Atmospheric
Chemistry
and Physics
Discussions

1 **Molecular distribution and stable carbon isotopic compositions of**

2 **dicarboxylic acids and related SOA from biogenic sources in the**

3 **summertime atmosphere of Mt. Tai in the North China Plain**

4

5

6 Jingjing Meng[1,3], Gehui Wang[2,3,4*], Zhanfang Hou[1,3], Xiaodi Liu[1], Benjie Wei[1], Can Wu[3],

7 Cong Cao[3], Jiayuan Wang[3], Jianjun Li[3], Junji Cao[3], Erxun Zhang[1], Jie Dong[1], Jiazhen Liu[1]

8

9

10

11

12

13

14 [1] School of Environment and Planning, Liaocheng University, Liaocheng 252000, China

15 [2] Key Laboratory of Geographic Information Science of the Ministry of Education, School

16 of Geographic Sciences, East China Normal University, Shanghai 200062, China

17 [3] State Key Laboratory of Loess and Quaternary Geology, Key Lab of Aerosol Chemistry

18 and Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075,

19 China

20 [4] School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, Xi'an

21   710049, China

22

23 *Corresponding author: Prof. Gehui Wang

24 E-mail address: wanggh@ieecas.cn, or ghwang@geo.ecnu.edu.cn

25

26

27

Atmospheric
Chemistry
and Physics
Discussions

28   **Abstract**: Molecular distributions and stable carbon isotopic (δ^{13}C values) compositions of

29   dicarboxylic acids and related SOA in PM$_{2.5}$ aerosols collected on a day/night basis at the

30   summit of Mt. Tai (1534 m a.s.l) in the summer of 2016 were analyzed to investigate the

31   sources and photochemical aging process of organic aerosols in the forested highland region

32   of North China Plain. The molecular distributions of dicarboxylic acids and related SOA are

33   characterized by the dominance of oxalic acid (C$_2$), followed by malonic (C$_3$), succinic (C$_4$)

34   and azelaic (C$_9$) acids. The concentration ratios of C$_2$/C$_4$, diacid-C/OC and C$_2$/total diacids

35   are larger in daytime than in nighttime, suggesting that the daytime aerosols are more

36   photochemically aged than those in nighttime due to the higher temperatures and stronger

37   solar radiation. Both ratios of C$_2$/C$_4$ (R^2>0.5) and C$_3$/C$_4$ (R^2>0.5) correlated strongly with the

38   ambient temperature, indicating that SOA in the mountaintop atmosphere are mainly derived

39   from the photochemical oxidation of local emissions rather than long-range transport. The

40   mass ratios of C$_9$/C$_6$, C$_9$/Ph, Gly/mGly and the strong linear correlation of major

41   dicarboxylic acids and related SOA with biogenic precursors further suggest that aerosols in

42   this region are mainly originated from biogenic sources (i.e., tree emissions).

43   C$_2$ concentrations correlated well with aerosol pH, indicating that particle acidity favors

44   the organic acid formation. The stable carbon isotopic compositions (δ^{13}C) of the

45   dicarboxylic acids are higher in daytime than in nighttime with the highest value

46   (−16.5±1.9‰) found for C$_2$ and the lowest value (−25.2±2.7‰) found for C$_9$. An increase in

47   δ^{13}C values of C$_2$ along with increases in C$_2$/Gly and C$_2$/mGly ratios was observed, largely

48   due to the isotopic fractionation during photochemical degradation of the precursors.

49

50   **Keywords**: Dicarboxylic acids; Glyoxal and methylglyoxal; Secondary organic aerosols

51   (SOA); Biogenic sources; Formation mechanisms

52

53

54

55

56   **1. Introduction**

57   Secondary organic aerosols (SOA) accounts for a substantial fraction (20-90%) of the

58   total $PM_{2.5}$ mass in the troposphere, and up to 80% of which are water-soluble (Hallquist et

59   al., 2009; Kroll and Seinfeld, 2008). Due to the low vapor pressures and high hygroscopicity

60   (approximately less than 10^{-7} Pa) (Bilde et al., 2015; Ehn et al., 2014), dicarboxylic acids

61   and related compounds are ubiquitously found in atmospheric waters and particles

62   (Kawamura and Bikkina, 2016; Sorooshian et al., 2007a). Because of the water-soluble and

63   hygroscopic properties, dicarboxylic acids and related compounds play important roles in

64   atmospheric aqueous chemistry and influence radiative forcing of aerosols via acting as

65   cloud condensation nuclei (CCN) (Hoque et al., 2017; Wang et al., 2016; Zhang et al.,

66   2016).

67   Although they can be emitted directly from sources such as incomplete combustion of

68   fossil fuels (Kawamura and Kaplan, 1987) and biomass burning (Kawamura et al., 2013a, b;

69   Narukawa et al., 1999), atmospheric dicarboxylic acids and related compounds are largely

70   produced by photochemical oxidation of unsaturated fatty acids, PAHs (Kawamura et al.,

71   1996) , cyclic alkanes and other compounds (Kawamura and Usukura, 1993). Oxalic acid

72   (C_2) is the smallest and the most abundant dicarboxylic acid (Wang et al., 2009, 2015).

73   Modeling studies and cloud measurements have suggested that C_2 are largely produced from

74   aqueous-phase oxidation of less oxygenated organic precursors such as glyoxal (Gly),

75   methyglyoxal (mGly) and pyruvic acid (Pyr) in clouds or wet aerosols as well as the

76   photochemical breakdown of longer-chain dicarboxylic acids (Wang et al., 2012, 2015).

77   There is a growing consensus on highlighting the significance of oxalic acid and related

78   SOA formation from the photochemical oxidation of anthropogenic/biogenic volatile

79   organic compounds (VOCs) via the aqueous phase in clouds or liquid water content

80   (LWC)-enriched aerosols from many field observations and laboratory experiments as well

81   as modeling studies (Bikkina et al., 2017; Cheng et al., 2017; Ervens et al., 2014; Fu et al.,

82   2008; Lim et al., 2005; Miyazaki et al., 2009; Mochizuki et al., 2017). A ubiquitous layer of

83   dicarboxylic acids was found above the clouds by aircraft measurements in US, indicating

Atmospheric
Chemistry
and Physics
Discussions

84   that organic acids are important CCN in the free troposphere (Sorooshian et al., 2007a, b).

85   Compared to the aerosols in lowland areas, alpine aerosols have a more important influence

86   on cloud formation, because they are more accessible to clouds due to higher elevation. Mt.

87   Tai is an independent peak located in the center of the North China Plain (NCP), one of the

88   severest air- polluted regions in the world (Wang et al., 2009; Yang et al., 2017). A few

89   studies have been performed on the molecular distributions and sources of dicarboxylic

90   acids at Mt. Tai, but most of them were conducted during the wheat straw burning period

91   (Kawamura et al., 2013a, b; Zhu et al., 2018), and very few information on dicarboxylic

92   acids in Mt. Tai during July and August is available when biogenic activity of vegetation is

93   dominant. Therefore, it is necessary to investigate the chemistry of SOA during the typical

94   summer season in this highland area.

95   The stable carbon isotopic composition (δ^{13}C) of specific organic acids can provide

96   very useful information on the sources and photochemical aging of organic aerosols,

97   because the isotopic fractionation of carbon occurs upon chemical reactions or phase transfer

98   (Pavuluri and Kawamura, 2016; Zhang et al., 2016). To our best knowledge, the stable

99   carbon isotopic compositions of dicarboxylic acids and related SOA in mountainous regions

100   have not been reported before. In the current work, we first investigated the diurnal

101   variations in molecular distributions and stable carbon isotopic compositions of dicarboxylic

102   acids and related compounds. Then we discussed the impact of temperature (T), relative

103   humidity (RH), particle acidity (pH_{IS}), liquid water content (LWC) and O_3 concentration on

104   oxalic acid and related SOA to explore their sources and formation mechanism in the

105   forested highland of the North China Plain.

106   **2. Experimental section**

107   **2.1 Aerosol sampling**

108        $PM_{2.5}$ samples were collected at the Meteorological Observation Station of Mt. Tai,

109   which is located at the summit of Mt. Tai (36.25° N, 117.10°E; 1534 m a.s.l.) in the North

110   China Plain (Fig. 1). About 80% of the mountainous land is covered by vegetation known to

111   comprise 989 species, which is densely wooded in summer (Fu et al., 2010). $PM_{2.5}$ samples

Atmospheric
Chemistry
and Physics
Discussions

112   were collected from July 20 to August 20, 2016 each lasting for 12h on a day/night basis

113   using a mid-volume air sampler (KC-120H, Qingdao Laoshan Company, China) equipped

114   with prebaked (450°C, 8 h) quartz fiber filters (Whatman, USA) at an airflow rate of 100 L

115   min^{-1}. The daytime samples were collected from 8:00 to 20:00, while nighttime samples

116   were collected from 20:00 to 8:00 of the next day. Field blank samples were also collected

117   by mounting the blank filter onto the sampler for 15 min without sucking any air before and

118   after the campaign. A total of 57 samples (daytime: 28; nighttime: 29) were collected during

119   the campaign. After sampling, each filter was sealed in an aluminum foil bag and stored at

120   −20°C prior to laboratory analyses. Moreover, the concentration of ozone was

121   simultaneously monitored at the side by an UV absorption analyzer (Model 49C, Thermo

122   Electron Corporation).

123   **2.2 Chemical analyses**

124   **2.2.1 Dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls**

125   Dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in $PM_{2.5}$ were determined

126   using the method described by previous studies (Kawamura et al.,1996; Meng et al., 2013,

127   2014). Briefly, one half of the filter was cut into pieces and extracted with pure Milli-Q

128   water under ultrasonication for three times each for 15 min. The water extracts were

129   concentrated to near dryness and then reacted with 14% BF_3/n-butanol at 100°C for 1 hr to

130   form butyl esters/dibutoxy acetals. After derivatization, n-hexane was added and washed

131   with pure water for three times. Finally, the hexane layer was concentrated to 200 µL and

132   determined using a capillary gas chromatography (GC; HP 6890) coupled with a

133   split/splitless injector and a flame ionization detector (FID). The GC oven temperature was

134   programmed from 50 (2 min) to 120°C at 15°C min^{-1}, and then to 300 at 5°C min^{-1} with a

135   final isothermal hold at 300°C for 16 min. Peak identification was performed by comparing

136   the GC retention time with that of authentic standards and confirmed by mass spectrum of

137   the sample using a GC-mass spectrometer (GC-MS). Recoveries of the target compounds

138   were 80% for oxalic acid and 85% to 110% for other species. The target compounds in the

139   field blank samples were lower than 4% of those in the ambient samples. Data presented

140   here were corrected for both field blanks and recoveries.

2.2.2 Stable carbon isotope composition of dicarboxylic acids and related SOA

142   The stable carbon isotopic compositions (δ^{13}C) of shorter-chain dicarboxylic acids and

143   related SOA were measured using the method developed by Kawamura and Watanabe

144   (2004). Briefly, the δ^{13}C values of the derivatized samples above were determined by gas

145   chromatography–isotope ratio mass spectrometry (GC-IR-MS; Thermo Fisher, Delta V

146   Advantage). The δ^{13}C values were then calculated for free organic acids using an isotopic

147   mass balance equation based on the measured δ^{13}C values of derivatives and the derivatizing

148   agent (BF_3/n-butanol) (Kawamura and Watanabe, 2004). To ensure the analytical error of

149   the δ^{13}C values less than 0.2 ‰, each sample was measured three times. The δ^{13}C data

150   reported here are averaged values of the triplicate measurements.

2.2.3 Elemental carbon (EC), organic carbon (OC), inorganic ions, water-soluble

organic carbon (WSOC), aerosol liquid water content (LWC), and particle in-situ pH

(pH_{IS}).

154   Briefly, EC and OC in the $PM_{2.5}$ samples were determined by using DRI Model 2001

155   Carbon Analyzer following the Interagency Monitoring of Protected Visual Environments

156   (IMPROVE) thermal/optical reflectance (TOR) protocol (Chow et al., 2004). As for the

157   measurement of inorganic ions and WSOC, an aliquot of the sample filters was extracted

158   with 30 mL Milli-Q water using an ultrasonic bath for three times each for 15min, and

159   filtered through PTFE filters to remove the particles and filter debris. The water extract was

160   then separated into two parts. One part was analyzed for inorganic ions using an ion

161   chromatography (Dionex 600, Dionex, USA), and the other part of the water extract was

162   used to determine WSOC using a Total Carbon Analyzer (TOC-L CPH, Shimadzu, Japan).

