



1 **Aircraft observations of water-soluble dicarboxylic acids in the aerosols over**

2 **China**

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18 **Abstract**

19 Vertical profiles of low molecular weight dicarboxylic acids, related organic
20 compounds and SOA tracer compounds in particle phase have not yet been simultaneously
21 explored in East Asia, although there is growing evidence that aqueous phase oxidation of
22 volatile organic compounds may be responsible for the elevated organic aerosols (OA) in the
23 free troposphere. Here, we found consistently good correlation of oxalic acid, the most
24 abundant organics globally, with its precursors as well as biogenic-derived secondary OA (SOA)
25 compounds in Chinese tropospheric aerosols by aircraft measurements. Anthropogenically
26 derived dicarboxylic acids (i.e., C₅ and C₆ diacids) at high altitudes were 4-20 times higher than
27 those from surface measurements and even occasionally dominant over oxalic acid at altitude
28 higher than 2 km, which is in contrast to the predominance of oxalic acid previously reported
29 globally including the tropospheric and surface aerosols. This indicates an enhancement of
30 tropospheric SOA formation from anthropogenic precursors. Furthermore, oxalic acid-to-
31 sulfate ratio maximized at altitude of ~2 km, explaining aqueous-phase SOA production that
32 was supported by good correlations with predicted liquid water content, organic carbon and
33 biogenic SOA tracers. These results demonstrate that elevated oxalic acid and related SOA
34 compounds from both the anthropogenic and biogenic sources may substantially contribute to
35 tropospheric OA burden over polluted regions of China, implying aerosol-associated climate
36 effects and intercontinental transport.

37 **1 Introduction**

38 Low molecular weight (LMW) dicarboxylic acids (diacids), one of the most abundant
39 organic aerosol (OA) constituents, have been reported in the marine (Kawamura and Sakaguchi,
40 1999), remote (Kawamura et al., 1996), mountainous, rural, semi-urban, and urban atmosphere
41 (Ho et al., 2007). LMW diacids play important roles in Earth's climate by directly scattering
42 sunlight or indirectly by enhancing the ability of OA to act as cloud condensation nuclei (CCN)
43 (Kumar et al., 2003). They can contribute from a few percent of the water-soluble mass



44 (Sorooshian et al., 2007b), which could serve as tracers for the atmospheric processing of water-
45 soluble OA (Ervens et al., 2011), to more than 10% of organic carbon (OC) in the remote marine
46 atmosphere (Kawamura and Sakaguchi, 1999).

47 LMW diacids in aerosols may be directly emitted from fossil fuel combustion (e.g.
48 vehicle exhaust) (Kawamura and Kaplan, 1987), biomass burning (Narukawa et al., 1999) and
49 cooking emissions (Rogge et al., 1991). They can also be formed by degradation from
50 unsaturated fatty acids (Kawamura et al., 1996) and cyclic alkenes (Hatakeyama et al., 1987).
51 Laboratory studies have provided direct experimental evidence that stepwise aqueous oxidation
52 of relatively longer-chain (n) dicarboxylic acids can yield the corresponding short-chain (n-1)
53 dicarboxylic acids (Enami et al., 2015). In addition, in-cloud and below-cloud measurements
54 as well as other field measurements have revealed that aqueous-phase oxidation of volatile
55 organic compounds (VOCs) and intermediates such as glyoxal (Gly), methylglyoxal (MeGly)
56 and pyruvic acid (Pyr) in wet aerosols or clouds and the subsequent gas-particle partitioning is
57 more important pathway for the production of small diacids such as oxalic and malonic acids
58 (Lim et al., 2013;Carlton et al., 2007;Lim et al., 2005;Carlton et al., 2006;Yu et al.,
59 2005;Sorooshian et al., 2007b;Sorooshian et al., 2006). Oxalic acid (C₂) is the most abundant
60 diacid with concentrations ranging from a few ng m⁻³ in remote locations (Kawamura et al.,
61 1996) to hundreds or even up to one thousand ng m⁻³ in urban regions (Ho et al., 2007) and
62 highly forested regions (Falkovich et al., 2005). Indeed, it has been reported that photochemical
63 oxidation of isoprene is a predominant formation pathway of oxalic acid (Myriokefalitakis et
64 al., 2011).

