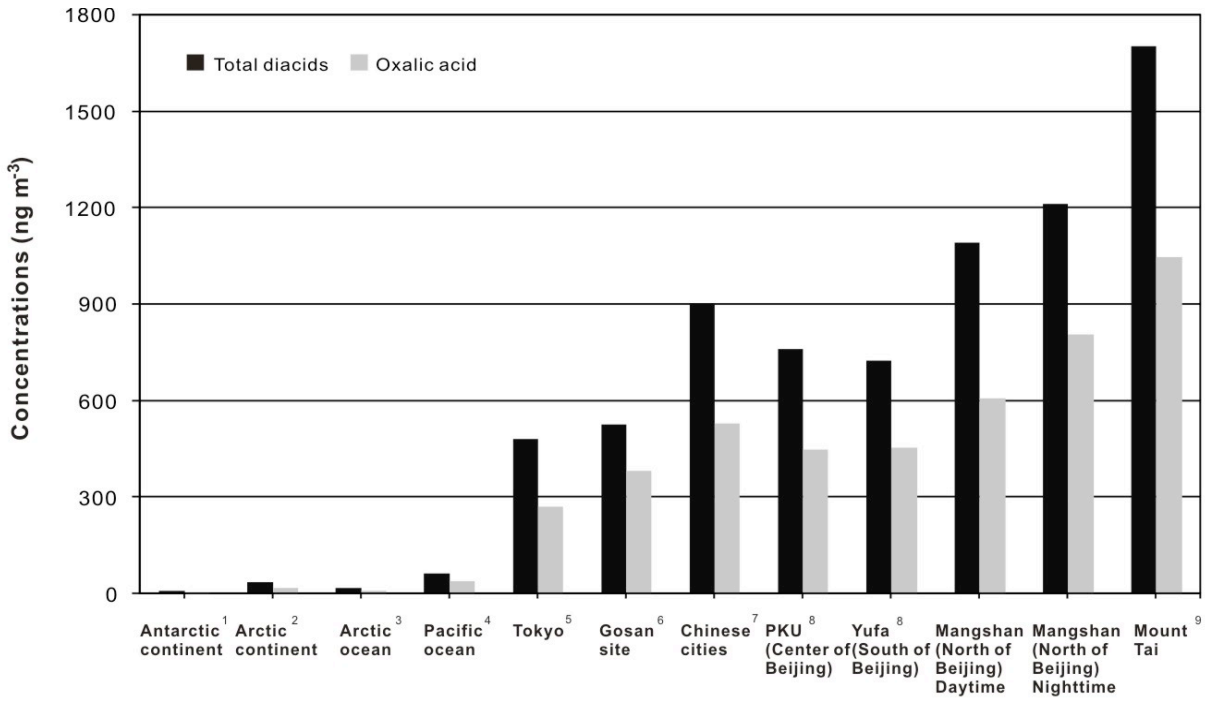

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Supporting Information

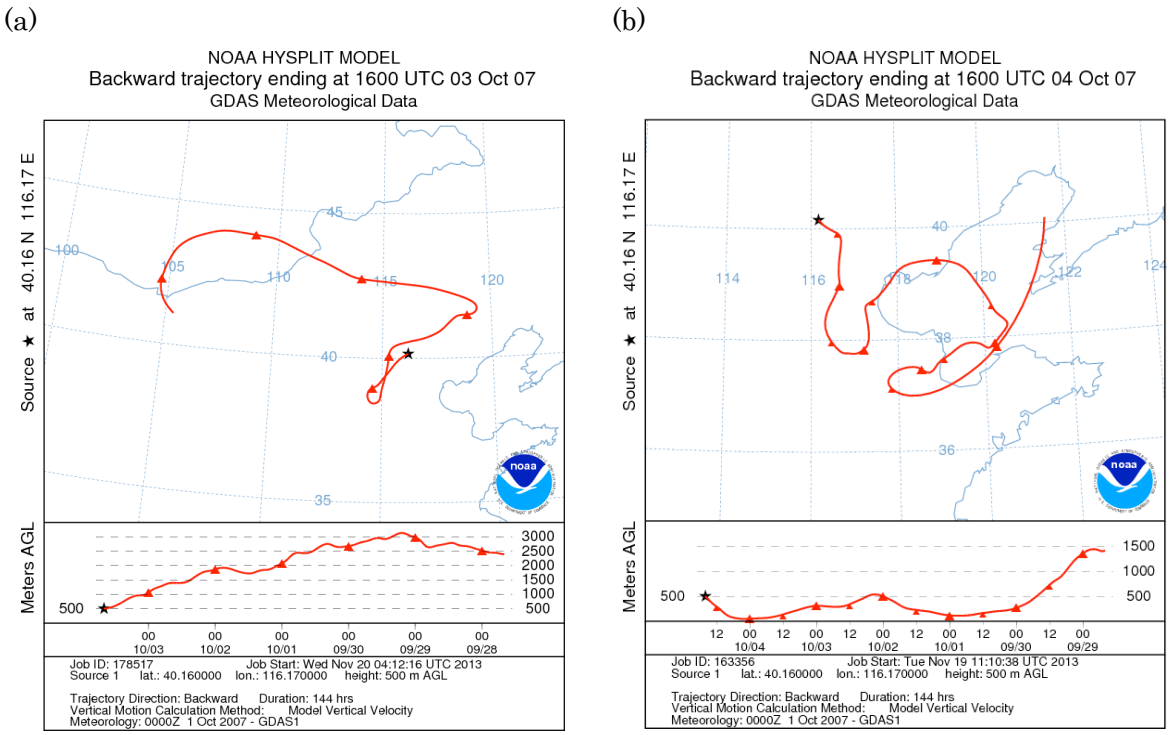

Figure S1. Backward air mass trajectories for the aerosol sample collected during (a) October 3-4 and (b) October 4-5, 2007 (local time is 00h) when higher peaks of diacid-C/TC were obtained (Figure 4). The trajectories were calculated for 6 days using the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (Draxler and Ralph, 2013; Rolph 2013).

