



Water soluble
diacids, ketoacids
and α -dicarbonyls

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High abundances of water-soluble dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls in the mountain aerosols over the North China Plain during wheat burning season

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Abstract

Aerosol (TSP) samples were collected at the summit of Mount Tai (elevation: 1534 m a.s.l., 36.25° N; 117.10° E) located in the North China Plain using a high-volume air sampler and pre-combusted quartz filters. Sampling was conducted on day/night or 3 h basis in the period from 29 May to 28 June 2006 during the field burning of wheat straw residue and the post-burning season. The filter samples were analyzed for low molecular weight dicarboxylic acids, ketoacids and α -dicarbonyls using capillary gas chromatography (GC) and GC-MS employing water extraction and butyl ester derivatization. Dicarboxylic acids (C_2 – C_{11} , 220–6070 ng m^{-3}) were characterized by a predominance of oxalic (C_2) acid (105–3920 ng m^{-3}) followed by succinic (C_4) or malonic (C_3) acid. Unsaturated aliphatic diacids, including maleic (M), isomaleic (iM) and fumaric (F) acid, were also detected together with aromatic diacids (phthalic, isophthalic and tere-phthalic acids). ω -Oxocarboxylic acids (C_2 – C_9 , 24–610 ng m^{-3}) were detected as the second most abundant compound class with the predominance of glyoxylic acid (11–360 ng m^{-3}), followed by α -ketoacid (pyruvic acid, 3–140 ng m^{-3}) and α -dicarbonyls (glyoxal, 1–230 ng m^{-3} and methylglyoxal, 2–120 ng m^{-3}). We found that these levels ($> 6000 \text{ ng m}^{-3}$ for diacids) are several times higher than those reported in Chinese megacities at ground levels. The concentrations of diacids increased from late May to early June showing a maximum on 7 June and then significantly decreased during 8–11 June when the wind direction shifted from northeasterly to northerly. Similar temporal trends were found for ketocarboxylic acids and α -dicarbonyls as well as total carbon (TC) and water-soluble organic carbon (WSOC). The temporal variations of water-soluble organics were interpreted by the direct emission from the field burning products of agricultural wastes (wheat straw) in the North China Plain and the subsequent photochemical oxidation of volatile and semi-volatile organic precursors emitted from field burning. This study demonstrates that the field burning of agricultural wastes in early summer strongly influenced the air quality of the free troposphere over the North China Plain.

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1 Introduction

Central East China (CEC) is one of the most polluted regions in the world due to the rapid economic growth for last two decades (Ohara et al., 2007). Very high levels of column NO_2 have been reported in the CEC region by satellite observation compared to those for the northeast of United States and north Europe (Richter et al., 2005). High levels of tropospheric ozone are also commonly obtained in this region based on the observations from ground sites (e.g. Gao et al., 2005) and satellite (e.g. Hayashida et al., 2008). Air pollutions are very serious in China as a result of increased usage of fossil fuels. One fourth of primary anthropogenic organic aerosols in the world is generated in China, ca. 70 % of which is derived from coal burning (Cooke et al., 1999; Streets et al., 2004). The air pollutants, in particular, dusts and anthropogenic aerosols are responsible to the degradation of visibility, health risks to human beings and climate changes in East Asia and the outflow regions including the North Pacific (Huebert et al., 2003). Recently, field burning of agricultural wastes is found as a source of serious air pollution in East China (Fu et al., 2008; Li et al., 2008; Wang et al., 2009).

High loadings of organic aerosols have been reported in Chinese cities (Wang and Kawamura, 2005; G. Wang et al., 2006), among which low molecular weight (LMW) dicarboxylic acids are recognized as most abundant organic compound class (Ho et al., 2007). In general, their molecular distributions are characterized by the predominance of oxalic acid (C_2) followed by malonic (C_3) and succinic (C_4) acids. LMW dicarboxylic acids have been reported in the urban (Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994; Rohrl and Lammel, 2001; Wang et al., 2002; Yao et al., 2002; Rompp et al., 2006; Kitanovski et al., 2011), mountainous (Legrand et al., 2007), marine (Kawamura and Sakaguchi, 1999; Mochida et al., 2003a,b), and Arctic and Antarctic atmospheres (Kawamura et al., 1996a, b, 2005, 2010; Kerminen et al., 1999; Narukawa et al., 2002, 2003). In general, concentrations of LMW diacids were found to be higher in Asian cities and its coastal regions in Asian Pacific region (Fu et al., 2013).

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Because small dicarboxylic acids and related polar compounds are highly water-soluble and abundant in atmospheric aerosols, they can significantly enhance the hygroscopicity of the particles. Previous studies have shown that the presence of dicarboxylic acids affect both deliquescence relative humidity and hygroscopicity of aerosol particles (Cruz and Pandis, 1998; Brooks et al., 2002). Although LMW diacids can be emitted from primary sources such as vehicular exhausts (Kawamura and Kaplan, 1987), biomass burning (Narukawa et al., 1999), cooking (Schauer et al., 2002), and natural marine sources (Rinaldi et al., 2011), they are mainly produced from the atmospheric photooxidation of various organic precursors (Kawamura and Gagosian, 1987; Stephanou, 1992; Kawamura and Sakaguchi, 1999) most likely in aqueous aerosol phase (e.g. Sorooshian et al., 2006; Carlton et al., 2007; Ervens et al., 2008; Ervens et al., 2011). LWM dicarboxylic acids and related compounds can contribute to 0.2–1.8 % of total carbon (TC) in urban Tokyo (Kawamura and Ikushima, 1993) and up to 16 % of TC in remote marine aerosols (Kawamura and Sakaguchi, 1999; H. B. Wang et al., 2006).

In this study, we collected atmospheric aerosols at the summit of Mt. Tai (elevation; 1534 m) located in CEC from late May to June in 2006 to characterize water-soluble organic aerosols at molecular levels during the field burning season of agricultural waste (wheat straw) and after. The sample collection was performed as part of the Mount Tai eXperiment 2006 campaign (MTX2006) in early summer. Kanaya et al. (2013) report an overview of the MTX2006 campaign with many outcomes of the project. Here, we report the molecular distributions of diacids, ketoacids and α -dicarbonyls in the atmospheric particles as well as total carbon (TC) and water-soluble organic carbon (WSOC). To better understand their sources, transport pathways and photochemical processing during long-range atmospheric transport, we compare the results of the mountaintop observation with those from Chinese urban sites and the outflow regions in East Asia and the Pacific Ocean. We also discuss the photochemical processing of organic aerosols in the free troposphere over the polluted regions of the North China

Plain based on the detailed analyses of molecular compositions of diacids and related compounds.

2 Samples and experiment

2.1 Sampling site and aerosol collection

5 Mt. Tai (36.25° N and 117.10° E) is located in Shandong Province, Central East China (30° N–40° N and 110° E–130° E), whose topography is characterized by flat lands of less than 200 m in altitude. Thus, Mt. Tai (elevation; 1534 m above sea level) is an independent peak in the CEC region (see Fig. 1) and the summit often stays within the free troposphere at night. As part of the MTX2006 campaign, daytime/nighttime and
10 three-hour aerosol samplings were performed from 28 May to 28 June, 2006 at the balcony of two-story building of the observatory (~ 10 m, above ground level) on the top of Mt. Tai. Eighty-one samples (including 5 whole-day, 19 daytime (6:00–18:00, local time), 20 nighttime (18:00–6:00), and 37 three-hour samples) were collected during the campaign using a high-volume air sampler and pre-combusted (450 °C for 6 h) quartz
15 fiber filters at a flow rate of 1.0 m³ min⁻¹. Four blanks were taken during the campaign by setting the filter on the filter cartridge without sucking air. The filter sample was placed in a clean glass bottle (150 mL) with a Teflon-lined screw cap and stored in a freezer at the observatory. After shipping to Sapporo, the samples were stored in a freezer room at –20 °C prior to analyses.

20 The heights of planetary boundary layer (PBL) around Mt. Tai were estimated during the campaign using a WRF/Chem model (Takigawa et al., unpublished data), which reached a maximum of ca. 4000 m at midday and a minimum of 200 m during night to early morning with average heights of 2200 m (daytime) and 600 m (nighttime). Thus, nighttime samples were most likely collected in the free troposphere.

25 The meteorological data are obtained at the Mt. Tai observatory located on the mountaintop. The results are summarized in Fig. 2. The ambient temperatures ranged from

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8 °C to 24 °C. Relative humidity in daytime was generally low (around 50 %) but increased over 95 % at night. Wind speeds ranged from less than 1 ms⁻¹ to 20 ms⁻¹. Winds generally came from the west or southwest, however, the northwest to north winds dominated during 8–11 June and 14–15 June when cold and dry air masses arrived over Mt. Tai from north China and Siberia (see Fig. 2). Weather conditions were generally clear or partly cloudy throughout the campaign, but minor rain events occurred on 7, 13 and 14, 21, 26 and 28 June. Major rain event occurred on 29 June. However, the filter sampling was ended just before the big rainstorm.

2.2 Analytical procedures

Aliquots of filter samples were extracted with organic-free pure water (Milli-Q) to separate water-soluble diacids and related organic compounds. The water extracts were concentrated using a rotary evaporator under vacuum and then converted to dibutyl esters and butoxy acetals employing the derivatization with 14 % BF₃ in *n*-butanol (Supelco). The derivatives were dissolved in *n*-hexane (100 or 200 μ L) and two μ L of the *n*-hexane solution were injected to a gas chromatograph (GC, Agilent 6980) installed with a split/splitless injector (250 °C), HP-5 column (0.2 mm \times 25 m, film thickness 0.5 μ m) and FID detector for the determination of dicarboxylic acids (C₂–C₁₀), ketocarboxylic acids (C₂–C₉) and α -dicarbonyls (glyoxal and methylglyoxal) (Kawamura, 1993; Kawamura and Ikushima, 1993). GC/mass spectrometer (Thermo Trace MS) was used to confirm the identification of the GC peaks (Kawamura et al., 1985; Kawamura, 1993). A spike experiment using authentic standards (oxalic, malonic, succinic and adipic acids) that were added into quartz filter showed that recoveries were 77 % for oxalic acid and better than 86 % for other diacids. Recoveries of glyoxylic acid, pyruvic acid, and methylglyoxal were 88 %, 72 %, and 47 %, respectively (Kawamura and Yasui, 2005). Recovery of glyoxal was 91 % (Kunwar and Kawamura, 2013). Field blank was analyzed as the actual samples. Although the blanks showed small peaks of oxalic acid and phthalic acid on the GC chromatogram, their amounts were less than 5 % of the actual samples. The concentrations of the compounds reported here are

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all corrected for the field blanks. Duplicate analyses of the sample showed that the analytical errors in the procedures were within 10 % for major components.