65 Most of the previous studies of diacids have been conducted at ground surface;
66 however, only a few aircraft observations that have been conducted over the arctic region
67 (Talbot et al., 1992), the western North Pacific (Narukawa et al., 1999), the western rim of the
68 Pacific Ocean (Kawamura et al., 2003), the coastal marine stratocumulus and cumulus clouds
69 over USA (Crahan et al., 2004;Sorooshian et al., 2013;Sorooshian et al., 2007a). These aircraft
70 experiments have revealed that water-soluble diacids may be produced by the photochemical



71 oxidation of anthropogenic organic compounds in the atmosphere and thus play an important
72 role in controlling the chemical and physical properties of OA in the troposphere. However, the
73 evidence of secondary production of LWM diacids (i.e., oxalic acid) in tropospheric aerosols
74 maybe not enough due to the lack of dataset from simultaneous measurements of their possible
75 precursors and/or intermediates such as particle-phase glyoxal (Gly), methylglyoxal (MeGly),
76 pyruvic acid (Pyr) and glyoxylic acid (ω C₂) as well as other secondary organic aerosol (SOA)
77 compounds from photochemical oxidation of VOCs such as isoprene and monoterpenes in the
78 aerosols collected from aircraft campaigns.

79 East Asia is one of the most important source regions of OA (Zhang et al., 2007), and
80 this is especially true for China due to the rapid urbanization, industrialization and energy
81 consumption (Huang et al., 2014; Zhang et al., 2015a; Zhang and Cao, 2015). Elevated OA were
82 found in the free troposphere (FT) from ACE-Asia aircraft observations, exceeding model-
83 predicted organic aerosols by a factor of 10-100 (Heald et al., 2011; Heald et al., 2005; Henze
84 and Seinfeld, 2006). There is growing evidence that SOA formation from aqueous phase
85 processing of VOCs, especially from isoprene may partially explain the missing OA in the
86 troposphere over East Asia (Heald et al., 2011; Heald et al., 2005; Henze and Seinfeld, 2006),
87 however, vertical profiles of LWM diacids, related organic compounds (i.e., ketoacids and α -
88 dicarbonyls) and SOA tracer compounds in particle phase have not yet been simultaneously
89 analyzed in this region. Additional chemical constraints are urgently required to investigate the
90 importance of SOA formation pathway to the global/regional budget of OA. Our previous
91 studies have reported the molecular composition of primary organic aerosols (POA) including
92 n-alkanes, fatty acids, sugars, and polycyclic aromatic hydrocarbons (PAHs) as well as biogenic
93 SOA tracers in aerosol particles over China (Wang et al., 2007; Fu et al., 2014). However,
94 chemical composition and molecular distribution of LMW diacids have never been reported by
95 aircraft measurements over mainland and coastal China, although only limited studies have
96 been conducted on their spatial distributions based ground observations (Ho et al., 2007).



97 In this study, we have collected aerosol samples over coastal to inland China using
98 aircraft during spring, summer and winter. The samples were analyzed for series of LWM
99 diacids and related compounds as well as SOA tracer compounds to investigate the vertical
100 profiles, possible sources and formation pathways of LWM diacids and related organic
101 compounds in the polluted troposphere over China. In light of these analyses, we identified that
102 production of oxalic acid and related compounds from anthropogenic and biogenic precursors
103 is enhanced at high altitudes in the troposphere.

104 **2 Materials and Methods**

105 **2.1 Aircraft Campaigns**

106 Aircraft measurements were carried out over the coastal East China Sea in winter
107 (12/25/2002–01/06/2003, n=18) and inland China during summer (08/08/2003–09/13/2003,
108 n=14) and spring (05/19/2004–06/10/2004, n=16) using Yun-12 and Yun-5 airplanes as
109 described elsewhere (Wang et al., 2007; Fu et al., 2014). The sampling heights were from 500
110 m to 3000 m above ground level across many major cities such as Changzhou, Nanjing, Hefei,
111 Wuhan, Chongqing and Chengdu for inland aerosol samples as well as Wenzhou, Ningbo,
112 Shanghai, Changzhou, Qingdao and Dalian for coastal aerosol samples. The detailed flight
113 tracks and flight information are shown in Figure 1 and Table S1 (see Supporting Information).
114 PM_{2.5} aerosols were collected on pre-heated quartz fiber filter (diameter of 90 mm) using a
115 medium-volume air sampler (Beijing Geological Instrument Factory, China). Aerosol samples
116 were collected for the sampling period from ca. 80 min. to two hours. Air was taken via an inlet
117 installed below the cabin of the aircraft at a flow rate of 78 L/min.