163   As for the calculation of aerosol liquid water content (LWC) and particle in-situ pH (pH_{IS}),

164   the Aerosol Inorganic Model (AIM) using a SO_4^{2-}-NO_3^-- NH_4^+-H^+ system (AIM-II) were

165   employed (Li et al., 2013).

166

167   **3 Results and discussion**

168   **3.1 General description of chemical components in Mt. Tai**

169   The concentrations of dicarboxylic acids and related SOA, EC, OC, WSOC and

170   inorganic ions in $PM_{2.5}$ samples from Mt. Tai are summarized in Table 1. During the

171   campaign the height of boundary layer at Mt. Tai was frequently reduced to ~600 m at night,

172   which kept the sampling site in the free troposphere at night. In contrast, the boundary layer

173   extended far above the mountaintop during the daytime (Zhu et al., 2018). However, as a

174   tracer of combustion source, EC concentration is very low and shows a similar level in the

175   day and night periods, suggesting that the impact of anthropogenic emissions from the

176   lowland region on the mountaintop atmosphere is insignificant. OC and WSOC in the $PM_{2.5}$

177   samples are higher in daytime than in nighttime (Table 1), largely due to the stronger

178   photochemical oxidation in daytime rather than the changes in the boundary layer heights.

179   OC/EC and WSOC/OC ratios are around 1.4 times higher in daytime than in nighttime (Fig.

180   4), indicating an enhancing SOA production due to the daytime photochemical oxidation

181   (Hegde and Kawamura, 2012).

182   The meteorological conditions in daytime can promote the secondary aerosol formation,

183   resulting in higher concentration of SO_4^{2-} ($13 \pm 6.9 \mu g\ m^{-3}$, Table 1) compared to that ($9.6 \pm$

184   $3.7 \mu g\ m^{-3}$) in nighttime (Kundu et al., 2010a). On the contrary, NO_3^- concentration is higher

185   in the nighttime ($4.2 \pm 2.3 \mu g\ m^{-3}$, Table 1) than in the daytime ($3.0 \pm 2.1 \mu g\ m^{-3}$), which is

186   probably caused by the evaporative loss of NH_4NO_3 due to the higher daytime temperature

187   (Table 1) (Pathak et al., 2009). Consequently, the concentrations of NH_4^+ also present higher

188   values in nighttime ($6.6 \pm 2.5 \mu g\ m^{-3}$, Table 1) compared to that in daytime ($5.3 \pm 2.9 \mu g\ m^{-3}$).

189   As shown in Table 1, the remaining four kinds of cations (K^+, Na^+, Ca^{2+} and Mg^{2+}), which

190   can be regarded as the key markers of primary sources, did not exhibit significant diurnal

191   variations, again suggesting that the effect of boundary layer heights is minor. In this work,

192   LWC and pH_{IS} are calculated by using AIM-II model, because both species cannot be

193   directly measured. LWC exhibits higher concentrations ($94 \pm 100 \mu g\ m^{-3}$) in daytime than

194   that ($75 \pm 69 \mu g\ m^{-3}$) in nighttime (Table 1). In contrast, pH_{IS} shows lower values (-0.04 ± 0.5)

Atmospheric
Chemistry
and Physics
Discussions

195   in daytime compared to that (0.4 ± 0.6) in nighttime (Table 1), indicating the daytime

196   aerosols are more acidic.

197   **3.2 Molecular distributions of dicarboxylic acids and related SOA**

198   A homologous series of dicarboxylic acids (C_2–C_{11}), ketocarboxylic acids (ωC_2–ωC_9

199   and pyruvic acid), and α-dicarbonyls (glyoxal and methylglyoxal) in $PM_{2.5}$ samples of Mt.

200   Tai were determined (Table 2). The molecular compositions of these compounds are

201   illustrated in Fig. 2.

202   Total dicarboxylic acids are 430 ± 282ng m^{-3} (27–944 ng m^{-3}, Table 2) in daytime,

203   around two times higher than those in nighttime (282 ± 161 ng m^{-3}, 73–671ng m^{-3}). The

204   average concentration levels (354 ± 239 ng m^{-3}) are lower than those in Asian lowland (e.g.

205   14 Chinese cities (892 ± 457 ng m^{-3}) (Ho et al., 2007); Chennai in India (502.9 ± 117.9 ng

206   m^{-3}) (Pavuluri et al., 2010)) and elevated regions (e.g. Mt. Hua in central China (744 ± 340

207   ng m^{-3}) (Meng et al., 2014); the central Himalayan in Nainital, India (430 ng m^{-3}) (Hegde

208   and Kawamura, 2012)), but higher than those in the continental background area such as

209   Qinghai Lake in Tibetan Plateau (231 ± 119 ng m^{-3}) (Meng et al., 2013) and marine regions

210   such as North Pacific (68 ng m^{-3}) (Hoque et al., 2017) and the western North Pacific (99.2 ±

211   86.4 ng m^{-3}) (Boreddy et al., 2017).

212   Interestingly, we found that the levels of dicarboxylic acids are equivalent to those at

213   Mt. Fuji in Japan in day and night (day: 424 ng m^{-3}; night: 266 ng m^{-3}) (Mochizuki et al.,

214   2017), which are dominantly derived from the oxidation of biogenic VOCs such as isoprene

215   and α-pinene in summer. Both mountains are located at the similar latitude in East Asia, and

216   the altitudes of the sampling sites at Mt. Tai and Mt. Fuji are almost the same. Thus, one

217   may expect that the emissions of biogenic VOCs at both sites during the same season are

218   similar. Moreover, O_3 level during the observation period in Mt. Tai is also similar to that at

219   Mt. Fuji, Japan ranging from a few ppb at night to about 60 ppb (Mochizuki et al., 2017) at

220   the noontime, which means that photochemical activity at both sites during the campaigns

221   are similar. Therefore, concentrations of dicarboxylic acids are comparable at both sites with

222   a similar diurnal difference.

Atmospheric
Chemistry
and Physics
Discussions

223   At the Mt. Tai site, the concentrations of dicarboxylic acids in daytime were about two

224   times higher than in nighttime, which can be ascribed to the stronger photochemical

225   production of dicarboxylic acids and/or higher emissions of the precursors in daytime. As

226   shown in Fig. 2, oxalic acid (C_2) is the dominant species in Mt. Tai, followed by malonic

227   acid (C_3), succinic acid (C_4), and azelaic acid (C_9) during the day and night, respectively.

228   These four species account for 60, 12, 7.2, and 6.9% of the total dicarboxylic acids in the

229   daytime and 53, 11, 8.5, and 7.6 % of the total in the nighttime, respectively. The molecular

230   compositions in Mt. Tai is similar to that in other remote areas such as Mt. Fuji, Japan, Mt.

231   Hua and Qinghai Lake, China in the summer (Meng et al., 2013, 2014; Mochizuki et al.,

232   2017), but different from that in urban regions where phthalic and/or tere-phthalic acids are

233   more abundant than C_9 because of higher emissions of anthropogenic precursors (e.g.,

234   aromatics and plasticizers) (Cheng et al., 2015; He et al., 2014; Jung et al., 2010; Wang et al.,

235   2002, 2017).

236   Ketocarboxylic acids are the major intermediates of aqueous phase photochemical

237   oxidation producing dicarboxylic acids in the atmosphere (Kawamura and Ikushima, 1993;

238   Pavuluri and Kawamura, 2016), which are 43 ± 28 ng m^{-3} in the daytime and 37 ± 19 ng m^{-3}

239   in the nighttime, respectively, with glyoxylic acid (ωC_2) being the dominant ω-oxoacid,

240   followed by pyruvic acid (Pyr) and 3-oxobutanoic acid (ωC_3) (Table 2 and Fig. 2). Previous

241   studies have proposed that ωC_2 can be initially formed from photochemical oxidation of

242   glyoxal with OH radical and other oxidants in aqueous phase and then further oxidized into

243   oxalic acid (Rapf et al., 2017; Wang et al., 2012). In contrast to the diurnal variations of

244   dicarboxylic and ketocarboxylic acids, the concentrations of α-dicarbonyls exhibit higher

245   concentrations in nighttime than those in daytime (Fig. 2). Because α-dicarbonyls are the

246   major precursors produced from the photochemical oxidation of isoprene and other VOCs in

247   the atmosphere (Carlton et al., 2006, 2007), the opposite pattern suggests that the aerosol

248   aqueous phase oxidation in nighttime is impressed in comparison with that in daytime. The

249   concentrations of Gly are less than mGly, largely because of the stronger biogenic sources

Atmospheric
Chemistry
and Physics
Discussions

250   and the lower oxidation rate of mGly with OH radical in aerosol phase compared to Gly

251   (Cheng et al., 2013; Meng et al., 2013).

252   Temporal variations in concentrations of total dicarboxylic acids, ketocarboxylic acids

253   and α-dicarbonyls are illustrated in Fig. 3, along with the meteorological parameters. During

254   the whole sampling periods, the concentrations of total daicarboxylic acids and related SOA

255   fluctuated significantly with a maximum (1060 ng m^{-3}) on August 4 and a minimum (33 ng

256   m^{-3}) on August 7. Our results showed that the levels of water-soluble organic compounds

257   decrease by 30-80% when it was rainy, suggesting that dicarboxylic acids and related SOA

258   can be removed efficiently by the wet precipitation, because these water-soluble compounds

259   are not only easily washed out but also can be efficiently removed by serving as cloud

260   condensation nuclei (CCN) during the wet deposition (Leaitch et al., 1996). Moreover, a

261   reduced secondary formation due to weaker solar radiation and a reduced biogenic emission

262   during the rainy days are also responsible for the lowest concentrations of dicarboxylic acid

263   and related SOA.

264   **3.3 Biogenic versus anthropogenic and local versus long-range transport sources**

265   Previous studies have proposed that C_2, C_3 and C_4 are produced by the photochemical

266   degradation of longer-chain diacids, while C_3 is produced by photooxidation of C_4 in the

267   atmosphere (Hoque et al., 2017; Kawamura and Usukura, 1993; Kunwar et al., 2017).

268   Therefore, both ratios of C_2/C_4 and C_3/C_4 can be regarded as indicators of photochemical

269   aging of organic aerosols. The C_2/C_4 and C_3/C_4 ratios in the mountainous atmosphere are 8.0

270    $\pm$ 2.7 and 1.6 $\pm$ 0.6, respectively, higher than aerosols freshly emitted from sources such as

271   vehicle exhausts (C_2/C_4: 7.1; C_3/C_4: 1.3) (Ho et al., 2006) and biomass burning plumes

272   (C_2/C_4: 5.0; C_3/C_4: 0.7) (Kundu et al., 2010b), but lower than photochemically aged aerosols

273   in remote regions such as a continental background site in Tibet Plateau (C_2/C_4: 11$\pm$7.2;

274   C_3/C_4: 2.2$\pm$1.3) (Meng et al., 2013) and the North and South Pacific (C_2/C_4: 8.7; C_3/C_4:

275   3.0)(Hoque et al., 2017). Compared with those in the nighttime, the higher ratios of C_2/C_4

276   and C_3/C_4 (Fig. 4) in the daytime again indicate that the photochemical modification of

277   aerosols is stronger. A few studies have found that when local sources are dominant over

Atmospheric
Chemistry
and Physics
Discussions

278   long-range transport, both ratios of C_2/C_4 and C_3/C_4 would correlate strongly with the

279   ambient temperatures (Meng et al., 2013; Pavuluri et al., 2010). In the current work, the

280   ratios of C_2/C_4 ($R^2>0.5$) (Fig. 5a) and C_3/C_4 ($R^2\geq0.5$) (Fig. 5b) correlated well with the

281   ambient temperatures in both the daytime and the nighttime, clearly suggesting that

282   dicarboxylic acids and related SOA at the Mt. Tai during the campaign are mostly derived

283   from the local photochemical oxidation of BVOCs rather than long-range transport.