Aerosol samples were also analyzed for total carbon (TC) and nitrogen (TN) contents. A small disc (area, 3.14 cm^2) was punched from aerosol filter samples and analyzed using an elemental analyzer (EA) (Carlo Erba, NA 1500) (Kawamura et al., 2004). The TC and TN contents are reported here after the blank correction. Reproducibility of TC and TN measurements was within 2 %.

For the measurements of water-soluble organic carbon (WSOC), another filter disc (1.4 cm in diameter) was extracted with organic-free MilliQ water for 15 min under ultrasonication. The water extracts were subsequently passed through a syringe filter (MillexGV, $0.22 \mu\text{m}$, Millipore), and WSOC was measured with a carbon analyzer (Shimadzu, TOC-5000A) equipped with a catalytic oxidation column/non-dispersive infrared detector (Aggarwal and Kawamura, 2008). The sample was measured three times and the average value was used. Before the sample analysis, external calibration was performed using a potassium hydrogen phthalate solution. The analytical error in the WSOC measurement was 15 % with a detection limit of 0.1 mg C m^{-3} .

3 Results and discussion

3.1 Variations of TC, TN and WSOC in the mountain aerosols

Figure 3 shows temporal variations of total carbon (TC) and total nitrogen (TN) contents in the Mt. Tai aerosols as well as C/N ratios. TC concentrations increased from the late May to mid June and then significantly decreased during 9–11 June when wind direction shifted to south or southwest over Mt. Tai (see Fig. 2). The TC concentrations again increased during 12–13 June when wind direction shifted to north. It is important to note that field burning of agricultural wastes (wheat straw) occurred in the south of Mt. Tai during the first half of sampling period (see Fig. 4a for the fire spot and air mass trajectories). As seen in Figs. 3a and 4, it is clear that TC concentrations are

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high when air masses arriving over Mt. Tai traveled over the fire spots (see the fire spots in Fig. 4b). The field burning activities in the CEC region maximized during 8–11 June (Fig. 4b), but TC concentrations were very low (Fig. 3a) because wind directions shifted to northerly and the air masses did not meet with the areas of intensive fire spots. In the second half of the campaign after mid June, the fire activities declined although the fire regions migrated from the south to north of the sampling site following the northward shift in the harvest areas of the wheat crops (Fig. 4c, d). Following the decrease in the fire activities (Fig. 4c), TC concentrations decreased in the second half of the campaign (Fig. 3a).

Interestingly, ranges of TC concentrations ($3\text{--}85\ \mu\text{g m}^{-3}$) obtained for Mt. Tai aerosols are comparable to those ($15\text{--}99\ \mu\text{g m}^{-3}$) reported for 14 Chinese cities during winter, but higher than those ($6\text{--}35\ \mu\text{g m}^{-3}$) during summer (G. Wang et al., 2006). High loadings in early June ($60\text{--}80\ \mu\text{g m}^{-3}$) are much higher than those reported in Tokyo ($10\text{--}44\ \mu\text{g m}^{-3}$, maximum in winter) (Kawamura and Ikushima, 1993). It is important to note that TC contents of Mt. Tai aerosols showed a good correlation with levoglucosan (a tracer of biomass burning, pyrolysis of cellulose) in the same aerosol samples (Fu et al., 2008), suggesting that the peaks of TC are mainly caused by a significant contribution from field burning of agricultural wastes (wheat straws). Thus, the field burning of agricultural wastes and the atmospheric transport of burning products significantly control the TC concentrations of atmospheric aerosols over Mt. Tai. Interestingly, TC did not show a correlation with dehydroabietic acid (a tracer for burning of pines) in the Mt. Tai aerosols (Fu et al., 2008). This supports that forest fires are not the source of the Mt. Tai aerosols, but the field burning in the CEC region is the major source of the high aerosol carbon.

Day/night samples did not show a diurnal trend of TC, although 3-h samples collected during 2–5, 23 and 25 June gave a peak in early morning, afternoon or evening; i.e. peaks were observed at 01:27 (center time) on 3 June, 19:34 on 3 June, 13:38 on 4 June, 13:28 on 23 June and 13:30 on 25 June (Fig. 3a). Such a peak of TC at different time may be associated with the transport of polluted air masses together with

the changes in the height of PBL over Mt. Tai, within which accumulation of biomass burning products occurs that are transported upwind from the ground surface in low lands. It is important to note that the two peaks appeared in the afternoon around 13:30 in late (23 and 25) June when the field burning of agricultural wastes is declined.

5 The daytime maxima of TC may be caused by photochemical secondary formation of organic aerosols under the less influence of field burning of agriculture wastes in low lands.

TN contents showed temporal variations similar to TC, except for relatively small peak in 12–13 June and relatively high peaks in late June (Fig. 3b). TN concentrations significantly declined during 8–11 June when winds from the north dominated over Mt. Tai and the fire spots located south of the sampling site (Fig. 4b). Clean air masses were probably transported over the sampling site during 8–11 June. However, when the wind direction changed to the north the TN levels again increased. Diurnal variations of TN were obtained during 3-h sampling, which showed a peak in late afternoon or evening (Fig. 3b), being consistent with the variation of TC (Fig. 3a) although amplitudes of the TN peaks in late June are a little higher than TC (Fig. 3b). Thus, C/N weight ratios stayed almost unchanged during the period of 31 May to 7 June (Fig. 3c). However, the ratios significantly increased up to 5.6 during 8–11 June when wind direction shifted to northerly (Figs. 3c and 4b). Further, C/N ratios decreased to the value of less than unity after 19 June when the activity of field burning declined (Figs. 3c and 4c). The lower C/N ratios may be derived from the relative increases in inorganic nitrogen (NO_3^- and NH_4^+) and organic nitrogen, the latter may include amino acids and proteins. During 22–23 June, the winds came from the east or southeast (Fig. 2), suggesting that contributions of marine organic matter enriched with organic nitrogen may result in the lower C/N ratios (Miyazaki et al., 2011).

25 Temporal variations of water-soluble organic carbon (WSOC) are shown in Fig. 5a. The WSOC variation pattern gave two peaks on 7 and 13 June, being very similar to that of TC (Fig. 3a). However, WSOC/TC ratios are not constant (Fig. 5b). Rather, the WSOC/TC ratios gradually increased from 0.3 in late May to 0.56 in 7 June, showing

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a diurnal variation with peaks early in the morning; i.e. 07:37 (center time) on 2 June, 07:38 on 3 June and 04:34 on 4 June (Fig. 5b). The enhanced WSOC/TC ratios may suggest aqueous phase production of WSOC in the aerosols early in the morning when relative humidity significantly increased (Fig. 2), a point to be discussed later.

5 Because biomass burning can produce water-soluble organic compounds such as sugar compounds (Simoneit et al., 1999; Simoneit, 2002; Engling et al., 2006), the higher WSOC/TC ratios may be associated with more contribution of field burning to atmospheric aerosols over the agricultural fields in CEC. In fact, significant influence of biomass burning was supported by high abundances of levoglucosan (tracer of biomass burning) over Mt. Tai (Fu et al., 2008). It is also consistent with both fire spots and air mass trajectories in 5–7 June (Fig. 4a). However, the WSOC/TC ratios significantly dropped in 8–12 June when wind direction shifted to south with minimum value of 0.2. This result indicates that the air masses delivered from the north (North China and Siberia) contain organic aerosols enriched with less water-soluble organic compounds, which may include biogenic lipid class compounds or fossil fuel combustion products. In fact, sterols, fatty alcohols and hopanes were relatively abundant in the Mt. Tai aerosols during the period of 8–10 June (Fu et al., 2008).

Diurnal variations of WSOC were observed during 3-h sampling periods of 2–5 June with peaks in late afternoon or evening; 19:37 on 2 June, 16:39 on 3 June, 13:38 on 4 June (Fig. 5a). This result may suggest that more water-soluble organic compounds are transported over Mt. Tai in late afternoon or evening by biomass burning plumes. In contrast, during 23–25 June maxima of WSOC were obtained around noontime at 13:28 on 23 June and 13:30 on 25 June when field burning activities declined. This may suggest that photochemical oxidation of organic precursors may produce more water-soluble organic species, which were probably accumulated over Mt. Tai. The latter point will be discussed in more details using the molecular composition of dicarboxylic acids and related compounds as tracers of photochemical processing.