118 **2.2 Measurement of LMW diacids**

119 LMW diacids and related organic compounds such as ω -oxocarboxylic acids (or
120 oxoacids), pyruvic acid and α -dicarbonyls were determined as described elsewhere (Kawamura
121 and Ikushima, 1993; Ho et al., 2010). Briefly, the sample and blank filters were extracted with
122 organic free ultrapure water (10 ml \times 3) in a glass vial for 10 min. To remove insoluble particles



123 and filter debris, the extracts were passed through a Pasteur pipette packed with quartz wool.
124 The combined extracts were concentrated using a rotary evaporator under a vacuum and then
125 further concentrated using a nitrogen blow-down system. The concentrated extracts were
126 reacted with 14% BF₃/n-butanol to derive carboxyl group to dibutyl ester and oxo group to
127 dibutoxy acetals.

128 The derivatives were extracted with n-hexane, concentrated to near dryness, dissolved
129 with n-hexane in 1.5 ml glass vials. The samples were finally determined using a gas
130 chromatography (GC, HP6980) with a split/splitless injection, fused silica capillary column
131 (HP-5, 0.2 mm i.d. x 25 m long x 0.52 μm film thickness) and a flame ionization detector.
132 Identification of the compounds was performed by GC retention times with those of authentic
133 standards and GC/mass spectrometry analyses. Recoveries of authentic standards spiked to a
134 pre-heated quartz fiber filter were generally better than 85% for all organic compound identified
135 except for oxalic acid (78%), pyruvic acid (72%), and methylglyoxal (55%). Duplicate analyses
136 of filter samples from other sites indicated that analytical errors are smaller than 15%. During
137 the aircraft campaigns, field blank filters were mounted onto the sampler for seconds without
138 pumping. Blank and sample filters were placed individually in a clean (pre-combusted at 450
139 °C for 6 h) glass jar sealed with a Teflon-lined screw cap, transported to the laboratory, and
140 stored at -20 °C prior to analysis (Wang et al., 2007).

141 Small peaks of oxalic, malonic and glyoxylic acids were found in the field and lab
142 blanks, but they were smaller than 10% of the real samples. The concentrations reported here
143 are all corrected for the field blanks but not for the recoveries. The method of SOA tracers
144 measurement was described elsewhere (Fu et al., 2014).

145 **2.3 Measurements of EC and OC**

146 The concentrations of organic carbon (OC) and elemental carbon (EC) were measured
147 with thermal-optical transmittance method by OC/EC Carbon Aerosol Analyzer (Sunset



148 Laboratory Inc., USA) following the IMPROVE protocol (Chow et al., 2004). All the analyses
149 of the filter samples were completed in 2006.

150 **2.4 Estimation of liquid water content and aerosol acidity**

151 Liquid water content (LWC) and aerosol acidity were predicted by ISORROPIA II,
152 which is a thermodynamic equilibrium model with robust and rapid convergence for all aerosol
153 types (Fountoukis and Nenes, 2007). Measured concentrations of water-soluble inorganic ions,
154 ambient temperature and relative humidity were used as input.

155 **3 Results and discussion**

156 **3.1 Concentrations and molecular distributions**

157 Total concentrations of LWM diacids and related compounds quantified in the inland
158 aircraft $PM_{2.5}$ (i.e., particulate matter with a diameter smaller than 2.5 μm) are 730 ± 328 and
159 586 ± 457 $ng\ m^{-3}$ during summer and spring, respectively, while in the coastal aerosols, the
160 average concentration is 254 ± 209 $ng\ m^{-3}$ in winter (Table 1). It is of great interest to note that
161 the concentrations of diacids in the FT over the Arctic and North Pacific are generally much
162 lower than those reported at ground levels (Kawamura et al., 1996; Kawamura and Sakaguchi,
163 1999); however, the concentrations in the troposphere over mainland China are within the range
164 of or even higher than those reported at ground levels in major cities (Ho et al., 2007; Kawamura
165 and Ikushima, 1993). Due to the enhanced anthropogenic emissions, concentrations of POA
166 (i.e., n-alkanes, fatty acids, sugars, lignin and resin products, sterols, PAHs, and phthalic acids)
167 are higher in winter than those in summer and spring (Wang et al., 2007). In contrast, the
168 concentrations of diacids in summer and spring are 2-15 times higher than those in winter,
169 indicating that these compounds are mostly of secondary origin via the oxidation of their
170 gaseous precursors such as isoprene and α/β -pinene (Kanakidou et al., 2005; Carlton et al.,
171 2006; Carlton et al., 2007; Carlton et al., 2009; Ervens et al., 2011) as discussed below.