284   Aggarwal et al., (2008) found that diacid-C/OC and C_2/total diacids should increase in

285   daytime when local emission and photooxidation are more significant than long-range

286   transport. In the summit of Mt. Tai the daytime ratios of diacid-C/OC and C_2/total diacids

287   are $5.5 \pm 2.6\%$ and $60 \pm 7.7\%$, which are about 1.2 and 1.3 times higher than those in the

288   nighttime, respectively (Fig. 4), further indicating the stronger photochemical oxidation in

289   daytime and the dominance of local sources for the SOA production in the troposphere of

290   Mt. Tai.

291   Both ratios of C_9/C_6 and C_9/Ph can be used as indicators to qualitatively evaluate the

292   source strength of anthropogenic versus biogenic precursors for producing dicarboxylic

293   acids and related SOA (Jung et al., 2010), because C_6 and Ph are largely produced by the

294   oxidation of anthropogenic cyclohexene (Hatakeyama et al., 1987) and aromatic

295   hydrocarbons such as naphthalene (Kawamura and Ikushima, 1993), respectively. In

296   contrast, C_9 is mainly produced by the oxidation of biogenic unsaturated fatty acids

297   containing a double bond at the C-9 position (Wang et al., 2010). As shown in Fig. 4, both

298   ratios of C_9/C_6 and C_9/Ph are higher in the daytime than those in the nighttime, which is

299   mainly attributed to the stronger biogenic activity of vegetation in daytime in the mountain

300   regions. The average values of C_9/C_6 (14 ± 9.0) and C_9/Ph (7.2 ± 2.2) at the mountaintop of Mt.

301   Tai are higher than those in urban regions such as Xi'an China (C_9/C_6: 3.1; C_9/Ph:

302   5.6)(Cheng et al., 2013) and also higher than other mountainous in summer such as Mt.

303   Himalayan, India (C_9/C_6: 2.1; C_9/Ph: 0.2)(Hedge and Kawamura, 2012) and Mt. Fuji, Japan

304   (C_9/C_6: 3.1) (Mochizuki et al., 2017). Model simulation (Fu et al., 2008) and field

305   observations (Meng et al., 2014) have suggested that the concentration ratio of particulate

Atmospheric
Chemistry
and Physics
Discussions

306   Gly/mGly is about 1:5 when biogenic sources are predominant and is about 1:1 when

307   anthropogenic sources are predominant such as in urban areas. As shown in Table 3, the

308   ratios of Gly/mGly in the Mt. Tai atmosphere are 1:5.1 in daytime and 1:4.8 in nighttime,

309   further suggesting that Gly and mGly in the Mt. Tai samples are mostly derived from

310   biogenic sources. This result is in agreement with the high abundance of C_9 relative to the

311   total dicarboxylic acids (7.2%), which is about two times higher than that (3.5%) in 14

312   Chinese megacities in the summer (Ho et al., 2007). Moreover, a trace amount of elemental

313   carbon (EC) was found for most of the samples (Table 1), suggesting that the impact of

314   pollutants derived from anthropogenic sources on the mountaintop atmosphere during the

315   campaign are negligible. Consequently, it can be concluded that the summertime SOA of Mt.

316   Tai are mainly derived from local photochemical oxidation of biogenic precursors rather

317   than long-range transport of anthropogenic precursors during the sampling period.

318   **3.4 Production of dicarboxylic acids and related SOA from biogenic sources**

319   A three-dimensional modeling study has proposed that 79% of oxalic acid is originated

320   from the photochemical oxidation of isoprene and other biogenic hydrocarbons in cloud

321   (Myriokefalitakis et al., 2011). Laboratory experiments and model simulations have

322   demonstrated that the photooxidaltaion of isoprene (Carlton et al., 2006, 2007; Huang et al.,

323   2011) and monoterpenes (Fick et al., 2003; Lee et al., 2006) can produce Gly and mGly via

324   reactions with OH radical and/or O_3 in the aerosol aqueous phase or the gas phase and

325   subsequently partition into cloud droplets, where both carbonyls are oxidized further by OH

326   radical to form oxalic acid (Lim et al., 2005; Tan et al., 2010).

327   In order to further ascertain the contribution of BVOCs to dicarboxylic acids and

328   related SOA during the high biological activity period in Mt. Tai, SOA tracers derived from

329   isoprene-, α-/β-pinene- and β-caryophyllene in the $PM_{2.5}$ samples collected at the Mt. Tai

330   site were determined. Their total concentrations (the sum of isoprene+ pinene+

331   caryophyllene derived SOA tracers) are 1.3 times higher in the daytime (106 ± 56 ng m^{-3})

332   than those in the nighttime (79 ± 38 ng m^{-3}) (unpublished data), which is consistent with the

333   diurnal variation patterns of dicarboxylic acids, ketocarboxylic acids and WSOC (Tables 1

Atmospheric
Chemistry
and Physics
Discussions

334   and 2). Previous studies reported that 2-methylglyceric acid, which is an isoprene oxidation

335   product, and 3-hydroxyglutaric acid, which is α-/β-pinene oxidation product, can serve as

336   organic precursors for the production of dicarboxylic acids and ketocarboxylic acids (Fu et

337   al., 2013). As shown in Table 4, major dicarboxylic acids and related SOA (e.g. C_2, C_2, Gly

338   and mGly) correlated positively with isoprene oxidation products during daytime and

339   nighttime ($R>0.60$, $P<0.01$), indicating that isoprene oxidation products can serve as

340   precursors for the production of oxalic acid via α-dicaronyls oxidation (Myriokefalitakis et

341   al., 2011). Moreover, both α-/β-pinene and caryophyllene oxidation products also presented

342   strong correlations with dicarboxylic acids and related SOA ($R>0.55$, $P<0.01$) (Table 4),

343   further highlighting the important contribution of BSOA to dicarboxylic acids and related

344   SOA in Mt. Tai during summer.

345   **3.5 Effects of temperature, relative humidity, and O_3 concentrations on the formation**

346   **of oxalic acid and related SOA**

347   Because oxidants such as OH radicals were not measured in Mt. Tai, O_3 is considered

348   here as an indicator of the total oxidant concentrations in this study. A significant linear

349   correlation of oxalic acid with O_3 concentrations is observed for the daytime samples

350   ($R^2=0.91$), but no correlation ($R^2=0.05$) was found for the nighttime samples (Fig.6a). Such a

351   phenomenon was also observed in Mt. Fuji, Japan (Mochizuki et al., 2017) and Beijing,

352   China (He et al., 2014). Additionally, C_2/ Gly, C_2/ mGly and C_2/total diacids ratios correlate

353   positively with O_3 concentrations in the daytime, but such correlations were not found in the

354   nighttime (Fig 8(a-c)). Mochizuki et al. (2017) have reported a robust correlation between

355   concentration ratios of oxalic acid to isoprene plus α-pinene (oxalic

356   acid/(isoprene+α-pinene)) and O_3 concentrations in a large forest region of Mt. Fuji, Japan

357   in the daytime. In the curren work, BSOA tracers correlate strongly with O_3 concentrations

358   in the daytime ($R>0.6$, $P<0.01$), but no correlation was found at night (Table 4). These

359   results suggest that the daytime oxalic acid and related SOA in the mountaintop of Mt. Tai

360   are largely derived from O_3 oxidation of BVOCs such as isoprene and α-pinene, while the

Atmospheric
Chemistry
and Physics
Discussions

361   nighttime oxalic acid and related SOA might be primarily produced by NO_3 radical and

362   other oxidizing agents such as H_2O_2 (Claeys et al., 2004; Herrmann et al., 1999).

363   As shown in Table 4, nearly all of the detected BSOA tracers including

364   2-methylglyceric acid, 3-hydorxyglutaric acid and β-caryophyllinic acid exhibit a strong

365   correlation with the ambient temperature, largely due to the increased production of BSOA

366   from enhanced emissions of BVOCs under the higher temperature conditions. The BSOA

367   tracer concentrations are higher in daytime than in nighttime, largely due to more abundant

368   BVOC emissions because of stronger biogenic activity of vegetation during the daytime. In

369   addition, oxalic acid and C_2/total diacids ratios correlated strongly with temperatures (Fig.6b

370   and Fig.8f), because higher temperature conditions can promote photochemical formation of

371   oxalic acid. Such a temperature dependence is also observed in other regions such as Mt.

372   Hua (Meng et al., 2014) and Beijing (Wang et al., 2017) in China.

373   Online measurements, field observations and chamber studies (Cheng et al., 2017; Gao

374   et al., 2004; McNeill, 2015; Meng et al., 2014; Wang et al., 2012, 2017) have suggested that

375   oxalic acid is primarily derived from the acid-catalyzed heterogeneous oxidation of glyoxal

376   and related precursors in the aqueous phase. Here we investigate the impact of LWC and

377   pH_{IS} on the formation of oxalic acid in Mt. Tai aerosols. As shown in Fig.6c, a strong linger

378   correlation between C_2 and SO_4^{2-} was found for the daytime (R^2=0.89) and nighttime

379   (R^2=0.76) samples, respectively, which is consistent with the measurements observed in

380   other mountainous region (Meng et al., 2014) and Chinese cities (Wang et al., 2002, 2010,

381   2012, 2017; Yu et al., 2005), indicating that oxalic acid and sulfate are formed via a similar

382   formation pathway such as in-cloud or aqueous-phase (Warneck, 2003). In this study, oxalic

383   acid does not exhibit correlations with relative humidity (RH) and LWC (Fig.6d and 6e), but

384   presents a significant negative correlation with pH_{IS} (R^2>0.60) (Fig.6f), largely due to the

385   fact that acidic conditions can promote the formation of oxalic acid and their precursors.

386   Therefore, a robust negative correlation was obtained for pH_{IS} and the precursors of oxalic

387   acid such as Gly, mGly and ωC_2 (R^2>0.50). A few studies have pointed out that aerosol

388   acidity are favorable for the formation of biogenic SOA (BSOA) derived from isoprene

Atmospheric
Chemistry
and Physics
Discussions

389   oxidation such as 2-methylglyceric acid, which can be oxidized into Gly and mGly and then

390   converted to oxalic acid (Meng et al., 2014; Surratt et al., 2007, 2010). Our previous studies

391   have revealed that enhanced RH can reduce particle acidity (pH$_{IS}$) and is thus unfavorable

392   for oxalic acid formation by acid-catalyzed reactions occurring in the aerosol aqueous phase

393   (Li et al., 2013, 2018; Meng et al., 2014). RH is a key factor controlling the aerosol LWC

394   (Bikkina et al., 2017). Deshmukh et al. (2017) and Bikkina et al. (2017) also found that RH

395   and LWC correlated well with oxalic acid, indicating that humid conditions are favorable for

396   the aqueous phase formation of C$_2$. Nevertheless, Zhang et al. (2011) pointed out that low

397   RH conditions can promote SOA yields via the oxidation of isoprene. Higher RH and LWC

398   can promote the partitioning of water-soluble semivolatile organic precursors of oxalic acid

399   (e.g., Gly and mGly) into the aerosol aqueous phase but can also suppress acid-catalyzed

400   formation of oxalic acid because of lower aerosol acidity due to dilution. Therefore, C$_2$ does

401   not present any correlations with RH or LWC in Mt. Tai.