3.2 Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls

In the Mt. Tai aerosols, we detected homologous series of α,ω -dicarboxylic acids (C_2 – C_{12}), branched chain diacids (iC_4 – iC_6), unsaturated diacids (maleic, fumaric and methylmaleic), aromatic diacids (phthalic, isophthalic and terephthalic) and hydroxy diacid (malic) as well as diacids with keto-group (ketomalonic and 4-ketopimelic). Their total concentrations range from 112 ng m^{-3} to 6070 ng m^{-3} . Table 1 summarizes the concentration ranges of dicarboxylic acids as well as ketoacids and α -dicarbonyls with their average and median concentrations. Figure 6 presents an averaged bar graph for these organic species in selected aerosol samples. Generally, oxalic acid (C_2) was found as the most abundant diacid species followed by malonic (C_3) and/or succinic (C_4) acids, being consistent with previous studies of continental aerosols (Kawamura and Ikushima, 1993; Kundu et al., 2010b). However, azelaic acid (C_9) was occasionally found to be very abundant in the aerosol samples (see Fig. 6e). We also detected ketocarboxylic acids including series of ω -oxocarboxylic acids (C_2 – C_9) and pyruvic acid, among which glyoxylic acid (ωC_2) was found as most abundant ketoacid (Table 1 and Fig. 6). Such a molecular signature has been reported in previous studies of ambient aerosols (Kawamura et al., 1996a; Kawamura and Yasui, 2005; Kundu et al., 2010a, b). Two α -dicarbonyls (glyoxal and methylglyoxal) were detected in the samples with a predominance of methylglyoxal in most samples. Concentrations of ketoacids and α -dicarbonyls are roughly one order of magnitude lower than those of diacids (Table 1).

The averaged concentrations of diacids (1702 ng m^{-3}), ketoacids (242 ng m^{-3}) and α -dicarbonyls (68.3 ng m^{-3}) in the Mt. Tai aerosols (Table 1) are 2–7 times higher than those (760 , 45 and 9 ng m^{-3} , respectively) reported in Beijing during August/September (Ho et al., 2010) and those (660 , 53 and 12 ng m^{-3} , respectively) from Gosan site, Jeju Island, outflow region of Chinese aerosols (Kundu et al., 2010b). In particular, ketoacids and α -dicarbonyls in Mt. Tai aerosols are very high compared with megacity

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aerosols (Ho et al., 2010). Further, the concentrations of Mt. Tai aerosols are 3 to 4 times higher than those (438, 43 and 11 ng m⁻³, respectively) reported in Pearl Delta River Region near Hong Kong, South China during winter and summer (Ho et al., 2011). Compared with European mountain sites (Legrand et al., 2007) and the high Arctic alert (Kawamura et al., 1996a), the concentrations of diacids in Mt. Tai aerosols are two orders of magnitude higher. These levels are significantly higher than those of remote marine aerosols from the Pacific (Kawamura and Sakaguchi, 1999; Miyazaki et al., 2010).

However, concentrations of diacids and related compounds in the Mt. Tai aerosols are equivalent to the levels reported in biomass burning aerosols from pasture site in Amazonia (Kundu et al., 2010a) and in urban aerosols from New Delhi, India in winter (Miyazaki et al., 2009). These comparisons demonstrate that the Mt. Tai aerosols are significantly enriched with diacids, ketoacids and α -dicarbonyls, showing the highest levels in the mountain aerosols.

3.3 Temporal variations of dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls and their contributions to TC and WSOC

Figure 7a presents temporal variations of total diacids. Their concentrations increase from 2 to 7 June, quickly decrease during 8–11 June and then increase in 12–13 June when the highest concentration of levoglucosan was reported (Fu et al., 2008). Interestingly, in 7 June, the concentrations of total diacids reached maximum (> 6000 ng m⁻³), which is the highest value ever reported in the aerosol samples collected in the world. These variations are similar to those of TC and WSOC (Figs. 3a and 5a, respectively), again suggesting that the diacid concentrations are closely associated with the field burning of agricultural wastes and changes in the wind direction. Their concentrations also decreased toward the end of field burning season in late June. These results suggest that diacids are largely produced as a result of biomass burning of agricultural crop wastes in the CEC region. This is supported by a positive correlation ($r = 0.70$) between total diacids (this study) and levoglucosan (Fu et al., 2008). Diacids have

been reported abundantly in biomass burning plumes of the forest fires in Indonesia (Narukawa et al., 1999) and Amazon (Kundu et al., 2010b).

Although we analyzed the day/night samples to discuss diurnal variations of diacids, no clear diurnal trend was detected for the diacid concentrations. However, the sample sets of 3-h sampling showed diurnal trend of the concentrations (Fig. 7a), although the peaking times are not consistent; i.e. the diacids concentrations peaked at 01:27 on 3 June (center time of sampling), 19:34 on 3 June, 10:38 on 4 June, and 04:29 on 5 June, except for the sample sets collected in the late period of the campaign, which showed a concentration peak at 13:28 23 June and 13:30 25 June (see Fig. 7a). These diurnal patterns are similar to those of TC and WSOC as described above.

Figure 7b, c presents contributions (%) of total diacids to total carbon (TC) and water-soluble organic carbon (WSOC), respectively. Total diacid-C/TC ratios ranged from 1.2% to 6.6% with an average of 2.4%. These values are much higher than those (range: 0.28 to 2.1%, average: 0.87%) reported in the marine aerosols from the Arctic Ocean in summer (Kawamura et al., 2012) and those (range: 0.18–1.8%, av. 0.95%) reported in the Tokyo urban aerosols (Kawamura and Ikushima, 1993). However, they are lower than those (1.5–7.0%, av. 4.0%) reported in the Arctic (Alert) aerosols from February to June (Kawamura et al., 2010) and are significantly lower than those (1.1–15.8%, av. 8.8%) reported in the remote marine aerosols collected in the North Central Pacific including tropics (Kawamura and Sakaguchi, 1999). Because diacid-C/TC ratios increase with photochemical aging of organic aerosols (Kawamura and Sakaguchi, 1999), the values obtained during MTX2006 campaign in the North China Plain suggest that the mountain organic aerosols are, to some extent, processed by photochemical oxidations during atmospheric transport. However, the degree of the photochemical ageing is not as strong as remote marine aerosols. We consider that the Mt. Tai aerosols are photochemically more aged than urban aerosols, but less aged than marine aerosols.

Contributions of total diacids to TC significantly dropped during 8–11 June when the air mass came from the north (Fig. 7b), suggesting that the aerosols were not

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photochemically aged. On 22 June, very high ratio (6.6%) was obtained partly due to the high abundance of azelaic acid (C_9) that is a specific oxidation product of unsaturated fatty acids (Kawamura and Gagosian, 1987; Stephanou, 1992). In contrast, the contributions of total diacids to WSOC are relatively constant around at 5% although a large peak was again observed on 22 June (Fig. 7b). We did not detect any diurnal trend in the contributions of total diacids to TC and WSOC (Figs. 7b, c), suggesting no serious photochemical production of diacids over the sampling site. The diacids-C/TC or WSOC ratios may have been determined prior to the atmospheric transport over the sampling site of Mt. Tai.

Figure 8a shows temporal variations in the concentrations of ketocarboxylic acids in the Mt. Tai aerosols. Total ketoacids showed the variation pattern similar to diacids (Fig. 7a) although the peak on 7 June is relatively small compared to diacids. We could not detect a systematic trend for the ketoacids concentrations between day and night samples. In contrast, the time-resolved samples collected each 3 h showed diurnal distributions (see Fig. 8a), however, we observed that the peaks appeared differently; total ketoacids peaked at 01:27 (center time) on 3 June, 22:28 on 3 June, 10:38 on 4 June and 04:29 on 5 June, 13:28 on 23 June and 13:30 on 25 June. These peak timings are similar to those of diacids. The variability of the concentration maxima may be caused by the complicated transport processes of polluted air masses over the mountaintop, coupled with the vertical movement of the PBL during the field-burning season. However, the last two peaks appeared in the early afternoon during late June when the field burning was weakened.

Figure 8b, c presents contributions of total ketoacids to TC and WSOC, respectively. Contributions of ketoacids to TC ranged from 0.17 to 0.81 (av. 0.43%) whereas those to WSOC ranged from 0.4 to 4.9% (av. 1.1%). These values (ketoacids-C/TC) are similar to those (0.2–0.6%) reported for the Arctic aerosols from Alert (Kawamura et al., 2010), but much higher than those (0.05–0.26%, av. 0.10%) reported for in the Arctic Ocean aerosols (Kawamura et al., 2012). This may suggest that these ketoacids are derived from biomass burning and anthropogenic sources. The ketoacids-C/TC ratios

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increased from 2 June to 5 June showing some diurnal peaks and then declined toward 8–11 June when the wind direction changed from southerly to northerly (Fig. 2). This trend is somewhat similar to that of diacids; however, the amplitude of the drop in 8–11 June is not as strong as diacids (Fig. 7b). This may suggest that ketoacids (semi-volatile species) may be more partitioned to aerosol phase due to the lower ambient temperature during 8–11 June (Fig. 2), causing the ketoacids-C/TC ratios relatively high. This trend seems much clearer for the temporal variation of ketoacids-C/WSOC ratios (Fig. 8c), which show more constant values around 1 %, except for high value on 21 June.

As shown in Fig. 9a, total α -dicarbonyls showed similar temporal variation with ketoacids although the peak on 7 June is very large mainly due to the high abundance of glyoxal (228 ng m⁻³). Diurnal variations of α -dicarbonyls were not clearly observed in the day/night samples, being similar to ketoacids. However, diurnal variations were obtained for 3-h samples with concentration peaks at 1:27 on 3 June, 19:34 on 3 June, 10:38 on 4 June and 1:31 on 5 June, 13:28 on 23 June and 13:30 on 25 June (Fig. 9a). These diurnal patterns are similar to those of diacids and ketoacids. Again the last two peaks of α -dicarbonyls appeared early in the afternoon when the field burning was weakened.

The relative abundance of α -dicarbonyls in TC and WSOC ranged from 0.03–0.37 % (av. 0.14 %) and 0.06–1.9 % (av. 0.35 %), respectively (Figs. 9b, c). These values (α -dicarbonyl-C/TC) are similar to those (0.05–0.26 %, av. 0.10 %) reported for the Arctic Ocean aerosols (Kawamura et al., 2012), but bit lower than those (0.2–0.6 %) reported in the Arctic Alert aerosols (Kawamura et al., 2010). The α -dicarbonyl-C/WSOC ratios of the Mt. Tai samples are higher than those (0.02–0.35 %) reported in the Arctic Alert aerosols that were collected in late winter to early summer including the season of polar sunrise (Kawamura et al., 2010). This result may suggest that Mt. Tai aerosols may be more contributed from anthropogenic sources than the Arctic aerosols and/or be more processed by photochemical reactions.