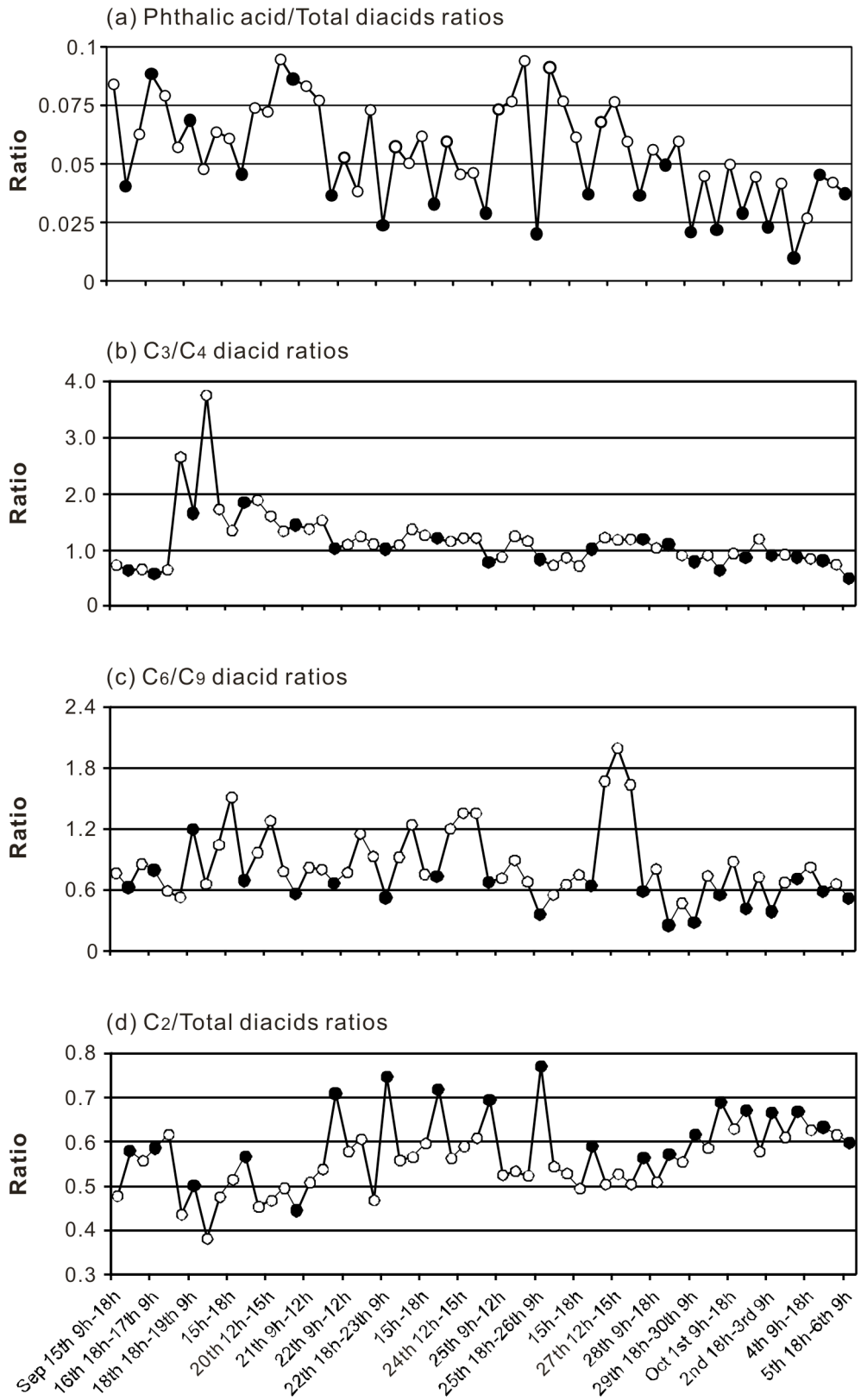

Figure S2. Temporal variations of (a) Ph/total diacid ratios, (b) C_3/C_4 diacid ratios, (c) C_6/C_9 diacid ratios and (d) C_2/total diacid ratios in Mangshan aerosols. The hollow circle represents daytime