402   **3.6 Stable carbon isotopic composition of oxalic acid and related SOA**

403   To further understand the formation mechanism of C$_2$ and related SOA, the stable

404   isotopic composition of major dicarboxylic acids and related SOA in the Mt. Tai aerosols

405   were investigated (Table 5). Generally, an increase in δ^{13}C values was observed with a

406   decrease in carbon numbers of dicarboxylic acids. The averaged δ^{13}C value (daytime:

407   −15.8±1.9‰; nighttime: −17.2±1.7‰) of C$_2$ is higher than other dicarboxylic acid and

408   related SOA in the Mt. Tai atmosphere, and also higher than those observed in the urban

409   regions such as Xi'an, China (−22.7‰ to −22.0‰) (Wang et al., 2012) and Sapporo, Japan

410   (18.8±2.0‰) (Aggarwal and Kawamura, 2008) and the rural regions such as Morogoro,

411   Tanzania (18.3±1.7‰) (Mkoma et al., 2014), but lower than those (11.5±2.8‰) (Zhang et

412   al., 2016) at a background supersite (the Korea Climate Observatory at Gosan) in East Asia

413   during the summer. Pavuluri et al. (2016) have reported that the average δ^{13}C values of C$_2$

414   from biogenic aerosols are higher than those from anthropogenic aerosols. The relatively

415   higher δ^{13}C values of C$_2$ observed in Mt. Tai further demonstrate that the contribution of

416   biogenic sources to C$_2$ and related SOA is more significant than anthropogenic sources,

Atmospheric
Chemistry
and Physics
Discussions

417   which is consistent with our discussion above. The average $\delta^{13}C$ values of C_4 are more

418   negative than C_2 and C_3 (Fig. 7). Such a phenomenon is also observed in other regions

419   (Aggarwal and Kawamura, 2008; Wang et al., 2012; Zhang et al., 2016). Photochemical

420   decomposition (or breakdown) of longer-chain diacarboxylic acids (e.g. C_3 or C_4) in aerosol

421   aqueous phase can form C_2 (Wang et al., 2017), during which C_3 or C_4 release CO_2/CO by

422   reaction with OH radical and other oxidants, resulting in C_2 more enriched in ^{13}C due to

423   kinetic isotope effects (KIE) (Wang et al., 2012). The ^{13}C enrichment in C_2 is more

424   distinguished in daytime than in nighttime (Table 5 and Fig. 7), largely due to the enhanced

425   photochemical oxidation. However, such diurnal variation was not found for C_3 and C_4.

426   ωC_2 is an important intermediate of aqueous phase photochemical oxidation of

427   precursors such as Gly, mGly, and Pyr during the C_2 formation process (Carlton et al., 2006;

428   Fu et al., 2008; Wang et al., 2012). Thus, the mass ratios of $C_2/\omega C_2$, C_2/Gly and $C_2/mGly$ are

429   indicative of organic aerosol aging (Wang et al., 2017). As shown in Fig. 8(g-i), $\delta^{13}C$ values

430   of C_2 correlate robustly with C_2/Gly, $C_2/mGly$, and $C_2/total$ diacids, suggesting an

431   enrichment of ^{13}C during the organic aerosol ageing process. During the campaign, ωC_2 is

432   less enriched in ^{13}C in comparison with Gly, mGly, and Pyr, because lighter isotope (^{12}C) is

433   preferentially enriched in the products due to KIEs during the aqueous phase irreversible

434   chemical reactions (Wang et al., 2012). As one of the major precursors of Gly, isoprene

435   emitted directly from vegetation is depleted in ^{13}C with a range from $-32‰$ to $-27‰$ (Affek

436   and Yakir, 2003), but during the transport process isoprene could gradually be enriched with

437   ^{13}C ($\delta^{13}C$ value$=-16.8‰$) due to isotope fractionation associated with the reaction with OH

438   radical (Rudolph et al., 2003). Moreover, chamber experiments have pointed out that

439   β-pinene is preferably enriched with ^{13}C during its ozonolysis due to KIE (Fisseha et al.,

440   2009). Therefore, the relatively higher values of Gly and mGly can be attributed to the

441   secondary formation from the oxidation of isoprene and other biogenic precursors with

442   stronger enrichment of ^{13}C.

443   **4. Summary and conclusions**

444   PM$_{2.5}$ aerosols from the summit of Mt. Tai (15340 m a.s.l) in the North China Plain

445   during the summer of 2016 were analyzed for dicarboxylic acids, ketocarboxylic acids,

446   α-dicarbonyls, EC, OC and WSOC. Molecular compositions of dicarboxylic acids and

447   related compounds in the forested highland are similar to those on the ground surface and

448   other mountainous regions. The concentrations of total dicarboxylic acids and

449   ketocarboxylic acids are higher in daytime than those in daytime, but α-dicarbonyls presents

450   lower values in daytime, suggesting the mountainous atmospheric environment is more

451   photochemically aged in daytime than in nighttime. The concentrations of oxalic acid and

452   BSOA traces and the mass ratios of C$_2$/Gly, C$_2$/mGly, and C$_2$/total diacids correlate

453   positively with O$_3$ concentrations in the daytime during the campaign, but such correlations

454   were not found at night, suggesting that in the mountaintop atmosphere O$_3$ oxidation is the

455   major formation pathway of oxalic acid and related SOA in daytime. Moreover, C$_2$, C$_2$/total

456   diacids ratios and BSOA tracers correlate strongly with temperatures, because higher

457   temperature conditions can enhance the emissions of BVOCs and further promote the

458   photochemical formation of C$_2$. C$_2$ has a robust correlation with pH$_{IS}$ and SO$_4^{2-}$ during the

459   whole sampling period, indicating that acidic conditions can favor the formation of oxalic

460   acid in aqueous phase.

461   A significant enrichment of ^{13}C in dicarboxylic aicds was observed as a function of

462   their carbon number. The observed larger δ^{13}C values of lower carbon numbered

463   dicarboxylic acids can be explained by isotopic fractionations resulting from the

464   atmospheric decomposition of relatively longer chain-diacids or their precursors. Increased

465   δ^{13}C values of C$_2$ relative to C$_2$/Gly and C$_2$/mGly ratios also suggested an important effect

466   of photochemical aging on the stable carbon isotopic composition of dicarboxylic acids.

467

468   **Acknowledgements**

Atmospheric
Chemistry
and Physics
Discussions

476   **References**

477   Affek, H. P., and Yakir, D.: Natural Abundance Carbon Isotope Composition of Isoprene Reflects Incomplete
478   Coupling between Isoprene Synthesis and Photosynthetic Carbon Flow, Plant Physiology, 131, 1727,
479   2003.
480   Aggarwal, S. G., and Kawamura, K.: Molecular distributions and stable carbon isotopic compositions of
481   dicarboxylic acids and related compounds in aerosols from Sapporo, Japan: Implications for
482   photochemical aging during long-range atmospheric transport, J. Geophys. Res., 113, D14301,
483   10.1029/2007jd009365, 2008.
484   Bikkina, S., Kawamura, K., and Sarin, M.: Secondary Organic Aerosol Formation over Coastal Ocean:
485   Inferences from Atmospheric Water-Soluble Low Molecular Weight Organic Compounds, Environmental
486   Science & Technology, 51, 4347-4357, 10.1021/acs.est.6b05986, 2017.
487   Bilde, M., Barsanti, K., Booth, M., Cappa, C. D., Donahue, N. M., Emanuelsson, E. U., McFiggans, G.,
488   Krieger, U. K., Marcolli, C., Topping, D., Ziemann, P., Barley, M., Clegg, S., Dennis-Smither, B.,
489   Hallquist, M., Hallquist, Å. M., Khlystov, A., Kulmala, M., Mogensen, D., Percival, C. J., Pope, F., Reid,
490   J. P., Ribeiro da Silva, M. A. V., Rosenoern, T., Salo, K., Soonsin, V. P., Yli-Juuti, T., Prisle, N. L.,
491   Pagels, J., Rarey, J., Zardini, A. A., and Riipinen, I.: Saturation Vapor Pressures and Transition Enthalpies
492   of Low-Volatility Organic Molecules of Atmospheric Relevance: From Dicarboxylic Acids to Complex
493   Mixtures, Chemical Reviews, 115, 4115-4156, 10.1021/cr5005502, 2015.
494   Boreddy, S. K. R., Kawamura, K., and Tachibana, E.: Long-term (2001–2013) observations of water-soluble
495   dicarboxylic acids and related compounds over the western North Pacific: trends, seasonality and source
496   apportionment, Scientific Reports, 7, 8518, 10.1038/s41598-017-08745-w, 2017.
497   Carlton, A. G., Turpin, B. J., Lim, H.-J., Altieri, K. E., and Seitzinger, S.: Link between isoprene and
498   secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds,
499   Geophysical Research Letters, 33, L06822, 10.1029/2005gl025374, 2006.
500   Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H.-J., and Ervens, B.: Atmospheric
501   oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments,
502   Atmospheric Environment, 41, 7588-7602, http://dx.doi.org/10.1016/j.atmosenv.2007.05.035, 2007.
503   Cheng, C., Wang, G., Zhou, B., Meng, J., Li, J., Cao, J., and Xiao, S.: Comparison of dicarboxylic acids and
504   related compounds in aerosol samples collected in Xi'an, China during haze and clean periods,
505   Atmospheric Environment, 81, 443-449, http://dx.doi.org/10.1016/j.atmosenv.2013.09.013, 2013.
506   Cheng, C., Wang, G., Meng, J., Wang, Q., Cao, J., Li, J., and Wang, J.: Size-resolved airborne particulate
507   oxalic and related secondary organic aerosol species in the urban atmosphere of Chengdu, China,
508   Atmospheric Research, 161–162, 134-142, http://dx.doi.org/10.1016/j.atmosres.2015.04.010, 2015.
509   Cheng, C., Li, M., Chan, C. K., Tong, H., Chen, C., Chen, D., Wu, D., Li, L., Wu, C., Cheng, P., Gao, W.,
510   Huang, Z., Li, X., Zhang, Z., Fu, Z., Bi, Y., and Zhou, Z.: Mixing state of oxalic acid containing particles
511   in the rural area of Pearl River Delta, China: implications for the formation mechanism of oxalic acid,
512   Atmos. Chem. Phys., 17, 9519-9533, 10.5194/acp-17-9519-2017, 2017.

Atmospheric
Chemistry
and Physics
Discussions

513   Chow, J. C., Watson, J. G., Chen, L. W. A., Arnott, W. P., Moosmüller, H., and Fung, K.: Equivalence of
514   Elemental Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature
515   Protocols, Environmental Science & Technology, 38, 4414-4422, 10.1021/es034936u, 2004.
516   Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae,
517   M. O., Artaxo, P., and Maenhaut, W.: Formation of Secondary Organic Aerosols Through Photooxidation
518   of Isoprene, Science, 303, 1173-1176, 10.1126/science.1092805, 2004.
519   Deshmukh, D. K., Kawamura, K., Deb, M. K., and Boreddy, S. K. R.: Sources and formation processes of
520   water-soluble dicarboxylic acids, ω-oxocarboxylic acids, α-dicarbonyls, and major ions in summer
521   aerosols from eastern central India, Journal of Geophysical Research: Atmospheres, 122, 3630-3652,
522   10.1002/2016jd026246, 2017.
523   Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann,
524   R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S.,
525   Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G.,
526   Canagaratna, M., Maso, M. D., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V.-M., Kulmala, M.,
527   Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol,
528   Nature, 506, 476, 10.1038/nature13032, 2014.
529   Ervens, B., Sorooshian, A., Lim, Y. B., and Turpin, B. J.: Key parameters controlling OH-initiated formation
530   of secondary organic aerosol in the aqueous phase (aqSOA), Journal of Geophysical Research:
531   Atmospheres, 119, 3997-4016, 10.1002/2013jd021021, 2014.
532   Fick, J., Pommer, L., Nilsson, C., and Andersson, B.: Effect of OH radicals, relative humidity, and time on the
533   composition of the products formed in the ozonolysis of α-pinene, Atmospheric Environment, 37,
534   4087-4096, https://doi.org/10.1016/S1352-2310(03)00522-3, 2003.
535   Fisseha, R., Spahn, H., Wegener, R., Hohaus, T., Brasse, G., Wissel, H., Tillmann, R., Wahner, A., Koppmann,
536   R., and Kiendler-Scharr, A.: Stable carbon isotope composition of secondary organic aerosol from
537   β-pinene oxidation, Journal of Geophysical Research: Atmospheres, 114, n/a-n/a, 10.1029/2008jd011326,
538   2009.
539   Fu, P., Kawamura, K., Kanaya, Y., and Wang, Z.: Contributions of biogenic volatile organic compounds to the
540   formation of secondary organic aerosols over Mt. Tai, Central East China, Atmospheric Environment, 44,
541   4817-4826, http://dx.doi.org/10.1016/j.atmosenv.2010.08.040, 2010.
542   Fu, P., Kawamura, K., Usukura, K., and Miura, K.: Dicarboxylic acids, ketocarboxylic acids and glyoxal in the
543   marine aerosols collected during a round-the-world cruise, Marine Chemistry, 148, 22-32,
544   http://dx.doi.org/10.1016/j.marchem.2012.11.002, 2013.
545   Fu, T.-M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global budgets of
546   atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, J.
547   Geophys. Res., 113, D15303, 10.1029/2007jd009505, 2008.
548   Gao, S., Ng, N. L., Keywood, M., Varutbangkul, V., Bahreini, R., Nenes, A., He, J., Yoo, K. Y., Beauchamp, J.
549   L., Hodyss, R. P., Flagan, R. C., and Seinfeld, J. H.: Particle Phase Acidity and Oligomer Formation in
550   Secondary Organic Aerosol, Environmental Science & Technology, 38, 6582-6589, 10.1021/es049125k,
551   2004.
552   Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue,
553   N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M.,
554   Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod,