3.4 Compositional changes of dicarboxylic acids

Molecular compositions of dicarboxylic acids have been used as tracers of source strength (biogenic vs. anthropogenic) or photochemical processing of organic aerosols. For example, adipic (C_6)/azelaic (C_9) acid ratios and phthalic (Ph)/ C_9 acid ratios are useful tracers to evaluate anthropogenic vs. biogenic contributions to organic aerosols because C_6 and Ph are produced by the oxidation of anthropogenic cyclic hexene (Hatakeyama et al., 1985) and aromatic hydrocarbons such as naphthalene (Kawamura and Ikushima, 1993) whereas C_9 is produced by the photooxidation of biogenic unsaturated fatty acids that have a double bond predominantly at C-9 position (Kawamura and Gagosian, 1987; Kawamura et al., 2005). As shown in Figs. 10a, b, C_6/C_9 and Ph/ C_9 ratios are higher in early June when the influence of field burning is significant, suggesting more contribution from anthropogenic sources. They are also high in 15–16 and 19–20 June as well as 23–25 June. In contrast, these ratios are significantly low during 8–11 and 21 June when the air masses came from North China and Siberia (Figs. 2 and 4b), suggesting that the aerosols are more influenced by biogenic sources. The Ph/ C_9 ratios of the Mt. Tai aerosols are similar to those reported for summer aerosols from Gosan site, Jeju Island (Kundu et al., 2010b), except for very high values (up to 9) in 23–25 June, which are similar to those reported from Gosan site in winter (Kundu et al., 2010b).

Malonic (C_3)/succinic (C_4) acid ratios can be used as a tracer to evaluate the photochemical processing of organic aerosols because the C_3/C_4 ratios significantly increased up to 3 in summer following the increase of ozone in the urban Tokyo atmosphere (Kawamura and Ikushima, 1993). The ratios are low in the fossil fuel combustion products due to the thermally unstable structure of malonic acid. Figure 10c show temporal variation of C_3/C_4 ratios in the Mt. Tai aerosols. During the first week of June, the period with an influence of field burning, the C_3/C_4 ratios were around 0.8–1.0 and decreased down to 0.2 in 7 June when total diacids maximized (Fig. 7a). The C_3/C_4 ratios increased during 8–11 June when the air masses came from the north. The higher

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ratios may be caused by photochemical production of C_3 from C_4 during a long-range atmospheric transport. The ratios declined around 13 June when diacids increased (Fig. 7a) due to the influence of field burning of wheat straw wastes. The ratios fluctuated with a peak in 15–16 June (winds came from the north) and a drop in 21–23 June (winds came from the south). The fluctuations of C_3/C_4 ratios seem to be consistent with the patterns of air mass origin and long-range transport. However, C_3/C_4 ratios (0.2–1.5) are much lower than those (up to 10) from remote marine aerosols where photochemical transformation is serious (Kawamura and Sakaguchi, 1999).

We detected unsaturated dicarboxylic acids, i.e. maleic (M) and fumaric (F) acids. Maleic acid (cis configuration) is produced by the oxidation of aromatic hydrocarbons such as toluene and benzene via combustion and/or photochemical processes and can be photo-isomerized to its trans isomer (F). The M/F ratios (0.22–5.1, av. 2.0) in the Mt. Tai aerosols were found to be > 1 except for one sample (7 June) (Fig. 10d), being much higher than those (0.06–1.3, av. 0.26) from the marine aerosols from the North Pacific (Kawamura and Sakaguchi, 1999). This comparison suggests that photochemical transformation is not so significant in the Mt. Tai aerosols as marine aerosols. It is of interest to note that M/F ratios of Mt. Tai aerosols are similar to those (0.9–4) from urban Tokyo aerosols (Kawamura and Ikushima, 1993). Interestingly, M/F ratios increased in the second half of the campaign (Fig. 10d). The higher ratios suggest that the aerosols of Mt. Tai were not seriously subjected to photochemical processing; rather they are derived from fresh aerosols either from fossil fuel combustion or biomass burning.

Glyoxylic acid (ωC_2) is an intermediate compound to produce oxalic acid (C_2) (Kawamura et al., 1996a; Warneck, 2003; Lim et al., 2005; Hegde and Kawamura, 2012; Wang et al., 2012); Thus, $\omega C_2/C_2$ ratios can serve as a tracer to evaluate the oxidation process of organic aerosols. Figure 10e present the temporal variation of $\omega C_2/C_2$ ratios in the Mt. Tai aerosols. Although the ratios varied significantly with the range of 0.04 to 2.2, we found that during 3-h sampling periods the $\omega C_2/C_2$ ratios maximized in late morning (center time around 10:30) or early afternoon (around 13:30) and minimized

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in late evening or night. The maxima of the ratios in daytime probably suggest that glyoxylic acid is preferentially formed by photochemical oxidations of various precursors including anthropogenic volatile organic compounds (VOC) as well as biogenic VOC such as isoprene during daytime when solar radiation and oxidants (e.g. ozone) are enhanced (Kanaya et al., 2013). This observations are consistent with the diurnal distributions of glyoxylic acid in the time-resolved aerosols from Tokyo, whose concentrations showed a positive correlation with ambient temperature and ozone (Kawamura and Yasui, 2005). In the late afternoon or evening, ω C₂ can be oxidized to oxalic acid possibly in aerosol aqueous phase (Warneck, 2003; Miyazaki et al., 2009; He and Kawamura, 2010).

3.5 Photochemical processing of diacids and related compounds as a function of relative abundance of oxalic acid (C₂ %)

Relative abundance of oxalic acid (C₂ %) in total *n*-saturated diacids (C₂–C₁₀) has been proposed as a tracer to evaluate the photochemical ageing of organic aerosols because C₂ is produced by the oxidation of longer chain diacids and other precursor compounds (Kawamura and Sakaguchi, 1999). Figure 11a–d provides relative abundances of C₂ and its precursors (e.g. pyruvic acid methylglyoxal) in TC or WSOC as a function of C₂ %. Relative contributions of C₂ to TC increased with an increase in C₂ % (Fig. 11a). Similar result was obtained for the contribution of C₂ to WSOC (Fig. 11b). These results support that oxalic acid is more produced during the photochemical ageing of organic aerosols. Intermediate compounds (e.g. pyruvic acid and methylglyoxal) that can serve as precursor of oxalic acid also show an increase relative to TC as a function of C₂ % (Fig. 11c, d) although the correlation coefficients are lower. These results again suggest that in addition to the formation of end product (i.e. oxalic acid) intermediate precursors are also produced in the atmosphere during the photochemical ageing of organic aerosols.

We found a negative correlation between ω C₂/C₂ ratio and C₂ % (Fig. 11e). This result suggests that glyoxylic acid is oxidized to oxalic acid in the course of photochemical

ageing that is expressed as C_2 %. Similar trend was obtained for glyoxal/oxalic acid ratios (Fig. 11f). Although the sources of aerosols and source regions of air masses are significantly variable during the campaign as discussed above, these relations demonstrate that the production of oxalic acid (end product) is closely linked with the photochemical behaviors of its precursor compounds (e.g. pyruvic acid, glyoxal, methylglyoxal) and intermediate (glyoxylic acid) that have similar chemical structures as described below.

Precursors (e.g. $CH_3COCOOH$, $HCO-CHO$, CH_3COCHO) → intermediate ($HCO-COOH$) → end product ($HOOC-COOH$)

Recently, a depletion of oxalic acid has been reported in the Arctic aerosols after polar sunrise (Kawamura et al., 2010) and the Arctic Ocean aerosols collected in summer (Kawamura et al., 2012). Although C_2 is generally the most abundant diacid in the atmospheric aerosols, C_2 became less abundant than C_3 and C_4 diacids during the C_2 -depletion events under the solar radiation in the presence of trace metals such as Fe (Pavuluri and Kawamura, 2012). However, in the Mt. Tai aerosols, we did not observe the depletion of oxalic acid; C_2 is always the most abundant diacid accounting for 50–85 % of total C_2 - C_{10} diacids. So far, depletion of oxalic acid has been observed in the Arctic and Antarctic regions (Kawamura et al., 1996b, 2010, 2012) but not in the low and mid latitudes. Because Mt. Tai is surrounded by pollution sources in low lands and contributed by fresh aerosols transported by upwind, photochemical processing may not be significant enough to decompose oxalic acid compared to atmospheric aerosols from the Polar Regions where halogen chemistry may be important.

4 Summary and conclusions

Aerosol samples collected at the summit (1534 m a.s.l.) of Mount Tai in Central East China (36.25° N; 117.10° E) showed high loadings of dicarboxylic acids, ketocarboxylic

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acids and α -dicarbonyls, whose concentrations are several times higher than those reported in Chinese megacities. Their concentrations are largely influenced by the field burning of agricultural wastes in the North China Plain and the air mass trajectories that transport the biomass burning products over the mountaintop as well as photochemical processes during the atmospheric transport. We found that total dicarboxylic acids accounted for 1.2 % to 6.5 % of TC and 5 % to 40 % of WSOC.

Although atmospheric photochemical processing over Mt. Tai is not as serious as remote marine aerosols, we detected a close link between the oxidation of glyoxylic acid and α -dicarbonyls and production of oxalic acid. Based on the detailed analyses of molecular compositions of the organic species and the ageing factor presented by the relative abundance of C_2 in total diacids (C_2 %), we conclude that chain-reactions of the oxidation of glyoxylic acid and methylglyoxal to result in oxalic acid is occurring in the aqueous aerosol phase in the atmosphere over the mountaintop.