172 Molecular distributions of diacids in our study are generally characterized by the
173 predominance of oxalic acid (C_2) followed by succinic (C_4) and malonic (C_3) acids during
174 spring and winter, being consistent with previous findings obtained in Chinese megacities (Ho
175 et al., 2007) (Figure 2a). However, in many summer samples collected at height of above 2
176 km, we found the predominance of glutaric (C_5) and adipic (C_6) acids (see Figure 2b), which
177 are the major organic compounds produced by the oxidation of anthropogenic cyclohexene and
178 methylenecyclohexane (Hamilton et al., 2006; Muller et al., 2007). Such a molecular
179 distribution has not been reported for the free tropospheric ^{21,27} and ground level aerosols
180 (Hatakeyama et al., 1987; Enami et al., 2015). In our measurements, the averaged
181 concentrations of C_5 and C_6 in summer are $159 \pm 79 \text{ ng m}^{-3}$ and $93.9 \pm 23.2 \text{ ng m}^{-3}$, which are 4-
182 20 times higher than those in ground measurements in many megacities in China (Ho et al.,
183 2007), Tokyo (Kawamura and Yasui, 2005) and Los Angeles (Kawamura and Kaplan, 1987).
184 Such high abundances of C_5 and C_6 observed in summer imply an important formation pathway
185 associated with enhanced photochemical oxidation of anthropogenic precursors in the polluted
186 troposphere over China.

187 3.2 C_3 (C_2) to C_4 ratio

188 The malonic to succinic acid (C_3/C_4) ratios can provide information on source,
189 formation pathways and photochemical aging of organic aerosols. C_3/C_4 ratios in aerosols
190 derived from vehicular exhausts (i.e., 0.25–0.44, av. 0.35) (Kawamura and Kaplan, 1987) have
191 lower values than those in ambient aerosols from Tokyo (i.e., 0.56–2.9, av. 1.6) (Kawamura
192 and Ikushima, 1993) and China's megacities (i.e., 0.6–1.1, average 0.74) (Ho et al., 2007). In
193 contrast, the ratios are substantially higher for aged aerosols because C_3 is more produced by
194 photochemical processing of C_4 (Kawamura and Ikushima, 1993). Actually, higher C_3/C_4 ratios
195 are observed for remote marine aerosols from the North Pacific including tropic (range: 1–11,
196 av. 3.9) which are subjected to extensive aging during the long-range atmospheric transport
197 (Kawamura and Sakaguchi, 1999). In this study, C_3/C_4 ratios are 0.5 ± 0.4 in summer, 0.9 ± 0.1
198 in spring (Table 1), and 0.7 ± 0.2 in winter, apparently smaller than those in aerosols affected by



199 atmospheric aging, but similar to that of urban aerosols in China (i.e., 0.9 in summer and 0.6 in
200 winter) (Ho et al., 2007).

201 C_2/C_4 ratios (2.0 in summer, 4.6 in spring and 4.6 in winter) in our study are found to
202 be much smaller than those from ground observations in China during summer (inland cities in
203 summer: av. 7.1) and winter (coastal cities in winter: av. 7.9). The lower C_2/C_4 and C_3/C_4 ratios
204 could be also resulting from degradation of C_2 and C_3 in high altitudes due to increased solar
205 radiation. However, no strong correlation ($p>0.05$) is found between C_2/C_4 (and C_3/C_4) and
206 sampling altitude although solar radiation is expected to increase with increasing altitudes.
207 These results suggest that the degradation of higher homologous diacids (i.e., C_4) is not an
208 important pathway for the production of tropospheric C_2 and C_3 in China, and primary fossil-
209 fuel emissions and/or secondary production from other precursors are major formation
210 pathways of these small diacids (i.e., C_2 , C_3 and C_4).