Atmospheric
Chemistry
and Physics
Discussions

555 A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties
556 and impact of secondary organic aerosol: current and emerging issues, Atmospheric Chemistry and
557 Physics, 9, 5155-5236, 2009.
558 Hatakeyama, S., Ohno, M., Weng, J., Takagi, H., and Akimoto, H.: Mechanism for the formation of gaseous
559 and particulate products from ozone-cycloalkene reactions in air, Environmental Science & Technology,
560 21, 52-57, 10.1021/es00155a005, 1987.
561 He, N., Kawamura, K., Okuzawa, K., Pochanart, P., Liu, Y., Kanaya, Y., and Wang, Z. F.: Diurnal and
562 temporal variations of water-soluble dicarboxylic acids and related compounds in aerosols from the
563 northern vicinity of Beijing: Implication for photochemical aging during atmospheric transport, Science of
564 The Total Environment, 499, 154-165, http://dx.doi.org/10.1016/j.scitotenv.2014.08.050, 2014.
565 Hegde, P., and Kawamura, K.: Seasonal variations of water-soluble organic carbon, dicarboxylic acids,
566 ketocarboxylic acids, and α-dicarbonyls in Central Himalayan aerosols, Atmos. Chem. Phys., 12,
567 6645-6665, 10.5194/acp-12-6645-2012, 2012.
568 Herrmann, H., Ervens, B., Nowacki, P., Wolke, R., and Zellner, R.: A chemical aqueous phase radical
569 mechanism for tropospheric chemistry, Chemosphere, 38, 1223-1232,
570 https://doi.org/10.1016/S0045-6535(98)00520-7, 1999.
571 Ho, K. F., Lee, S. C., Cao, J. J., Kawamura, K., Watanabe, T., Cheng, Y., and Chow, J. C.: Dicarboxylic acids,
572 ketocarboxylic acids and dicarbonyls in the urban roadside area of Hong Kong, Atmospheric Environment,
573 40, 3030-3040, http://dx.doi.org/10.1016/j.atmosenv.2005.11.069, 2006.
574 Ho, K. F., Cao, J. J., Lee, S. C., Kawamura, K., Zhang, R. J., Chow, J. C., and Watson, J. G.: Dicarboxylic
575 acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China, Journal of Geophysical
576 Research: Atmospheres, 112, D22S27, 10.1029/2006jd008011, 2007.
577 Hoque, M. M. M., Kawamura, K., and Uematsu, M.: Spatio-temporal distributions of dicarboxylic acids,
578 ω-oxocarboxylic acids, pyruvic acid, α-dicarbonyls and fatty acids in the marine aerosols from the North
579 and South Pacific, Atmospheric Research, 185, 158-168, http://dx.doi.org/10.1016/j.atmosres.2016.10.022,
580 2017.
581 Huang, D., Zhang, X., Chen, Z. M., Zhao, Y., and Shen, X. L.: The kinetics and mechanism of an aqueous
582 phase isoprene reaction with hydroxyl radical, Atmos. Chem. Phys., 11, 7399-7415,
583 10.5194/acp-11-7399-2011, 2011.
584 Jung, J., Tsatsral, B., Kim, Y. J., and Kawamura, K.: Organic and inorganic aerosol compositions in
585 Ulaanbaatar, Mongolia, during the cold winter of 2007 to 2008: Dicarboxylic acids, ketocarboxylic acids,
586 and α-dicarbonyls, Journal of Geophysical Research: Atmospheres, 115, D22203, 10.1029/2010jd014339,
587 2010.
588 Kawamura, K., and Kaplan, I. R.: Motor exhaust emissions as a primary source for dicarboxylic acids in Los
589 Angeles ambient air, Environmental Science & Technology, 21, 105-110, 10.1021/es00155a014, 1987.
590 Kawamura, K., and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban
591 atmosphere, Environmental Science & Technology, 27, 2227-2235, 10.1021/es00047a033, 1993.
592 Kawamura, K., and Usukura, K.: Distributions of low molecular weight dicarboxylic acids in the North Pacific
593 aerosol samples, Journal of Oceanography, 49, 271-283, 10.1007/bf02269565, 1993.
594 Kawamura, K., Kasukabe, H., and Barrie, L. A.: Source and reaction pathways of dicarboxylic acids, ketoacids
595 and dicarbonyls in arctic aerosols: One year of observations, Atmospheric Environment, 30, 1709-1722,
596 http://dx.doi.org/10.1016/1352-2310(95)00395-9, 1996.

Atmospheric
Chemistry
and Physics
Discussions

597 Kawamura, K., and Watanabe, T.: Determination of Stable Carbon Isotopic Compositions of Low Molecular
598   Weight Dicarboxylic Acids and Ketocarboxylic Acids in Atmospheric Aerosol and Snow Samples,
599   Analytical Chemistry, 76, 5762-5768, 10.1021/ac049491m, 2004.
600 Kawamura, K., Okuzawa, K., Aggarwal, S. G., Irie, H., Kanaya, Y., and Wang, Z.: Determination of gaseous
601   and particulate carbonyls (glycolaldehyde, hydroxyacetone, glyoxal, methylglyoxal, nonanal and decanal)
602   in the atmosphere at Mt. Tai, Atmos. Chem. Phys., 13, 5369-5380, 10.5194/acp-13-5369-2013, 2013a.
603 Kawamura, K., Tachibana, E., Okuzawa, K., Aggarwal, S. G., Kanaya, Y., and Wang, Z. F.: High abundances
604   of water-soluble dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in the mountain aerosols over
605   the North China Plain during wheat burning season, Atmos. Chem. Phys. , 13, 3695-3734,
606   10.5194/acpd-13-3695-2013, 2013b.
607 Kawamura, K., and Bikkina, S.: A review of dicarboxylic acids and related compounds in atmospheric aerosols:
608   Molecular distributions, sources and transformation, Atmospheric Research, 170, 140-160,
609   http://dx.doi.org/10.1016/j.atmosres.2015.11.018, 2016.
610 Kroll, J. H., and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of
611   low-volatility organics in the atmosphere, Atmospheric Environment, 42, 3593-3624,
612   https://doi.org/10.1016/j.atmosenv.2008.01.003, 2008.
613 Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: Diurnal variation in the
614   water-soluble inorganic ions, organic carbon and isotopic compositions of total carbon and nitrogen in
615   biomass burning aerosols from the LBA-SMOCC campaign in Rondônia, Brazil, Journal of Aerosol
616   Science, 41, 118-133, http://dx.doi.org/10.1016/j.jaerosci.2009.08.006, 2010a.
617 Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: Molecular distributions of
618   dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in biomass burning aerosols:
619   implications for photochemical production and degradation in smoke layers, Atmos. Chem. Phys., 10,
620   2209-2225, 10.5194/acp-10-2209-2010, 2010b.
621 Kunwar, B., Torii, K., and Kawamura, K.: Springtime influences of Asian outflow and photochemistry on the
622   distributions of diacids, oxoacids and α-dicarbonyls in the aerosols from the western North Pacific Rim,
623   Tellus B: Chemical and Physical Meteorology, 69, 1369341, 10.1080/16000889.2017.1369341, 2017.
624 Leaitch, W. R., Li, S. M., Liu, P. S. K., Banic, C. M., Macdonald, A. M., Isaac, G. A., Couture, M. D., and
625   Strapp, J. W.: Relationships among ccn, aerosol size distribution and ion chemistry from airborne
626   measurements over the bay of fundy in august-september, 1995 A2 - Kulmala, Markku, in: Nucleation
627   and Atmospheric Aerosols 1996, edited by: Wagner, P. E., Pergamon, Amsterdam, 840-843, 1996.
628 Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.:
629   Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes,
630   Journal of Geophysical Research: Atmospheres, 111, n/a-n/a, 10.1029/2006jd007050, 2006.
631 Li, J. J., Wang, G. H., Cao, J. J., Wang, X. M., and Zhang, R. J.: Observation of biogenic secondary organic
632   aerosols in the atmosphere of a mountain site in central China: temperature and relative humidity effects,
633   Atmos. Chem. Phys., 13, 11535-11549, 10.5194/acp-13-11535-2013, 2013.
634 Li, J., Wang, G., Wu, C., Cao, C., Ren, Y., Wang, J., Li, J., Cao, J.-j., Zeng, L., and Zhu, T.: Characterization
635   of isoprene-derived secondary organic aerosols at a rural site in North China Plain with implications for
636   anthropogenic pollution effects, Scientific Reports, 8, 535, DOI: 510.1038/s41598-41017-18983-41597,
637   2018.

638   Lim, H.-J., Carlton, A. G., and Turpin, B. J.: Isoprene Forms Secondary Organic Aerosol through Cloud
639   Processing: Model Simulations, Environmental Science & Technology, 39, 4441-4446,
640   10.1021/es048039h, 2005.
641   McNeill, V. F.: Aqueous Organic Chemistry in the Atmosphere: Sources and Chemical Processing of Organic
642   Aerosols, Environmental Science & Technology, 49, 1237-1244, 10.1021/es5043707, 2015.
643   Meng, J., Wang, G., Li, J., Cheng, C., and Cao, J.: Atmospheric oxalic acid and related secondary organic
644   aerosols in Qinghai Lake, a continental background site in Tibet Plateau, Atmospheric Environment, 79,
645   582-589, http://dx.doi.org/10.1016/j.atmosenv.2013.07.024, 2013.
646   Meng, J., Wang, G., Li, J., Cheng, C., Ren, Y., Huang, Y., Cheng, Y., Cao, J., and Zhang, T.: Seasonal
647   characteristics of oxalic acid and related SOA in the free troposphere of Mt. Hua, central China:
648   Implications for sources and formation mechanisms, Science of The Total Environment, 493, 1088-1097,
649   http://dx.doi.org/10.1016/j.scitotenv.2014.04.086, 2014.
650   Miyazaki, Y., Aggarwal, S. G., Singh, K., Gupta, P. K., and Kawamura, K.: Dicarboxylic acids and
651   water-soluble organic carbon in aerosols in New Delhi, India, in winter: Characteristics and formation
652   processes, Journal of Geophysical Research: Atmospheres, 114, D19206, 10.1029/2009jd011790, 2009.
653   Mkoma, S. L., Kawamura, K., and Tachibana, E.: Stable carbon isotopic compositions of
654   low-molecular-weight dicarboxylic acids, glyoxylic acid and glyoxal in tropical aerosols: implications for
655   photochemical processes of organic aerosols, Tellus B: Chemical and Physical Meteorology, 66, 23702,
656   10.3402/tellusb.v66.23702, 2014.
657   Mochizuki, T., Kawamura, K., Miyazaki, Y., Wada, R., Takahashi, Y., Saigusa, N., and Tani, A.: Secondary
658   formation of oxalic acid and related organic species from biogenic sources in a larch forest at the northern
659   slope of Mt. Fuji, Atmospheric Environment, 166, 255-262,
660   https://doi.org/10.1016/j.atmosenv.2017.07.028, 2017.
661   Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K., Segers, A., and
662   Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D modeling study, Atmos.
663   Chem. Phys., 11, 5761-5782, 10.5194/acp-11-5761-2011, 2011.
664   Narukawa, M., Kawamura, K., Takeuchi, N., and Nakajima, T.: Distribution of dicarboxylic acids and carbon
665   isotopic compositions in aerosols from 1997 Indonesian forest fires, Geophysical Research Letters, 26,
666   3101-3104, 10.1029/1999gl010810, 1999.
667   Pathak, R. K., Wu, W. S., and Wang, T.: Summertime PM2.5 ionic species in four major cities of China:
668   nitrate formation in an ammonia-deficient atmosphere, Atmos. Chem. Phys., 9, 1711-1722,
669   10.5194/acp-9-1711-2009, 2009.
670   Pavuluri, C. M., Kawamura, K., and Swaminathan, T.: Water-soluble organic carbon, dicarboxylic acids,
671   ketoacids, and α-dicarbonyls in the tropical Indian aerosols, Journal of Geophysical Research:
672   Atmospheres, 115, D11302, 10.1029/2009jd012661, 2010.
673   Pavuluri, C. M., and Kawamura, K.: Enrichment of (13)C in diacids and related compounds during
674   photochemical processing of aqueous aerosols: New proxy for organic aerosols aging, Scientific Reports,
675   6, 36467, 10.1038/srep36467, 2016.
676   Rapf, R. J., Dooley, M. R., Kappes, K., Perkins, R. J., and Vaida, V.: pH Dependence of the Aqueous
677   Photochemistry of α-Keto Acids, The Journal of Physical Chemistry A, 121, 8368-8379,
678   10.1021/acs.jpca.7b08192, 2017.