This study demonstrated that the enhanced field burning of agriculture residues in early summer often enhanced water-soluble organic acids in the mountain aerosols in the free troposphere over the Northern China Plain. The field burning of agricultural wastes in this region not only controls the high loading of organic aerosols in Central East China, but also affects the air quality and atmospheric chemistry in the outflow regions of Chinese aerosols in the western North Pacific.

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References

- Aggarwal, S. G. and Kawamura, K.: Molecular distributions and stable carbon isotopic compositions of dicarboxylic acids and related compounds in aerosols from Sapporo, Japan: implications for photochemical aging during long-range atmospheric transport, *J. Geophys. Res.-Atmos.*, 113, D14301, doi:10.1029/2007jd009365, 2008.
- Brooks, S. D., Wise, M. E., Cushing, M., and Tolbert, M. A.: Deliquescence behavior of organic/ammonium sulfate aerosol, *Geophys. Res. Lett.*, 29, 1917, doi:10.1029/2002GL014733, 2002.
- Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H. J., and Ervens, B.: Atmospheric oxalic acid and SOA production from glyoxal: results of aqueous photooxidation experiments, *Atmos. Environ.*, 41, 7588–7602, 2007.
- Cooke, W. F., Liousse, C., Cachier, H., and Feichter, J.: Construction of a 1 degrees × 1 degrees fossil fuel emission data set for carbonaceous aerosol and implementation and radiative impact in the ECHAM4 model, *J. Geophys. Res.*, 104, 22137–22162, 1999.
- Cruz, C. N. and Pandis, S. N.: The effect of organic coatings on the cloud condensation nuclei activation of inorganic atmospheric aerosol, *J. Geophys. Res.*, 103, 13111–13123, 1998.
- Engling, G., Carrico, C. M., Kreidenweis, S. M., Collett, J. L., Day, D. E., Malm, W. C., Lincoln, E., Hao, W. M., Iinuma, Y., and Herrmann, H.: Determination of levoglucosan in biomass combustion aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection, *Atmos. Environ.*, 40, S299–S311, 2006.
- Ervens, B., Carlton, A. G., Turpin, B. J., Altieri, K. E., Kreidenweis, S. M., and Feingold, G.: Secondary organic aerosol yields from cloud-processing of isoprene oxidation products, *Geophys. Res. Lett.*, 35, GL031828, doi:10.1029/2007GL031828, 2008.
- Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.*, 11, 11069–11102, doi:10.5194/acp-11-11069-2011, 2011.
- Fu, P. Q., Kawamura, K., Okuzawa, K., Aggarwal, S. G., Wang, G., Kanaya, Y. and Wang, Z.: Organic molecular compositions and temporal variations of summertime mountain aerosols over Mt. Tai, North China Plain, *J. Geophys. Res.*, 113, D19107, doi:10.1029/2008JD009900, 2008.

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Fu, F., Kawamura, K., Usukura, K., and Miura, K.: Dicarboxylic acids and related polar compounds in the marine aerosols collected during a round-the-world cruise, *Mar. Chem.*, 148, 22–32, 2013.

Gao, J., Wang, T., Ding, A. J., and Liu, C. B.: Observational study of ozone and carbon monoxide at the summit of mount Tai (1534 m a.s.l.) in central-eastern China, *Atmos. Environ.*, 39, 4779–4791, 2005.

Hatakeyama, S., Tanonaka, T., Weng, J. H., Bandow, H., Takagi, H., and Akimoto, H.: Ozone cyclohexene reaction in air – quantitative-analysis of particulate products and the reaction-mechanism, *Environ. Sci. Technol.*, 19, 935–942, 1985.

Hayashida, S., Urita, N., Noguchi, K., Liu, X., and Chance, K.: Spatiotemporal variation in tropospheric column ozone over East Asia observed by GOME and ozonesondes, *Sola*, 4, 117–120, 2008.

He, N. and Kawamura, K.: Distributions and diurnal changes of low molecular weight organic acids and alpha-dicarbonyls in suburban aerosols collected at Mangshan, North China, *Geochem. J.*, 44, E17–E22, 2010.

Hegde, P. and Kawamura, K.: Seasonal variations of water-soluble organic carbon, dicarboxylic acids, ketocarboxylic acids, and alpha-dicarbonyls in Central Himalayan aerosols, *Atmos. Chem. Phys.*, 12, 6645–6665, doi:10.5194/acp-12-6645-2012, 2012.

Ho, K. F., Cao, J. J., Lee, S. C., Kawamura, K., Zhang, R. J., Chow, J. C., and Watson, J. G.: Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China, *J. Geophys. Res.-Atmos.*, 112, D22s27, doi:10.1029/2006jd008011, 2007.

Ho, K. F., Lee, S. C., Ho, S. S. H., Kawamura, K., Tachibana, E., Cheng, Y., and Zhu, T.: Dicarboxylic acids, ketocarboxylic acids, alpha-dicarbonyls, fatty acids, and benzoic acid in urban aerosols collected during the 2006 Campaign of Air Quality Research in Beijing (CAREBeijing-2006), *J. Geophys. Res.-Atmos.*, 115, 2197–2208, doi:10.1029/2009jd013304, 2010.

Ho, K. F., Ho, S. S. H., Lee, S. C., Kawamura, K., Zou, S. C., Cao, J. J., and Xu, H. M.: Summer and winter variations of dicarboxylic acids, fatty acids and benzoic acid in PM_{2.5} in Pearl Delta River Region, China, *Atmos. Chem. Phys.*, 11, 2197–2208, doi:10.5194/acp-11-2197-2011, 2011.

Huebert, B. J., Bates, T., Russell, P. B., Shi, G. Y., Kim, Y. J., Kawamura, K., Carmichael, G., and Nakajima, T.: An overview of ACE-Asia: strategies for quantifying the relationships

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between Asian aerosols and their climatic impacts, *J. Geophys. Res.*, 108, D23, doi:10.1029/2003JD003550, 2003.

Kanaya, Y., Akimoto, H., Wang, Z.-F., Pochanart, P., Kawamura, K., Liu, Y., Li, J., Komazaki, Y., Irie, H., Pan, X.-L., Taketani, F., Yamaji, K., Tanimoto, H., Inomata, S., Kato, S., Suthawaree, J., Okuzawa, K., Wang, G., Aggarwal, S. G., Fu, P. Q., Wang, T., Gao, J., Wang, Y., and Zhuang, G.: Overview of the Mount Tai Experiment (MTX2006) in Central East China in June 2006: studies of significant regional air pollution, *Atmos. Chem. Phys. Discuss.*, 13, 1527–1573, doi:10.5194/acpd-13-1527-2013, 2013.

Kawamura, K.: Identification of C2–C10 ω -oxocarboxylic acids, pyruvic acid, and C2–C3 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.: Implications 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 distributions 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., Steinberg, S., and Kaplan, I. R.: Capillary GC determination of short-chain dicarboxylic-acids in rain, fog, and mist, *Int. J. Environ. Anal. Chem.*, 19, 175–188, 1985.

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.*, 30, 1709–1722, 1996a.

Kawamura, K., Sempéré, R., Imai, Y., Fujii, Y., and Hayashi, M.: Water soluble dicarboxylic acids and related compounds in Antarctic aerosols, *J. Geophys. Res.-Atmos*, 101, 18721–18728, 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

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of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, in: *Geochemical Investigations in Earth and Space Science: A Tribute to Isaac R. Kaplan*, edited by: Hill, R. J., Leventhal, J., Aizenshtat, Z., Baedecker, M. J., Claypool, G., Eganhouse, R., Goldhaber, M., and Peters, K., The Geochemical Society, Publication No. 9, 243–265, 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., Kasukabe, H., and Barrie, L. A.: Secondary formation of water-soluble organic acids and α -dicarbonyls and their contributions to total carbon and water-soluble organic carbon: Photochemical aging of organic aerosols in the Arctic spring, *J. Geophys. Res.-Atmos.*, 115, D21306, doi:10.1029/2010jd014299, 2010.

Kawamura, K., Ono, K., Tachibana, E., Charrière, B., and Sempéré, R.: Distributions of low molecular weight dicarboxylic acids, ketoacids and alpha-dicarbonyls in the marine aerosols collected over the Arctic Ocean during late summer, *Biogeosciences*, 9, 4725–4737, 2012, <http://www.biogeosciences.net/9/4725/2012/>.

Kerminen, V. M., Teinila, K., Hillamo, R., and Makela, T.: Size-segregated chemistry of particulate dicarboxylic acids in the Arctic atmosphere, *Atmos. Environ.*, 33, 2089–2100, 1999.

Kitanovski, Z., Grgic, I., and Veber, M.: Characterization of carboxylic acids in atmospheric aerosols using hydrophilic interaction liquid chromatography tandem mass spectrometry, *J. Chromatogr. A*, 1218, 4417–4425, 2011.

Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α -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, 2010a.

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.-Atmos.*, 115, D19307, doi:10.1029/2010jd013973, 2010b.

Legrand, M., Preunkert, S., Oliveira, T., Pio, C. A., Hammer, S., Gelencser, A., Kasper-Giebl, A., and Laj, P.: Origin of C2–C5 dicarboxylic acids in the European atmosphere inferred from year-round aerosol study conducted at a west-east transect, *J. Geophys. Res.-Atmos.*, 112, D23s07, doi:10.1029/2006jd008019, 2007.