sample and the solid circle represents nighttime sample.

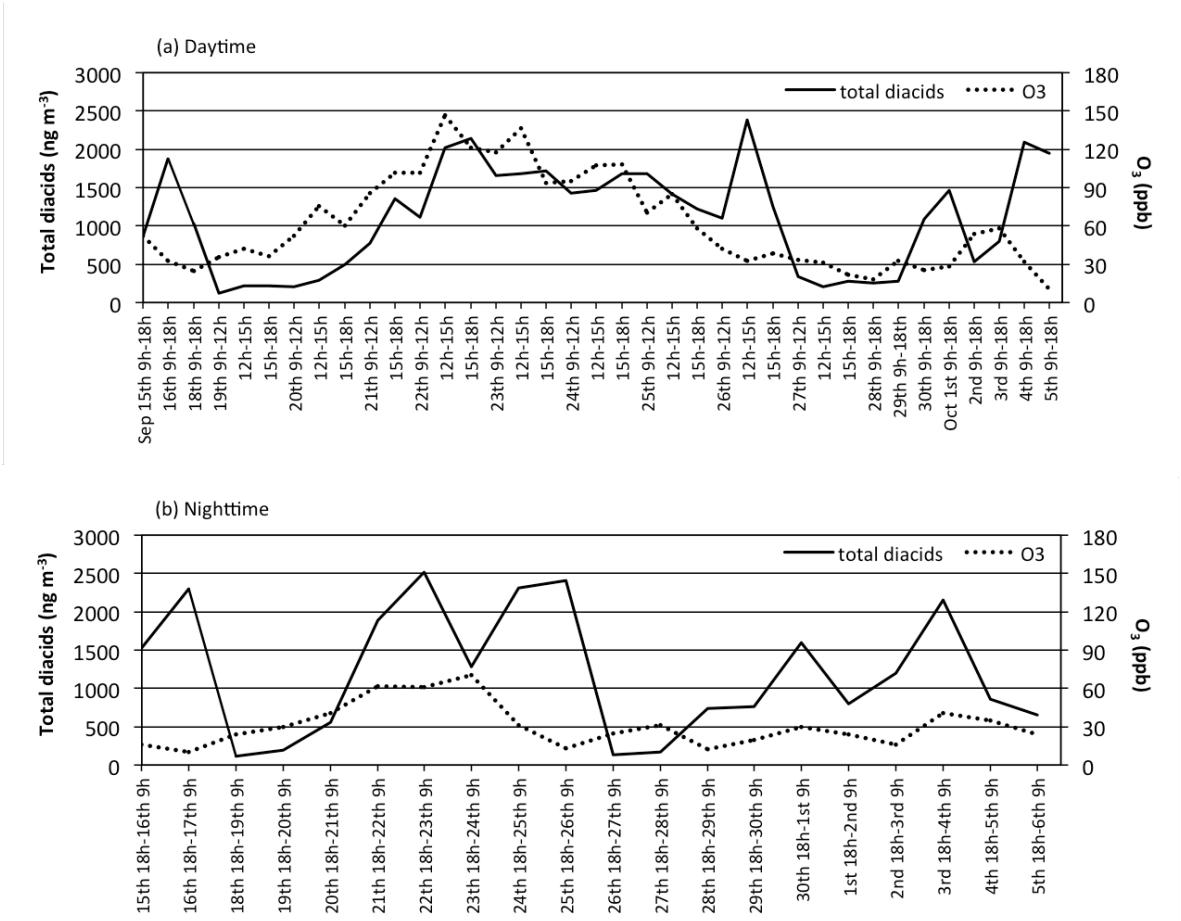

Figure S3. Temporal variations in the concentrations of total dicarboxylic acids and ozone in the atmosphere of Mangshan for (a) daytime and (b) nighttime.