Atmospheric
Chemistry
and Physics
Discussions

679   Rudolph, J., Anderson, R. S., Czapiewski, K. V., Czuba, E., Ernst, D., Gillespie, T., Huang, L., Rigby, C., and
680   Thompson, A. E.: The Stable Carbon Isotope Ratio of Biogenic Emissions of Isoprene and the Potential
681   Use of Stable Isotope Ratio Measurements to Study Photochemical Processing of Isoprene in the
682   Atmosphere, Journal of Atmospheric Chemistry, 44, 39-55, 10.1023/a:1022116304550, 2003.
683   Sorooshian, A., Lu, M.-L., Brechtel, F. J., Jonsson, H., Feingold, G., Flagan, R. C., and Seinfeld, J. H.: On the
684   Source of Organic Acid Aerosol Layers above Clouds, Environmental Science & Technology, 41,
685   4647-4654, 10.1021/es0630442, 2007a.
686   Sorooshian, A., Ng, N. L., Chan, A. W. H., Feingold, G., Flagan, R. C., and Seinfeld, J. H.: Particulate organic
687   acids and overall water-soluble aerosol composition measurements from the 2006 Gulf of Mexico
688   Atmospheric Composition and Climate Study (GoMACCS), J. Geophys. Res., 112, D13201,
689   10.1029/2007jd008537, 2007b.
690   Surratt, J. D., Lewandowski, M., Offenberg, J. H., Jaoui, M., Kleindienst, T. E., Edney, E. O., and Seinfeld, J.
691   H.: Effect of Acidity on Secondary Organic Aerosol Formation from Isoprene, Environmental Science &
692   Technology, 41, 5363-5369, 10.1021/es0704176, 2007.
693   Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R.
694   C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol
695   formation from isoprene, Proceedings of the National Academy of Sciences, 107, 6640-6645,
696   10.1073/pnas.0911114107, 2010.
697   Tan, Y., Carlton, A. G., Seitzinger, S. P., and Turpin, B. J.: SOA from methylglyoxal in clouds and wet
698   aerosols: Measurement and prediction of key products, Atmospheric Environment, 44, 5218-5226,
699   http://dx.doi.org/10.1016/j.atmosenv.2010.08.045, 2010.
700   Wang, G., Kawamura, K., Umemoto, N., Xie, M., Hu, S., and Wang, Z.: Water-soluble organic compounds in
701   PM2.5 and size-segregated aerosols over Mount Tai in North China Plain, Journal of Geophysical
702   Research: Atmospheres, 114, D19208, 10.1029/2008jd011390, 2009.
703   Wang, G., Xie, M., Hu, S., Gao, S., Tachibana, E., and Kawamura, K.: Dicarboxylic acids, metals and isotopic
704   compositions of C and N in atmospheric aerosols from inland China: implications for dust and coal
705   burning emission and secondary aerosol formation, Atmos. Chem. Phys., 10, 6087-6096,
706   10.5194/acp-10-6087-2010, 2010.
707   Wang, G., Kawamura, K., Cheng, C., Li, J., Cao, J., Zhang, R., Zhang, T., Liu, S., and Zhao, Z.: Molecular
708   Distribution and Stable Carbon Isotopic Composition of Dicarboxylic Acids, Ketocarboxylic Acids, and
709   α-Dicarbonyls in Size-Resolved Atmospheric Particles From Xi'an City, China, Environmental Science &
710   Technology, 46, 4783-4791, 10.1021/es204322c, 2012.
711   Wang, G., Cheng, C., Meng, J., Huang, Y., Li, J., and Ren, Y.: Field observation on secondary organic aerosols
712   during Asian dust storm periods: Formation mechanism of oxalic acid and related compounds on dust
713   surface, Atmospheric Environment, 113, 169-176, http://dx.doi.org/10.1016/j.atmosenv.2015.05.013,
714   2015.
715   Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J.,
716   Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P.,
717   Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y.,
718   Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P. S.,
719   Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese

720   haze, Proceedings of the National Academy of Sciences, 113, 13630-13635, 10.1073/pnas.1616540113,
721   2016.
722   Wang, G. H., Niu, S. L., Liu, C., and Wang, L. S.: Identification of dicarboxylic acids and aldehydes of PM10
723   and PM2.5 aerosols in Nanjing, China, Atmospheric Environment, 36(12), 1941-1950, 2002.
724   Wang, J., Wang, G., Gao, J., Wang, H., Ren, Y., Li, J., Zhou, B., Wu, C., Zhang, L., Wang, S., and Chai, F.:
725   Concentrations and stable carbon isotope compositions of oxalic acid and related SOA in Beijing before,
726   during, and after the 2014 APEC, Atmos. Chem. Phys., 17, 981-992, 10.5194/acp-17-981-2017, 2017.
727   Warneck, P.: In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere,
728   Atmospheric Environment, 37, 2423-2427, http://dx.doi.org/10.1016/S1352-2310(03)00136-5, 2003.
729   Yang, X., Xue, L., Yao, L., Li, Q., Wen, L., Zhu, Y., Chen, T., Wang, X., Yang, L., Wang, T., Lee, S., Chen, J.,
730   and Wang, W.: Carbonyl compounds at Mount Tai in the North China Plain: Characteristics, sources, and
731   effects on ozone formation, Atmospheric Research, 196, 53-61,
732   https://doi.org/10.1016/j.atmosres.2017.06.005, 2017.
733   Yu, J. Z., Huang, X.-F., Xu, J., and Hu, M.: When Aerosol Sulfate Goes Up, So Does Oxalate: Implication for
734   the Formation Mechanisms of Oxalate, Environmental Science & Technology, 39, 128-133,
735   10.1021/es049559f, 2005.
736   Zhang, H., Surratt, J. D., Lin, Y. H., Bapat, J., and Kamens, R. M.: Effect of relative humidity on SOA
737   formation from isoprene/NO photooxidation: enhancement of 2-methylglyceric acid and its corresponding
738   oligoesters under dry conditions, Atmos. Chem. Phys., 11, 6411-6424, 10.5194/acp-11-6411-2011, 2011.
739   Zhang, Y.-L., Kawamura, K., Cao, F., and Lee, M.: Stable carbon isotopic compositions of
740   low-molecular-weight dicarboxylic acids, oxocarboxylic acids, α-dicarbonyls, and fatty acids:
741   Implications for atmospheric processing of organic aerosols, Journal of Geophysical Research:
742   Atmospheres, 121, 3707-3717, 10.1002/2015jd024081, 2016.
743   Zhu, Y., Yang, L., Chen, J., Kawamura, K., Sato, M., Tilgner, A., van Pinxteren, D., Chen, Y., Xue, L., Wang,
744   X., Herrmann, H., and Wang, W.: Molecular distributions of dicarboxylic acids, oxocarboxylic acids, and
745   α-dicarbonyls in PM2.5 collected at Mt. Tai, in North China in 2014, Atmos. Chem. Phys. Discuss., 2018,
746   1-31, 10.5194/acp-2017-1240, 2018.
747
748
749

Atmospheric
Chemistry
and Physics
Discussions

750   Table 1. Meteorological parameters and concentrations of inorganic ions, ozone, water
751   soluble organic carbon (WSOC), organic carbon (OC), elemental carbon (EC), liquid water
752   content (LWC), and in-situ pH (pH_{IS}) of $PM_{2.5}$ from Mt. Tai in the summer.

	Daytime (n=28)	Nighttime (n=29)	Total (n=57)
I. Meteorological parameters and ozone			
Temperature (°C)	23 ± 2.9 (17–28)	19 ± 2.9 (12–25)	21 ± 3.6 (12–28)
Relative humidity (%)	92 ± 5.0 (80–98)	77 ± 8.2 (65–193)	84 ± 9.9 (65–98)
O_3 (ppb)	32 ± 16 (7.8–61)	22 ± 12 (6.0–48)	27 ± 15 (6.0–61)
II. Inorganic ions (µg m^{-3})			
K^+	0.4 ± 0.2 (0.1–0.8)	0.4 ± 0.2 (0.1–0.7)	0.4 ± 0.2 (0.1–0.8)
Na^+	0.3 ± 0.1 (0.1–0.9)	0.3 ± 0.2 (0.1–1.0)	0.3 ± 0.2 (0.1–1.0)
NH_4^+	5.3 ± 2.9 (0.5–12)	6.6 ± 2.5 (1.2–11)	5.9 ± 2.8 (0.5–12)
Mg^{2+}	0.2 ± 0.1 (0–0.3)	0.2 ± 0.1 (0.1–0.3)	0.2 ± 0.1 (0–0.3)
Ca^{2+}	0.3 ± 0.1 (0–0.5)	0.3 ± 0.2 (0.1–0.7)	0.3 ± 0.2 (0–0.7)
NO_3^-	3.0 ± 2.1 (0.1–8.4)	4.2 ± 2.3 (0.9–10)	3.6 ± 2.3 (0.1–10)
SO_4^{2-}	13 ± 6.9 (3.0–33)	9.6 ± 3.7 (2.9–18)	12 ± 5.8 (2.9–33)
Subtotal	23 ± 12 (4.6–54)	22 ± 8.2 (6.6–40)	22 ± 10 (4.6–54)
III. Other species (µg m^{-3})			
EC	0.2 ± 0.2 (0–0.6)	0.2 ± 0.2 (0–0.8)	0.2 ± 0.2 (0–0.8)
OC	2.4 ± 0.8 (1.1–3.9)	2.1 ± 0.3 (1.5–2.8)	2.2 ± 0.6 (1.1–3.9)
WSOC	1.9 ± 0.8 (0.8–3.6)	1.4 ± 0.5 (0.7–2.3)	1.7 ± 0.7 (0.7–3.6)
pH_{IS}	-0.04 ± 0.5 (-0.9–1.0)	0.4 ± 0.6 (-1.0–1.2)	0.2 ± 0.6 (-1.0–1.2)
LWC	94 ± 100 (10–313)	75 ± 69 (6.3–199)	84 ± 86 (6.3–313)
$PM_{2.5}$	38 ± 19 (6.1–83)	36 ± 14 (11–66)	37 ± 16 (6.1–83)

753
754
755

756   Table 2. Concentrations (ng m^{-3}) of dicarboxylic acids, ketocarboxylic acids and
757   α-dicarbonyls of PM$_{2.5}$ from Mt. Tai in the summer.