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- Li, J., Wang, Z., Akimoto, H., Yamaji, K., Takigawa, M., Pochanart, P., Liu, Y., Tanimoto, H. and Kanaya, Y.: Near-ground ozone source attributions and outflow in central eastern China during MTX2006, *Atmos. Chem. Phys.*, 8, 7335–7351, doi:10.5194/acp-8-7335-2008, 2008.
- 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.
- 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.
- Miyazaki, Y., Kawamura, K., and Sawano, M.: Size distributions and chemical characterization of water-soluble organic aerosols over the western North Pacific in summer, *J. Geophys. Res.-Atmos.*, 115, D23210, doi:10.1029/2010jd014439, 2010.
- Miyazaki, Y., Kawamura, K., Jung, J., Furutani, H., and Uematsu, M.: Latitudinal distributions of organic nitrogen and organic carbon in marine aerosols over the western North Pacific, *Atmos. Chem. Phys.*, 11, 3037–3049, doi:10.5194/acp-11-3037-2011, 2011.
- Mochida, M., Kawabata, A., Kawamura, K., Hatsushika, H., and Yamazaki, K.: Seasonal variation and origins of dicarboxylic acids in the marine atmosphere over the western North Pacific, *J. Geophys. Res.*, 108, 4193, doi:10.1029/2002JD002355, 2003a.
- Mochida, M., Kawamura, K., Umemoto, N., Kobayashi, M., Matsunaga, S., Lim, H. J., Turpin, B. J., Bates, T. S., and Simoneit, B. R. T.: Spatial distributions of oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine aerosols over the western Pacific and off the coast of East Asia: continental outflow of organic aerosols during the ACE-Asia campaign, *J. Geophys. Res.*, 108, 8638, doi:10.1029/2002JD003249, 2003b.
- 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.
- Narukawa, M., Kawamura, K., Li, S. M., and Bottenheim, J. W.: Dicarboxylic acids in the Arctic aerosols and snowpacks collected during ALERT 2000, *Atmos. Environ.*, 36, 2491–2499, 2002.
- Narukawa, M., Kawamura, K., Anlauf, K. G., and Barrie, L. A.: Fine and coarse modes of dicarboxylic acids in the Arctic aerosols collected during the Polar Sunrise Experiment 1997, *J. Geophys. Res.*, 108, 4575, doi:10.1029/2003JD003646, 2003.

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- Ohara, T., Akimoto, H., Kurokawa, J., Horii, N., Yamaji, K., Yan, X., and Hayasaka, T.: An Asian emission inventory of anthropogenic emission sources for the period 1980–2020, *Atmos. Chem. Phys.*, 7, 4419–4444, doi:10.5194/acp-7-4419-2007, 2007.
- 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.
- Richter, A., Burrows, J. P., Nuss, H., Granier, C., and Niemeier, U.: Increase in tropospheric nitrogen dioxide over China observed from space, *Nature*, 437, 129–132, 2005.
- Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Fuzzi, S., Ceburnis, D., O'Dowd, C. D., Sciare, J., Burrows, J. P., Vrekoussis, M., Ervens, B., Tsigaridis, K., and Facchini, M. C.: Evidence of a natural marine source of oxalic acid and a possible link to glyoxal, *J. Geophys. Res.*, 116, D16204, doi:10.1029/2011JD015659, 2011.
- Rohrl, A. and Lammel, G.: Low molecular weight dicarboxylic acids and glyoxylic acid: seasonal and air mass characteristics, *Environ. Sci. Tech.*, 35, 95–101, 2001.
- Rompp, A., Winterhalter, R., and Moortgat, G. K.: Oxodicarboxylic acids in atmospheric aerosol particles, *Atmos. Environ.*, 40, 6846–6862, 2006.
- Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emission from air pollution sources. 4. C_1 - C_{27} organic compounds from cooking with seed oils, *Environ. Sci. Technol.*, 36, 567–575, 2002.
- Sempéré, R. and Kawamura, K.: Comparative distributions of dicarboxylic-acids and related polar compounds in snow rain and aerosols from urban atmosphere, *Atmos. Environ.*, 28, 449–459, 1994.
- Simoneit, B. R. T.: Biomass burning—a review of organic tracers for smoke from incomplete combustion, *Appl. Geochem.*, 17, 129–162, 2002.
- Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., Rogge, W. F., and Cass, G. R.: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, *Atmos. Environ.*, 33, 173–182, 1999.
- Sorooshian, A., Varutbangkul, V., Brechtel, F. J., Ervens, B., Feingold, G., Bahreini, R., Murphy, S. M., Holloway, J. S., Atlas, E. L., Buzorius, G., Jonsson, H., Flagan, R. C., and Seinfeld, J. H.: Oxalic acid in clear and cloudy atmospheres: analysis of data from International Consortium for Atmospheric Research on Transport and Transformation 2004, *J. Geophys. Res.-Atmos.*, 111, D23, doi:10.1029/2005jd006880, 2006.

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Stephanou, E. G.: α,ω -Dicarboxylic acid salts and α,ω -dicarboxylic acids – photooxidation products of unsaturated fatty acids present in marine aerosols and marine sediments, *Naturwissenschaften*, 79, 128–131, 1992.

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.

Wang, G. and Kawamura, K.: Molecular characteristics of urban organic aerosols from Nanjing: a case study of a mega-city in China, *Environ. Sci. Technol.*, 39, 7430–7438, 2005.

Wang, G., Niu, S., Liu, C., and Wang, L.: Identification of dicarboxylic acids and aldehyde of PM₁₀ and PM_{2.5} aerosols in Nanjing, China, *Atmos. Environ.*, 36, 1941–1950, 2002.

Wang, G., Kawamura, K., Lee, S., Ho, K. F., and Cao, J. J.: Molecular, seasonal, and spatial distributions of organic aerosols from fourteen Chinese cities, *Environ. Sci. Technol.*, 40, 4619–4625, 2006.

Wang, G. H., Kawamura, K., Xie, M. J., Hu, S. Y., Cao, J. J., An, Z. S., Weston, J. G., and Chow, J. C.: Organic molecular compositions and size distributions of Chinese summer and autumn aerosols from Nanjing: characteristic haze event caused by wheat straw burning, *Environ. Sci. Technol.*, 43, 6493–6499, 2009.

Wang, G. H., Kawamura, K., Cheng, C. L., Li, J. J., Cao, J. J., Zhang, R. J., Zhang, T., Liu, S. X., and Zhao, Z. Z.: Molecular distribution and stable carbon isotopic composition of dicarboxylic acids, ketocarboxylic acids, and alpha-dicarbonyls in size-resolved atmospheric particles from Xi'an City, China, *Environ. Sci. Technol.*, 46, 4783–4791, 2012.

Wang, H. B., Kawamura, K., and Yamazaki, K.: Water-soluble dicarboxylic acids, ketoacids and dicarbonyls in the atmospheric aerosols over the Southern Ocean and western Pacific Ocean, *J. Atmos. Chem.*, 53, 43–61, 2006.

Warneck, P.: In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, *Atmos. Environ.*, 37, 2423–2427, 2003.

Yao, X. H., Fang, M., and Chan, C. K.: Size distributions and formation of dicarboxylic acids in atmospheric particles, *Atmos. Environ.*, 36, 2099–2107, 2002.

Table 1. Concentrations (ng m^{-3}) of dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls as well as concentrations ($\mu\text{g m}^{-3}$) of TC, TN and WSOC in the aerosols collected over Mt. Tai during 29 May to 28 June 2006.

Components, abbreviation	Concentrations (ng m^{-3})			
	Minimum	Maximum	Average	Median
Dicarboxylic acids				
Oxalic, C2	61.0	3920	1046	863
Malonic, C3	7.4	475	152	130
Succinic, C4	7.0	829	194	149
Glutaric, C5	0.7	137	39.9	33.3
Adipic, C6	0.6	68.0	21.7	18.5
Pimelic, C7	0.5	70.1	18.7	15.3
Sebacic, C8	0.0	38.0	7.2	3.7
Azelaic, C9	1.8	313	31.7	24.1
Decanedioic, C10	0.0	19.5	3.8	2.9
Undecanedioic, C11	0.0	18.0	3.8	2.9
Dodecanedioic, C12	0.0	3.5	0.6	0.5
Methylmalonic, iC4	0.0	11.9	3.1	2.6
Methylsuccinic, iC5	1.1	80.8	17.2	13.1
2-Methylglutaric, iC6	0.0	10.3	3.4	2.6
Maleic, M	0.6	91.0	12.6	10.4
Fumaric, F	0.3	37.5	7.6	5.6
Methylmaleic, mM	0.0	61.5	15.6	14.3
Phthalic, Ph	4.8	131.4	52.0	45.0
Isophthalic, iPh	0.0	21.4	6.2	5.2
Terephthalic, tPh	0.6	112	22.7	16.3
Malic, hC4	0.0	43.9	10.2	6.5
Oxomalonic, kC3	3.1	68.0	19.2	16.2
4-Oxopimelic, kC7	0.8	31.6	13.8	13.3
Sub total	112	6073	1702	1385
Ketocarboxylic acids				
Pyruvic, Pyr	3.0	140	50.5	42.9
Glyoxylic (2-oxoethanoic), ω C2	10.6	359	106	86.4
3-Oxopropanoic, ω C3	2.0	51.9	19.9	19.5
4-Oxobutanoic, ω C4	1.2	71.1	21.8	16.5
5-Oxopentanoic, ω C5	0.3	16.2	4.4	3.2
7-Oxoheptanoic, ω C7	1.1	42.5	14.3	12.4
8-Oxooctanoic, ω C8	0.0	70.9	19.2	13.5
9-Oxononanoic, ω C9	0.0	49.1	6.0	4.4
Sub total	26.6	742	242	210
α-Dicarbonyls				
Glyoxal, Gly	1.0	228	23.1	17.1
Methylglyoxal, mGly	1.8	118	45.2	42.0
Sub total	2.8	325	68.3	64.1
TC	3.1	85.4	24.4	21.6
TN	1.7	40.5	16.5	15.9
WSOC	0.5	37.2	10.4	8.4
C/N ratio	0.5	5.6	1.7	1.5

BDL: Below detection limit. BDL is ca. 0.01 ng m^{-3} .