211 3.3 Cis/trans ratio

212 It has been revealed that maleic acid (M, *cis* configuration) is produced by
213 photochemical oxidation of anthropogenic aromatic hydrocarbons such as benzene and toluene,
214 which is predominant over fumaric acid (F, *trans* configuration) (Sempere and Kawamura,
215 1996). M can be photo-isomerized to its *trans* isomer (F) in the atmosphere under solar
216 radiation. M/F ratios (4.9, 4.5 and 6.8 for summer, spring and winter, respectively) are much
217 higher in the present study than those reported in marine region (0.1-1.5) (Fu et al., 2013) and
218 Chinese megacities at ground levels (2.0 and 2.2 for summer and winter, respectively) (Ho et
219 al., 2007). This indicates that only a small fraction of maleic acid is isomerized to fumaric acid
220 by photochemical transformation and thus SOA produced from anthropogenic emissions in the
221 low troposphere in China is mostly fresh without substantially photochemical processing (Cong
222 et al., 2015).

223 3.4 C_5 (C_6) to C_9 diacid ratio



224 C_6 (or C_5) to azelaic acid (C_9) ratio (i.e., C_6/C_9 or C_5/C_9) is often used as an indicator
225 of relative contribution from anthropogenic and biogenic sources to OA (Kawamura and Yasui,
226 2005). C_6/C_9 and C_5/C_9 ratios during the summer aircraft campaign are on average 17 and 28,
227 respectively, which are >15 times higher than those reported at the ground surface from major
228 Chinese cities (Ho et al., 2007; Wang et al., 2002). This comparison further supports that
229 anthropogenic sources are an important source of OA in the high altitudes over China. Taken
230 together with other possible SOA components (e.g., oligomers with MW > 250 Da) produced
231 during the oxidation of anthropogenic VOCs, our result implies that SOA formation plays an
232 important role in OA budget in the troposphere especially during summer when atmospheric
233 oxidation capacity is significantly enhanced. It is important to note that the correlation
234 coefficient of C_6 (or C_5) with C_2 during summer ($r^2=0.39$ or 0.49) is lower than that obtained in
235 winter ($r^2=0.76$ or 0.59) and spring ($r^2=0.95$ or 0.96), suggesting that C_2 has a different
236 formation pathway and/or its precursors are mostly from biogenic origins (i.e., isoprene) in
237 summer.

238 3.5 Correlation of diacids with SOA tracers

239 In the urban atmosphere, dicarboxylic acids can be emitted as primary particles from
240 motor exhausts (Kawamura and Kaplan, 1987), biomass burning (Cong et al., 2015; Falkovich
241 et al., 2005), and cooking emissions (Rogge et al., 1991). However, recent field, laboratory and
242 model studies have demonstrated that aqueous-phase SOA formation from isoprene or other
243 precursors photooxidation is a major formation pathway of LMW diacids (Myriokefalitakis et
244 al., 2011; Carlton et al., 2006; Ervens et al., 2011). Furthermore, significant correlations ($r>0.70$,
245 $p<0.05$) are obtained between C_2 and its possible precursors and intermediates such as glyoxylic
246 acid (ωC_2), pyruvic acid (Pyr), glyoxal (Gly) and methylglyoxal (MeGly) in all three campaigns
247 (Table 2). This demonstrates that C_2 is produced from its precursor compounds such as Pyr,
248 Gly, MeGly and ωC_2 through the following formation pathways: ($CH_3COCOOH$, $HCO-CHO$,
249 CH_3COCHO) \rightarrow $HCO-COOH$ \rightarrow $HOOC-COOH$ (Carlton et al., 2009; Carlton et al.,
250 2007; Carlton et al., 2006). Based on the GEOS-Chem Global 3-D chemical transport model,



251 Gly may be derived from both biogenic and anthropogenic VOCs whereas MeGly is more
252 specific to biogenic isoprene (Fu et al., 2008). We found that the correlation coefficient between
253 Gly and C₂ is higher than that between MeGly and C₂ for winter and spring samples, suggesting
254 a substantial contribution of SOA formation from anthropogenic VOCs during these two
255 seasons.

256 Similarly, C₂ also shows better correlations with both anthropogenic-derived SOA such
257 as C₅ and C₆ for winter ($r^2=0.76$ or 0.59) and spring ($r^2=0.95$ or 0.96) samples than summer
258 samples ($r^2=0.39$ or 0.49), further supporting that anthropogenic VOCs play a more important
259 role in SOA formation than biogenic VOCs during winter and spring. No significant correlation
260 ($r^2=0.28$, $p>0.05$) is found between EC (i.e., a primary tracer for fossil fuel biomass combustion
261 (Zhang et al., 2015b)) and C₂ in summer aerosols, whereas a good correlation is found in spring.
262 These results indicate that primary emissions are not major sources of C₂ during summer, but
263 their contribution may be more important in spring.