Compounds	Daytime (n=28)	Nighttime (n=29)	Total (n=57)
I. Dicarboxylic acids			
Oxalic, C_2	272± 190 (11–623)	156 ± 105 (34–415)	213 ± 162 (11–623)
Malonic, C_3	49 ± 30 (4.0–101)	31 ±17 (7.4–69)	40 ± 26 (4.0–101)
Succinic, C_4	30 ± 23 (2.0–83)	24 ± 16 (4.7–67)	27 ± 20 (2.0–83)
Glutaric, C_5	7.0 ± 5.5 (0.4–19)	5.6 ± 3.9 (1.1–14)	6.3 ± 4.8 (0.4–19)
Adipic, C_6	2.2 ± 1.7 (0.1–5.6)	2.2 ± 1.8 (0.2–7.7)	2.2 ± 1.7 (0.1–7.7)
Pimelic, C_7	3.0 ±1.9 (0.3–7.3)	2.9 ± 1.3 (0.3–6.1)	3.0 ± 1.6 (0.3–7.3)
Suberic, C_8	4.3 ± 2.2 (0.9–9.0)	3.8 ± 2.8 (0.4–13)	4.0 ± 2.5 (0.4–13)
Azelaic, C_9	24 ± 14 (4.2–55)	19 ± 8.6 (4.5–41)	22 ± 12 (4.2–55)
Sebacic, C_{10}	5.9 ± 4.3 (0.1–14)	5.6 ± 2.7 (0.7–11)	5.8 ± 3.6 (0.1–14)
Undecanedioic, C_{11}	2.4 ± 1.7 (0.2–5.8)	1.1 ± 0.8 (0–3.8)	1.7 ± 1.4 (0–5.8)
Methylmalonic, iC_4	2.1 ±1.7 (0.1–5.2)	2.1 ± 1.5 (0–5.3)	2.1 ± 1.6 (0–5.3)
Mehtylsuccinic, iC_5	2.7 ± 2.0 (0.1–7.1)	2.2 ± 1.7 (0.2–6.1)	2.4 ± 1.8 (0.1–7.1)
Methyglutaric, iC_6	2.6 ± 2.1 (0.5–9.1)	2.3 ± 1.9 (0–9.0)	2.5 ± 2.0 (0–9.1)
Maleic, M	2.0 ±1.2 (0.1–4.3)	3.0 ± 2.0 (0.7–8.2)	2.5 ± 1.7 (0.1–8.2)
Fumaric, F	4.2 ± 2.7 (0.2–9.4)	4.0 ± 3.0 (0.5–13)	4.1 ± 2.8 (0.2–13)
Methylmaleic, mM	2.9 ± 1.7 (0.1–6.6)	2.7 ± 2.1 (0.5–9.9)	2.8 ± 1.9 (0.1–9.9)
Phthalic, Ph	3.0 ± 1.5 (0.6–5.6)	3.3 ± 2.3 (0.7–11.2)	3.2 ± 1.9 (0.6–11.2)
Isophthalic, iPh	1.6 ± 1.0 (0.1–3.3)	1.3 ± 0.8 (0.2–3.5)	1.4 ± 0.9 (0.1–3.5)
Terephthalic, tPh	1.9 ± 1.3 (0.1–5.0)	2.4 ±1.5 (0.1–6.1)	2.2 ± 1.4 (0.1–6.1)
Ketomalonic, kC_3	2.6 ± 1.5 (0–5.8)	2.7 ± 1.5 (0.5–6.4)	2.7 ± 1.5 (0–6.4)
Ketopimelic, kC_7	3.6 ± 2.8 (0.2–9.3)	3.9 ± 2.6 (0.2–12)	3.7 ± 2.7 (0.2–12)
Subtotal	430 ± 282 (27–944)	282 ± 161 (73–671)	354 ± 239 (27–944)
II. Ketocarboxylic acids			
Pyruvic, Pyr	14 ± 8.8 (1.4–28)	11 ± 5.5 (2.2–23)	12 ± 7.4 (1.4–28)
Glyoxylic, ωC_2	18 ± 12 (0.9–38)	15 ± 9.5 (3.5–35)	16 ± 11(0.9–38)
3-Oxopropanoic, ωC_3	4.0 ± 2.7 (0.1–7.7)	4.1 ± 2.2 (0.5–8.3)	4.1 ± 2.4 (0.1–8.3)
4-Oxobutanoic, ωC_4	2.9 ± 1.9 (0.2–6.8)	2.5 ± 1.7 (0.6–7.1)	2.7 ± 1.8 (0.2–7.1)
7-Oxoheptanoic, $\omega C7$	1.0 ±0.6 (0–2.7)	1.3 ± 1.0 (0.1–4.8)	1.2 ± 0.9 (0.0–4.8)
8-Oxooctanoic, ωC_8	1.5 ± 0.9 (0.1–3.3)	1.5 ± 0.7 (0.2–3.4)	1.5 ± 0.8 (0.1–3.4)
9-Oxononanoic, ωC_9	2.0 ± 1.4 (0.1–4.4)	1.8 ± 1.1 (0.2–4.3)	1.9 ± 1.3 (0.1–4.4)
Subtotal	43 ± 28 (2.9–88)	37 ± 19 (7.6–77)	40 ± 24 (2.9–88)
III. α-Dicarbonyls			
Glyoxal, Gly	3.1 ± 1.8 (0.3–6.0)	4.6 ± 2.6 (0.4–12)	3.8 ± 2.3 (0.3–12)
Methyglyoxal, mGly	16 ± 9.5 (1.8–33)	22 ± 15 (1.4–62)	19 ± 13 (1.4–62)
Subtotal	19 ± 11 (2.6–39)	27 ± 17 (2.1–69)	23 ± 15 (2.1–69)
Total detected	491 ± 320 (33–1060)	346 ± 194 (96–807)	417 ± 271 (33–1060)

758

759 Table 3. Concentrations of α-dicarbonyls in PM$_{2.5}$ from Mt. Tai and Mt. Hua in China and
760 the global budgets of atmospheric Gly and mGly.

Site	Sources/Season	Abundance		Mass ratio
		Gly	mGly	Gly/mGly
Global budget (Tg a^{-1})	Biogenic	22.8[a]	113.5[a]	1:5
	Anthropogenic	22.2[a]	26.5[a]	1:1
Mt. Hua (ngm^{-3})	Biogenic, Summer	2.3[b]	10[b]	1:4.4
	Anthropogenic, Winter	8.8[b]	1.3[b]	1:1.5
Mt. Tai (ngm^{-3}, this study)	Summer, Daytime	3.1	15.8	1:5.1
	Summer, Nighttime	4.6	22.1	1:4.8

761 Note: [a] Data are calculated from Fu et al., 2008;
762 [b] Data are cited from Meng et al., 2014.
763

764 Table 4. Correlation coefficients (*R*) matrix among major low molecular weight dicarboxylic
765 acids and related SOA, BSOA tracers, temperature (T), and O$_3$ concentrations in Mt. Tai
766 during the summer campaign.

	C$_2$	C$_3$	C$_4$	ωC$_2$	Pyr	Gly	mGly	O$_3$	T
(a) Daytime									
2-methylglyceric acid	0.98[a]	0.96[a]	0.86[a]	0.95[a]	0.73[a]	0.96[a]	0.94[a]	0.92[a]	0.85[a]
2-methylthreitol	0.83[a]	0.80[a]	0.64[a]	0.74[a]	0.77[a]	0.77[a]	0.82[a]	0.85[a]	0.72[a]
2-methylerthritol	0.84[a]	0.87[a]	0.70[a]	0.78[a]	0.83[a]	0.83[a]	0.84[a]	0.80[a]	0.71[a]
cis-pinonic acid	0.83[a]	0.75[a]	0.73[a]	0.75[a]	0.74[a]	0.71[a]	0.77[a]	0.80[a]	0.72[a]
3-hydroxyglutaric acid	0.81[a]	0.76[a]	0.69[a]	0.74[a]	0.78[a]	0.74[a]	0.73[a]	0.73[a]	0.75[a]
MBTCA	0.84[a]	0.77[a]	0.83[a]	0.82[a]	0.75[a]	0.74[a]	0.77[a]	0.82[a]	0.67[a]
β-Caryophyllinic acid	0.75[a]	0.70[a]	0.79[a]	0.70[a]	0.70[a]	0.71[a]	0.72[a]	0.65[a]	0.57[a]
(b) Nighttime									
2-methylglyceric acid	0.87[a]	0.72[a]	0.74[a]	0.70[a]	0.64[a]	0.44[b]	0.51[a]	0.09	0.59[a]
2-methylthreitol	0.81[a]	0.71[a]	0.58[a]	0.71[a]	0.66[a]	0.60[a]	0.47[b]	0.05[a]	0.65[a]
2-methylerthritol	0.83[a]	0.72[a]	0.62[a]	0.79[a]	0.73[a]	0.67[a]	0.61[a]	0.23	0.74[a]
cis-pinonic acid	0.83[a]	0.65[a]	0.57[a]	0.75[a]	0.61[a]	0.56[a]	0.54[a]	0.22	0.63[a]
3-hydroxyglutaric acid	0.79[a]	0.62[a]	0.69[a]	0.71[a]	0.60[a]	0.58[a]	0.50[a]	0.43[b]	0.62[a]
MBTCA[c]	0.82[a]	0.80[a]	0.78[a]	0.73[a]	0.75[a]	0.61[a]	0.55[a]	0.30	0.60[a]
β-caryophyllinic acid	0.68[a]	0.74[a]	0.61[a]	0.73[a]	0.71[a]	0.73[a]	0.58[a]	0.32[a]	0.53[a]

767 [a] *P*<0.01; [b] *P*<0.05.
768 [c] MBTCA: 3-Methyl-1,2,3-butanetricarboxylic acid.
769
770
771
772
773

774 Table 5. Stable carbon isotopic compositions ($\delta^{13}C$, ‰) of major dicarboxylic acids and
775 related SOA in $PM_{2.5}$ of Mt. Tai in the North China Plain.

| Compounds	Daytime (n=28)	Nighttime (n=29)	Total (n=57)
I. Dicarboxylic acids			
Oxalic, C_2	−15.8±1.9 (−19.4 to −13.0)	−17.2±1.7 (−20.1 to −12.1)	−16.5±1.9 (−20.1 to −12.1)
Malonic, C_3	−19.1±2.3 (−23.8 to−15.9)	−18.5±1.8 (−21.1 to−15.3)	−18.8±2.0 (−23.8 to−15.3)
Succinic, C_4	−22.0±2.3 (−25.6 to−18.5)	−21.4±2.2 (−24.6 to −18.4)	−21.7±2.2 (−25.6 to −18.4)
Adipic, C_6	−23.7±2.5 (−27.3 to −19.9)	−24.8±2.4 (−27.9 to −21.4)	−24.2±2.5 (−27.9 to −19.9)
Azelaic, C_9	−24.7±2.6 (−28.7 to−21.0)	−25.7±2.7 (−30.3 to−21.9)	−25.2±2.7 (−30.3 to −21.0)
Phthalic, Ph	−24.3±2.5 (−28.1 to−20.6)	−25.2±2.6 (−29.2 to−20.9)	−24.8±2.5 (−29.2 to −20.6)
II. Ketocarboxylic acids			
Pyruvic, Pyr	−19.4±2.1 (−23.1 to −16.5)	−21.2±2.2 (−24.5 to −17.8)	−20.3±2.3 (−24.5 to −16.5)
Glyoxylic, ωC_2	−18.6.8±1.9 (−21.5 to −15.6)	−20.2±2.1 (−23.1 to−16.9)	−19.4±2.2 (−23.1 to−15.6)
3-Oxopropanoic, ωC_3	−20.2±2.1 (−23.5 to−17.0)	−24.0±2.5 (−27.7 to − 20.8)	−22.2±3.0 (−27.7 to−17.0)
III. α-Dicarbonyls			
Glyoxal, Gly	−16.7±1.7 (−19.4 to−14.0)	−18.1±1.8(−21.3 to −15.2)	−17.4±1.9 (−21.3 to −14.0)
Methyglyoxal, mGly	−17.9±1.8 (−21.0 to−15.0)	−19.6±2.0 (−22.5 to−16.5)	−18.8±2.1 (−22.5 to−15.0)