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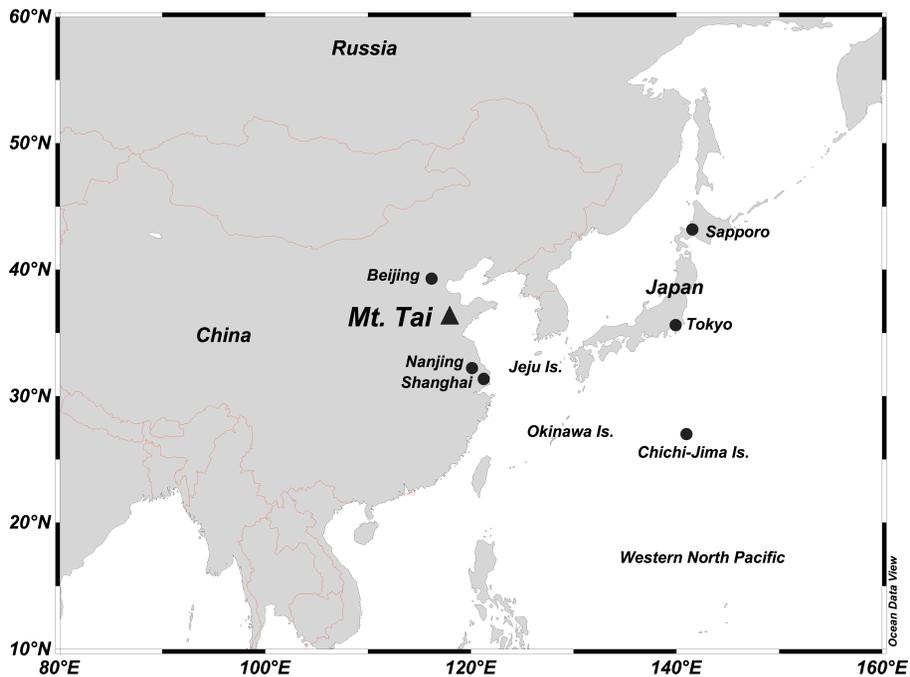


Fig. 1. A map of East Asia with the location of Mt. Tai (sampling site, triangle) and major megacities in Asia.

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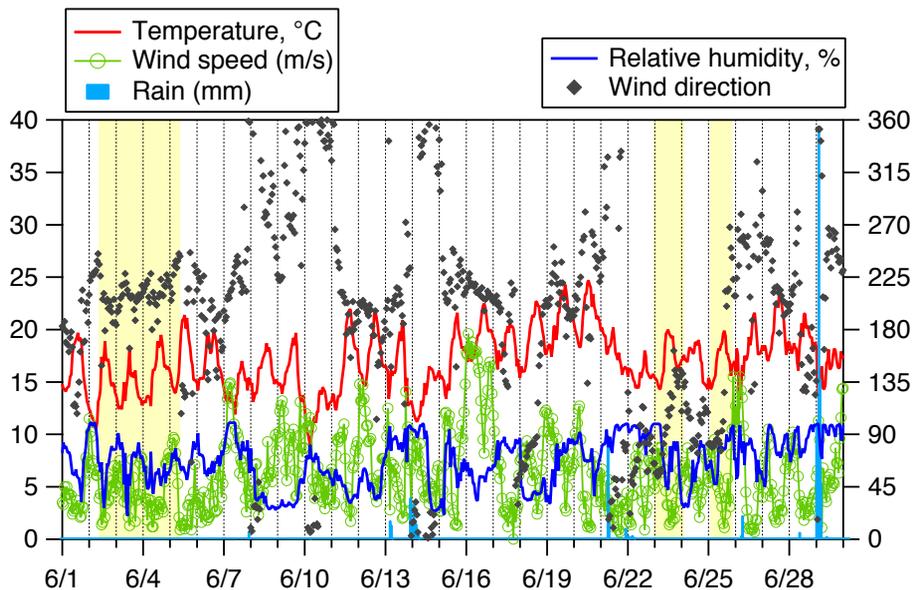


Fig. 2. Summary of meteorological data obtained at Mt. Tai Observatory in Central East China.

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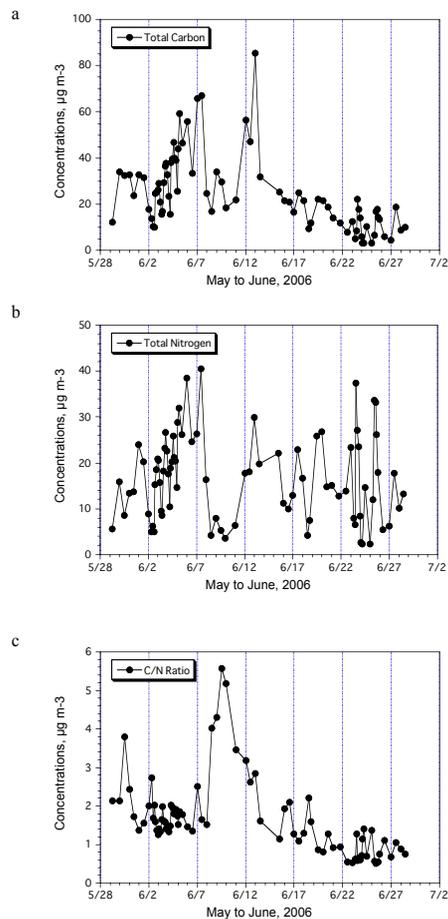


Fig. 3. Temporal variations of **(a)** total carbon (TC), **(b)** total nitrogen (TN) and **(c)** C/N ratios for the atmospheric aerosols collected from Mt. Tai.

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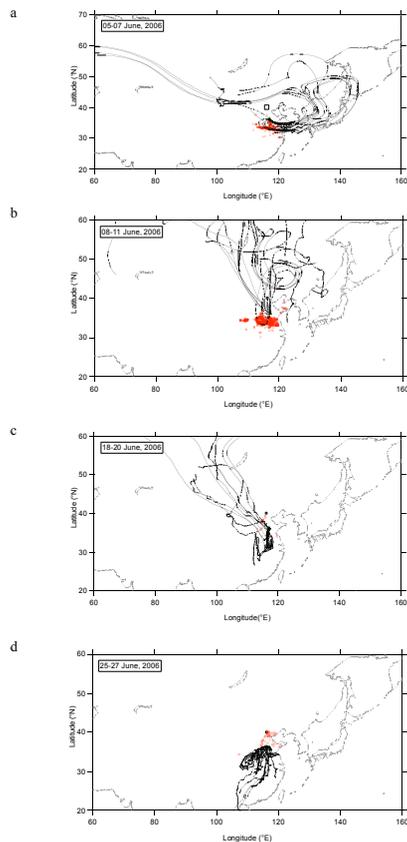


Fig. 4. Fire spots and backward air mass trajectories at Mt. Tai for selected periods in June 2006. Fire spot data were obtained from MODIS fire spot website (<http://earthdata.nasa.gov/data/near-real-time-data/firms>). Air mass trajectories were drawn by the data obtained by HYSPLIT4 model from NOAA ARL website (<http://ready.arl.noaa.gov/HYSPLIT.php>).

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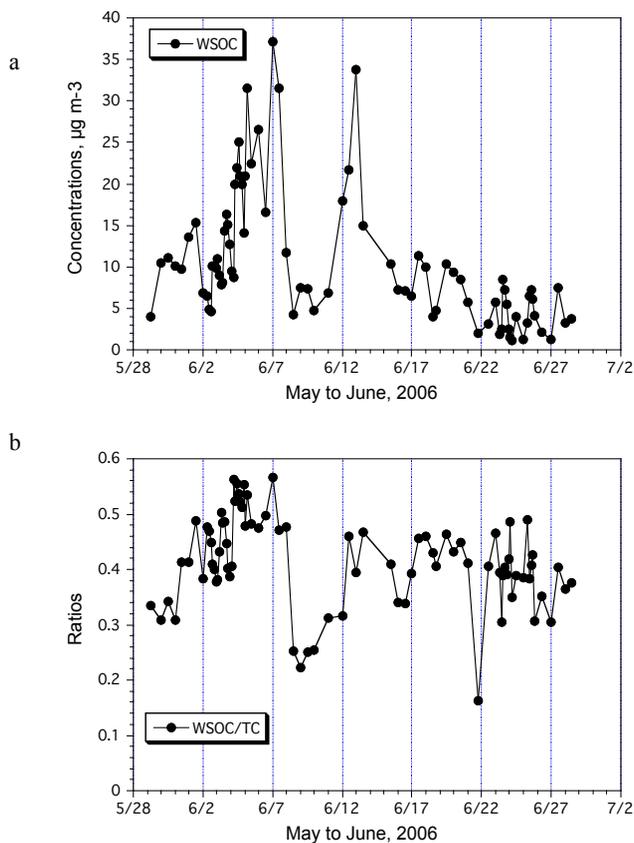


Fig. 5. Temporal variations of (a) water-soluble organic carbon (WSOC) and (b) WSOC/TC.

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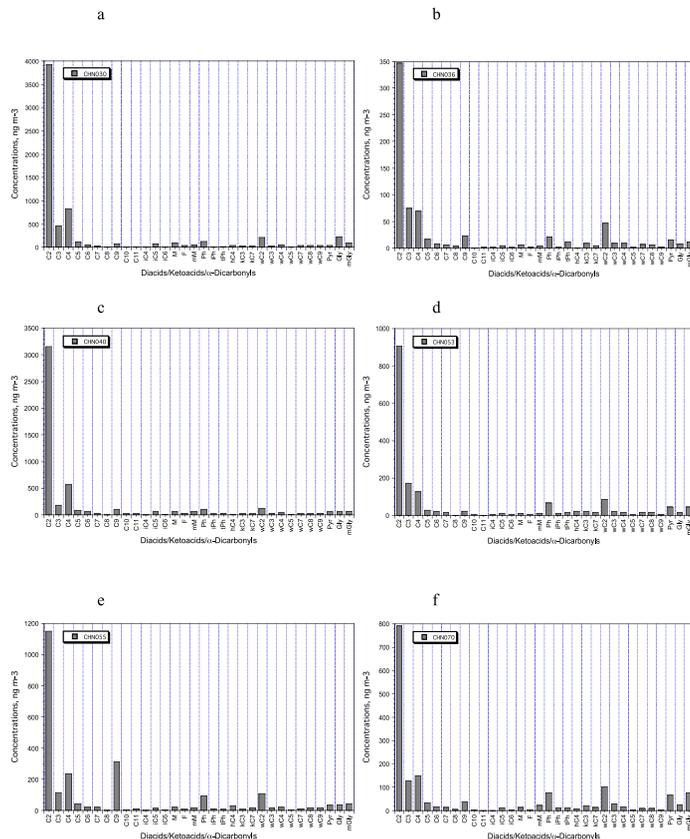


Fig. 6. Molecular distributions of dicarboxylic acids, ketocarboxylic acids and dicarbonyls detected in the selected atmospheric aerosol samples collected at the summit of Mt. Tai (**a**) Sample ID: CHN030 (sampling center time and date: 00:02, 7 June), (**b**) CHN036 (00:01, 10 June), (**c**) CHN040 (00:05, 13 June), (**d**) CHN053 (12:01, 20 June), (**e**) CHN055 (18:14, 21 June) and (**f**) CHN070 (13:30, 25 June).