264 Oxalic acid shows a strong positive correlation with isoprene-derived SOA tracers such
265 as 2-methylglyceric acid (2-MGA) and C₅-alkene triols (cis-2-methyl-1,3,4-trihydroxy-1-
266 butene, 3-methyl-2,3,4-trihydroxy-1-butene plus trans-2-methyl-1,3,4-trihydroxy-1-butene)
267 (Figure 3), but a very weak correlation ($r^2 = 0.26$, $p>0.05$) with 2-methyltetrols (2-
268 methylthreitol and 2-methylerythritol). Previous studies have revealed that 2-methyltetrols
269 could be formed through diepoxy derivatives of isoprene through acid-catalyzed hydrolysis
270 (Wang et al., 2005), whereas 2-MGA is produced by further oxidation of its intermediates such
271 as methacrolein and methacrylic acid from isoprene (Claeys et al., 2004; Surratt et al., 2006).
272 Such a good correlation between 2-MGA and oxalic acid could demonstrate that oxalic acid
273 has a very close link with the higher-generation products of isoprene, which could serve as
274 precursors of oxalic acid over China. Oxalic acid also significantly correlates with α/β -pinene-
275 SOA tracers (i.e., pinonic, pinic, 3-hydroxyglutaric, and 3-methyl-1,2,3-butanetricarboxylic
276 acid) and β -caryophyllene tracer (β -caryophyllinic acid, see Figure 3) (Jaoui et al., 2013).



277 Overall, both oxalic acid and SOA tracers are more abundant in summer than in spring,
278 suggesting that production of these organics is associated with higher oxidation capacity,
279 emission strength and solar radiation in summer. Based on the consistent good correlations of
280 oxalic acid with SOA tracers derived from isoprene, monoterpene and β -caryophyllene, we
281 propose that a large fraction of oxalic acid detected within the atmospheric boundary layer over
282 China is of secondary origin, i.e., mostly via atmospheric oxidation of gaseous precursors
283 uplifted aloft from ground surface. This study highlights that oxalic acid should serve as an
284 important tracer of SOA formation not only on the ground surface but also at high altitudes
285 within the lower FT. Therefore, the high abundances of LWM diacids (C_2 - C_6) observed in this
286 study imply an important contribution to the OA budget from SOA production from both
287 biogenic and anthropogenic precursors emitted from the ground surface to high altitudes over
288 inland China.

289 The observed total concentrations of oxalic acid and other LWM diacids identified in
290 this study (Table 1) show the same magnitude as the levels of SOA (i.e., 299 ± 173 ng m^{-3} in
291 summer and 257 ± 210 ng m^{-3} in spring) estimated by SOA-tracer methods (Fu et al., 2014). It
292 should be noted that oxalic acid is not included in the traditional “SOA tracer method”
293 (Kleindienst et al., 2007) and therefore SOA may be underestimated if SOA is calculated by
294 this approach. Inclusion of oxalic acid (and also other LWM diacids) as major products from
295 atmospheric oxidation of biogenic (and also anthropogenic) VOCs may partially reduce the
296 discrepancy between modeled and observed tropospheric OA during the ACE-Asia campaign
297 (Heald et al., 2005), although further studies are still required to investigate other SOA
298 compounds (e.g., oligomeric components) produced from anthropogenic and biogenic VOCs
299 in the reactions to fully understand the associated formation pathway and mechanism.

300 **3.6 Vertical profiles of LWM-diacids**

301 As shown in Figure 4, the highest concentrations of oxalic acid and total diacids are
302 observed around at 2 km in altitude during summer with a sharp decrease toward 3 km.



303 However, during spring and winter, their concentrations decrease with increasing altitudes due
304 to the atmospheric dilution during upward transport. Much clear trends are observed in the
305 vertical profiles of oxalic acid normalized by anthropogenic tracers such as sulfate (SO_4^{2-}),
306 vanadium, and bulk OC. Interestingly, similar trends are also found in spring and winter
307 samples, but the trends are weaker, suggesting that a secondary production of oxalic acid is
308 largely enhanced in summer at higher altitudes of the lower troposphere. Similar vertical pattern
309 has been also reported for biogenic SOA-tracers such as 2-MGA, 3-HGA and MBTCA (3-
310 methyl-1,2,3-butanetricarboxylic acid), but not for POA such as biomass burning tracers (e.g.,
311 levoglucosan), fungal spore tracers (arabitol and mannitol), sucrose, and trehalose (Fu et al.,
312 2014). These results further demonstrate that oxalic acid is mostly likely produced by secondary
313 process in the troposphere.