776

777
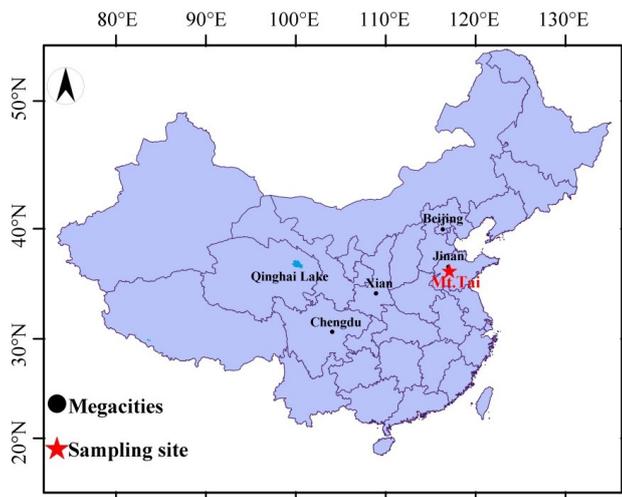
779   Fig.1. Location of the sampling site (Mt. Tai; 36.25° N, 117.10°E; 1534 m a.s.l.).
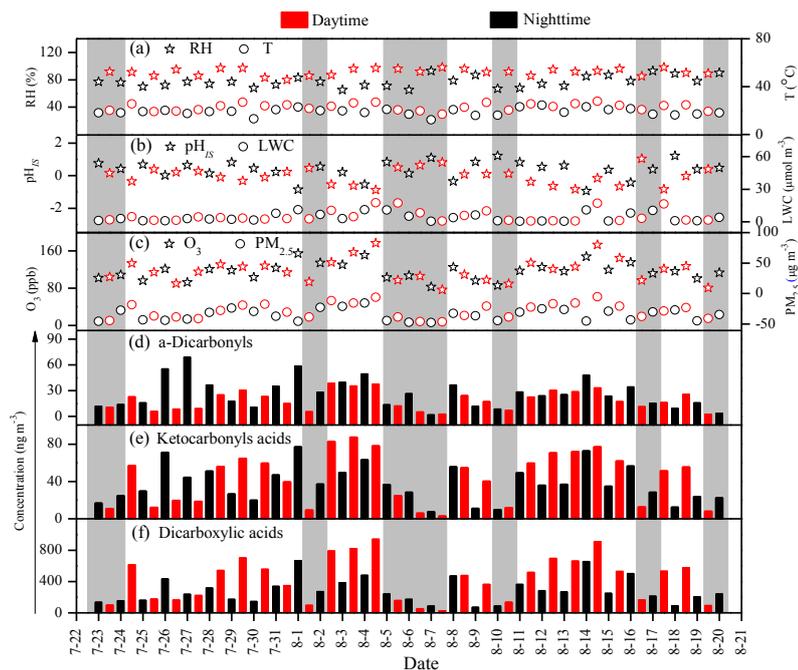
780
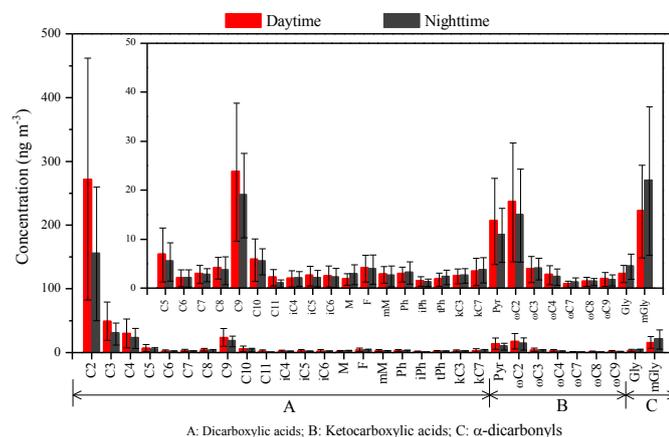
781

782   Fig.2. Molecular distributions of dicarboxylic acids and related compounds in PM$_{2.5}$ of Mt.
783   Tai in North China Plain.

Atmospheric
Chemistry
and Physics
Discussions

784

785 Fig.3. Diurnal variations of relative humidity (RH), temperature (T), in-situ acidity of
786 particles (pH$_{IS}$), liquid water content of particles (LWC), concentrations of O$_3$, PM$_{2.5}$,
787 α-dicarbonyls, ketocarboxylic acids, and dicarboxylic acids (rainy days are highlighted in
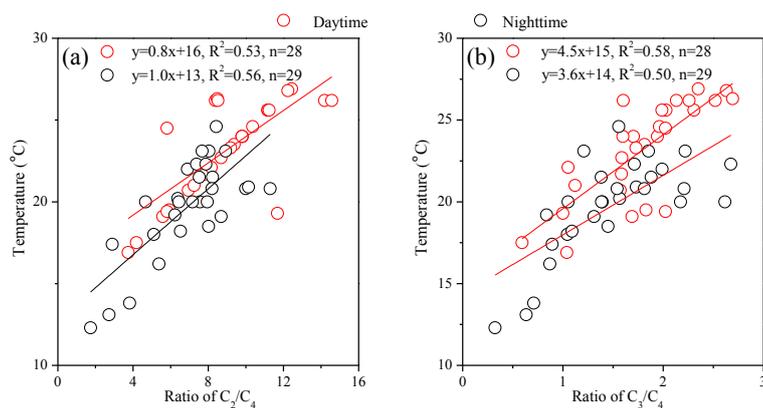788 shadow).
789

Atmospheric
Chemistry
and Physics
Discussions

790
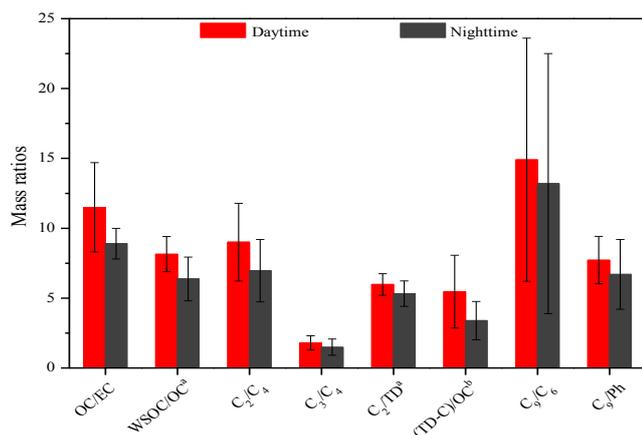
Fig.4. Diurnal variations of mass ratios of OC/EC, WSOC/OC, C_2/C_4, C_3/C_4, C_2/TD,

(TD-C)/OC, C_9/C_6, $C_9/$Ph. (TD: total dicarboxylic acids; TD-C: the carbon concentration of

total dicarboxylic acids; [a] the mass ratios expanding 10 times; [b] the mass ratios expanding

100 times).

795

796

Fig.5. Linear fit regression for temperature (T) with mass ratios of (**a**) C_2/C_4 and (**b**) C_3/C_4
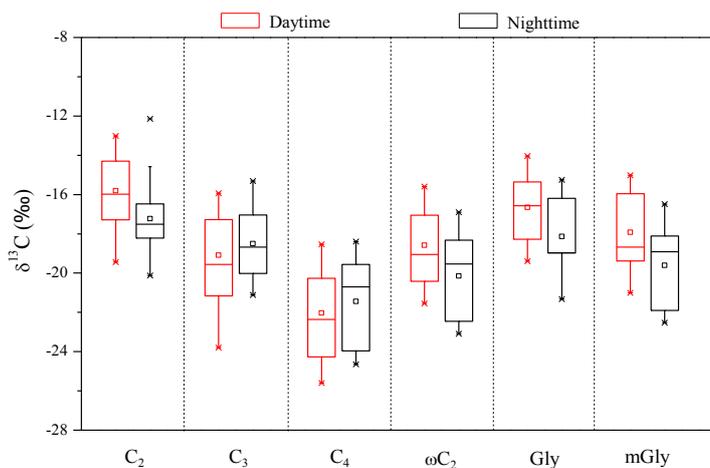
(See the abbreviations in Table 1).

Atmospheric
Chemistry
and Physics
Discussions

Open Access
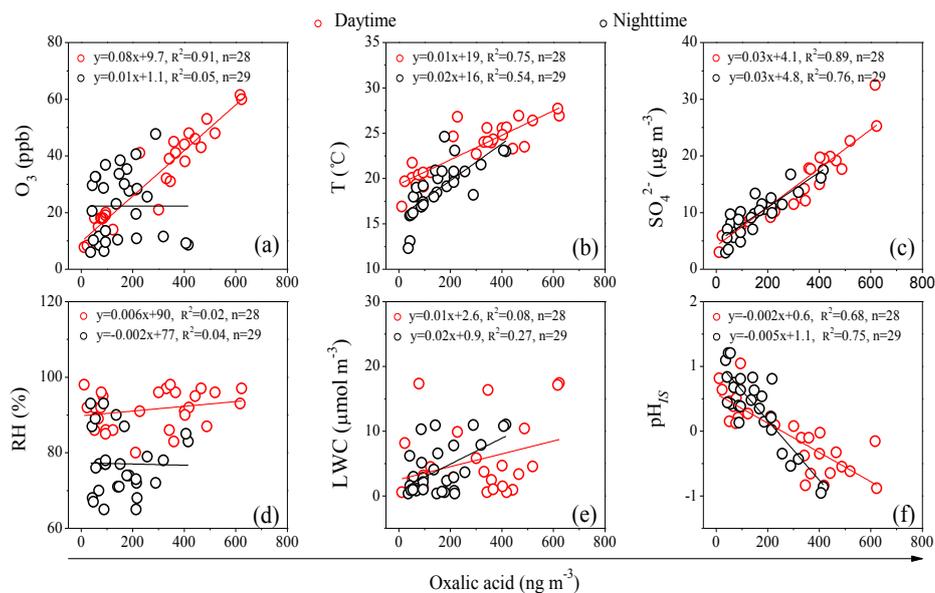
799
800   Fig.6. Linear fit regressions of oxalic acid (C_2) with (**a**) O_3, (**b**) temperature (T), (**c**)SO_4^{2-}, (**d**)
801   relative humidity (RH), (**e**) aerosol liquid water content (LWC), and (**f**) in-situ acidity of
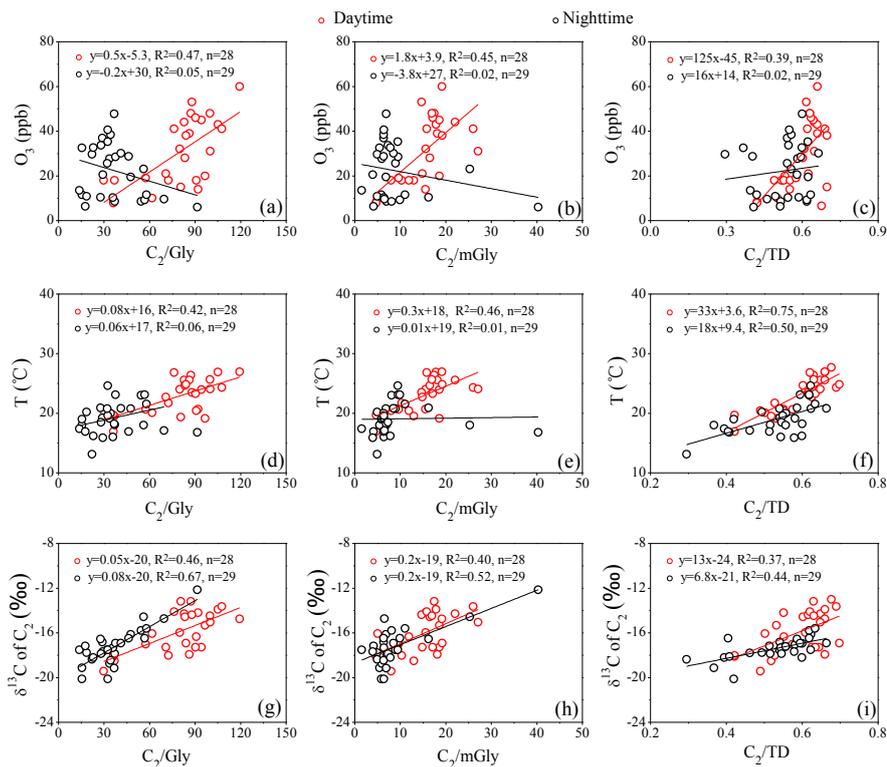802   particles (pH_{IS}).
803

804
805   Fig.7. Diurnal variations of stable carbon isotope composition of low molecular weight
806   dicarboxylic acids (C_2−C_4), the smallest ketocarboxylic acids (ωC_2) and α-dicarbonyls (Gly,
807   mGly) in $PM_{2.5}$ collected at the summit of Mt. Tai during the summer.

Atmospheric
Chemistry
and Physics
Discussions

808

809   Fig.8. Correlation analysis for the mass ratios of C_2/Gly, C_2/mGly and C_2/TD with (**a-c**)

810   concentrations of O_3; (**d-f**) temperature and (**g-i**) $\delta^{13}C$ of C_2 during the daytime and

811   nighttime (C_2/TD: mass ratio of oxalic acid to total dicarboxylic acids; T: temperature).

812

813

814

815

816