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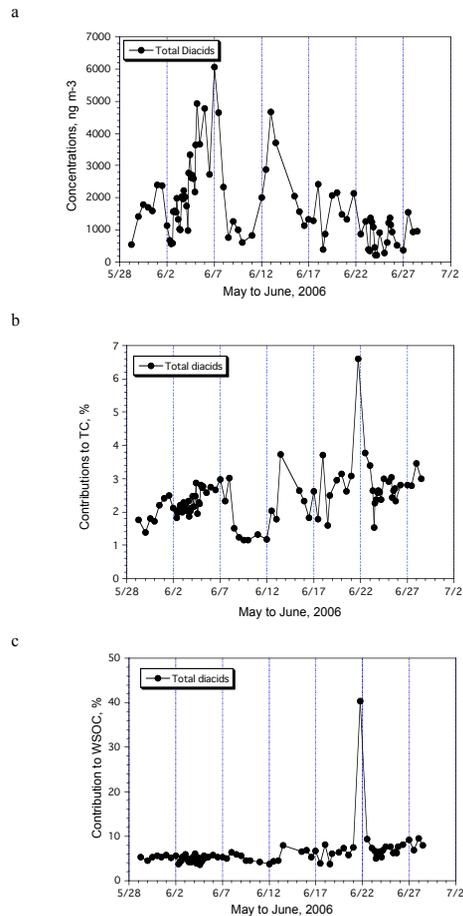


Fig. 7. Temporal variation of **(a)** total dicarboxylic acids (ng m^{-3}), **(b)** their contributions to TC (%), and **(c)** the contributions to WSOC (%) for the aerosol samples collected at Mt. Tai.

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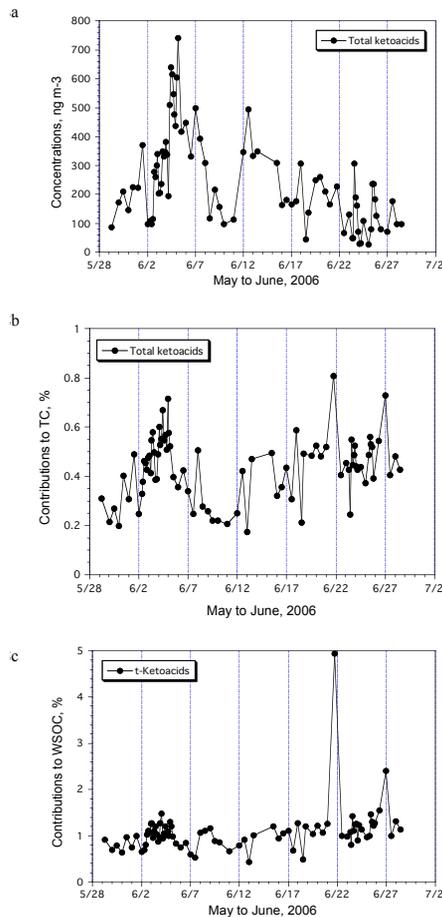


Fig. 8. Temporal variation of **(a)** total ketocarboxylic acids (ng m^{-3}), **(b)** their contributions to TC (%), and **(c)** the contributions to WSOC (%) for the aerosol samples collected at Mt. Tai.

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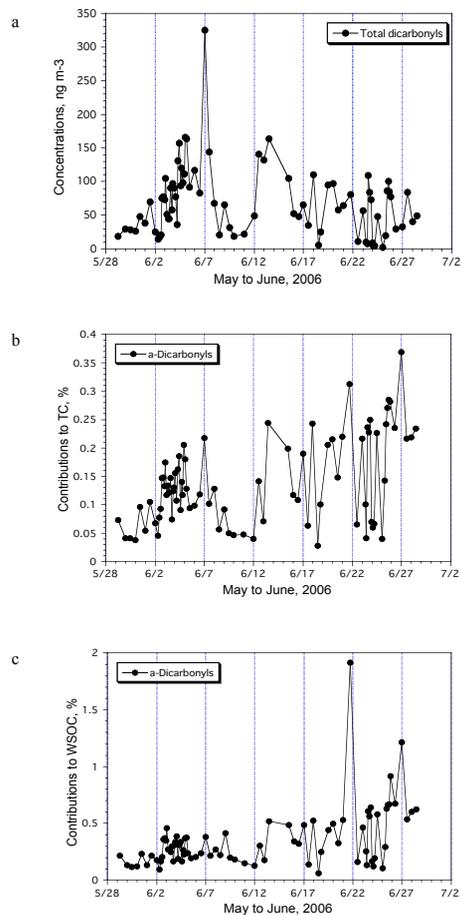


Fig. 9. Temporal variation of **(a)** total α -dicarbonyls (ng m⁻³), **(b)** their contributions to TC (%), and **(c)** the contributions to WSOC (%) for the aerosol samples collected at Mt. Tai.

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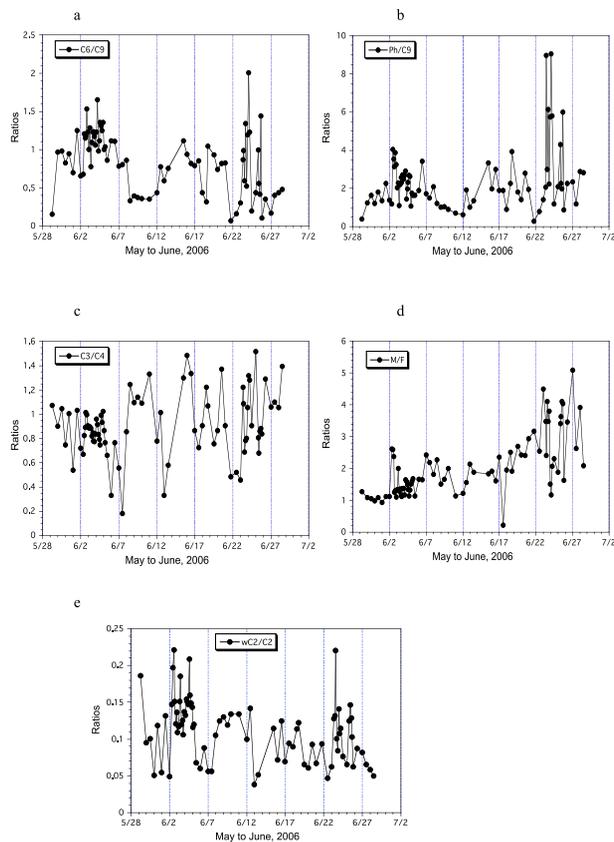


Fig. 10. Changes in concentration ratios of (a) adipic (C_6)/azelaic (C_9) acid ratios, (b) phthalic (Ph)/ C_9 acid ratios, (c) malonic (C_3)/succinic (C_4) acid ratios, (d) maleic (M)/fumaric (F) acid ratios, and (e) glyoxylic (wC_2)/oxalic (C_2) acid ratios in the Mt. Tai aerosols.

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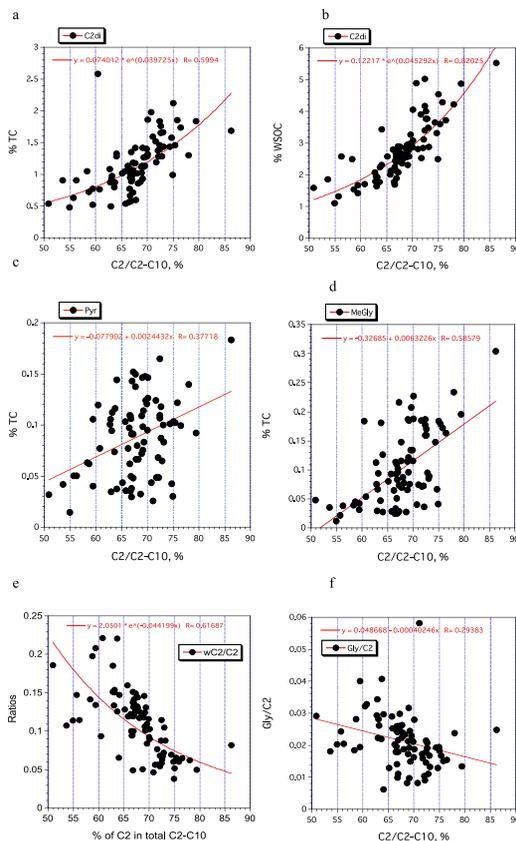


Fig. 11. Changes of contributions of **(a)** oxalic acid (C₂) to total carbon (TC), **(b)** C₂ to water-soluble organic carbon (WSOC), **(c)** pyruvic acid (Pyr) to TC, and **(d)** methylglyoxal (mGly) to TC, and of **(e)** glyoxylic acid (ω C₂)/oxalic (C₂) acid ratios and **(f)** glyoxal (Gly)/C₂ ratios as a function of relative abundance of C₂ in C₂-C₁₀ diacids in the Mt. Tai aerosols.