314 Oxalic acid and related organic species identified in the high altitudes could not be
315 simply explained by uplifting transport of pre-existing SOA produced on the ground surface
316 because these SOA compounds relative to anthropogenic tracers such as SO_4^{2-} , vanadium, and
317 OC significantly increased with altitude as stated above. This finding suggests that in-situ SOA
318 production by the oxidation of VOCs lifted from ground surface substantially contributes to the
319 observed levels of oxalic acid and related species. Therefore, SOA formation in cloud or wet
320 aerosol via the oxidation of biogenic and anthropogenic VOCs may increase concentrations of
321 oxalic acid in the lower FT. There is growing evidence to support of in-cloud formation of
322 oxalic acid and related SOA. Many studies suggest that oxalic acid is mostly produced via
323 aqueous-phase oxidation of water-soluble organics such as glyoxal, methylglyoxal, pyruvic
324 acid and glyoxylic acid, which are oxidation intermediates of various VOCs (Ervens et al.,
325 2004;Carlton et al., 2006;Ervens et al., 2011). Indeed, a good correlation (Figure 5) was found
326 between predicted liquid water content with both OC and oxalic acid, indicating an important
327 contribution from SOA formation via cloud processing and/or aqueous-phase oxidation. This
328 formation pathway is also supported by the consistently good correlation among these species
329 identified in our study as discussed previously. Aqueous-phase production of oxalic acid and



330 related compounds may increase the abundances of SOA at the lower FT (around 2 km in this
331 study). With the GEOS-Chem model based on the Fu et al. (2008) scheme (Fu et al., 2008),
332 aqueous-phase SOA has a pronounced enhancement in the lower FT (2-6 km) (Heald et al.,
333 2011), which may explain to some extent the elevated levels of oxalic acid around at ~2 km in
334 altitude.

335 **4 Conclusions**

336 Based on three aircraft measurements over East Asia, this study demonstrates an
337 aqueous-phase mechanism for SOA productions of diacids in the troposphere following
338 correlation analysis of oxalic acid in tropospheric aerosols with other measured chemical
339 variables including its precursors and its intermediate as well as biogenic-derived SOA from
340 isoprene, monoterpenes and β -caryophyllene. In addition to biogenic-derived SOA compounds,
341 anthropogenic-derived dicarboxylic acids (e.g. C5 and C6 diacids) are 4-20 times higher than
342 those from ground measurements and even occasionally dominant over oxalic acid at altitudes
343 higher than 2 km in summer, which is in contrast to the predominance of oxalic acid previously
344 reported globally including the tropospheric and surface aerosols. The results suggest an
345 important formation pathway associated with enhanced photochemical oxidation of
346 anthropogenic precursors in the polluted troposphere over China. Their relative contribution of
347 anthropogenic and biogenic sources is subject to future studies. The combination of radiocarbon
348 (^{14}C) measurement of water-soluble organic carbon (WSOC) and specific SOA compounds
349 (e.g., oxalic acid) may provide better insights on biogenic and fossil sources of SOA (Zhang et
350 al., 2014; Zhang et al., 2015a; Noziere et al., 2015) .

351 The present study demonstrates that secondary formation of oxalic acid in aqueous
352 phase plays an important role in the SOA budget from the near surface to the lower FT (i.e., 2
353 km) over inland China, whereas dilution of pre-existing particles and VOCs, photochemical
354 decomposition and aerosol processing may decrease the levels of oxalic acid and related
355 compounds at higher altitudes (>2 km). Our findings also highlight that water-soluble LMW



356 diacids and other SOA components may control the chemical compositions, physical properties
357 and budget of OA in the polluted troposphere over China, and thus significantly affect the
358 regional/global climate and intercontinental transport especially over the Pacific Ocean.

359

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369 **References**

- 370 Carlton, A. G., Turpin, B. J., Lim, H. J., Altieri, K. E., and Seitzinger, S.: Link between
371 isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility
372 organic acids in clouds, *Geophys. Res. Lett.*, 33, L06822, 2006.
- 373 Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H. J., and Ervens, B.:
374 Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous
375 photooxidation experiments, *Atmos. Environ.*, 41, 7588-7602, 2007.
- 376 Carlton, A. G., Wiedinmyer, C., and Kroll, J. H.: A review of Secondary Organic Aerosol
377 (SOA) formation from isoprene, *Atmos. Chem. Phys.*, 9, 4987-5005, 2009.
- 378 Chow, J. C., Watson, J. G., Chen, L. W. A., Arnott, W. P., Moosmüller, H., and Fung, K.:
379 Equivalence of elemental carbon by thermal/optical reflectance and transmittance with
380 different temperature protocols, *Environ. Sci. Technol.*, 38, 4414-4422, 2004.
- 381 Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J.,
382 Guyon, P., Andreae, M. O., Artaxo, P., and Maenhaut, W.: Formation of secondary organic
383 aerosols through photooxidation of isoprene, *Science*, 303, 1173-1176, 2004.



- 384 Cong, Z. Y., Kawamura, K., Kang, S. C., and Fu, P. Q.: Penetration of biomass-burning
385 emissions from South Asia through the Himalayas: new insights from atmospheric organic
386 acids, *Scientific Reports*, 5, 9580, 2015.
- 387 Crahan, K. K., Hegg, D., Covert, D. S., and Jonsson, H.: An exploration of aqueous oxalic
388 acid production in the coastal marine atmosphere, *Atmos. Environ.*, 38, 3757-3764, 2004.
- 389 Enami, S., Hoffmann, M. R., and Colussi, A. J.: Stepwise Oxidation of Aqueous Dicarboxylic
390 Acids by Gas-Phase OH Radicals, *J. Phys. Chem. Lett.*, 6, 527-534, 2015.
- 391 Ervens, B., Feingold, G., Frost, G. J., and Kreidenweis, S. M.: A modeling study of aqueous
392 production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass
393 production, *J. Geophys. Res.*, 109, D15205, 2004.
- 394 Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud
395 droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies,
396 *Atmos. Chem. Phys.*, 11, 11069-11102, 2011.
- 397 Falkovich, A. H., Graber, E. R., Schkolnik, G., Rudich, Y., Maenhaut, W., and Artaxo, P.:
398 Low molecular weight organic acids in aerosol particles from Rondonia, Brazil, during the
399 biomass-burning, transition and wet periods, *Atmos. Chem. Phys.*, 5, 781-797, 2005.
- 400 Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic
401 equilibrium model for K^+ - Ca^{2+} - Mg^{2+} - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O aerosols,
402 *Atmos. Chem. Phys.*, 7, 4639-4659, 2007.
- 403 Fu, P., Kawamura, K., Usukura, K., and Miura, K.: Dicarboxylic acids, ketocarboxylic acids
404 and glyoxal in the marine aerosols collected during a round-the-world cruise, *Mar. Chem.*,
405 148, 22-32, 2013.
- 406 Fu, P. Q., Kawamura, K., Cheng, Y. F., Hatakeyama, S., Takami, A., Li, H., and Wang, W.:
407 Aircraft measurements of polar organic tracer compounds in tropospheric particles (PM10)
408 over central China, *Atmos. Chem. Phys.*, 14, 4185-4199, 2014.
- 409 Fu, T. M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global
410 budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of
411 secondary organic aerosols, *J. Geophys. Res.*, 113, D15303, 2008.
- 412 Hamilton, J. F., Lewis, A. C., Reynolds, J. C., Carpenter, L. J., and Lubben, A.: Investigating
413 the composition of organic aerosol resulting from cyclohexene ozonolysis: low molecular
414 weight and heterogeneous reaction products, *Atmos. Chem. Phys.*, 6, 4973-4984, 2006.
- 415 Hatakeyama, S., Ohno, M., Weng, J. H., Takagi, H., and Akimoto, H.: Mechanism for the
416 Formation of Gaseous and Particulate Products from Ozone-Cycloalkene Reactions in Air,
417 *Environ. Sci. Technol.*, 21, 52-57, 1987.
- 418 Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H.,
419 and Weber, R. J.: A large organic aerosol source in the free troposphere missing from current
420 models, *Geophys. Res. Lett.*, 32, L18809, 2005.



- 421 Heald, C. L., Coe, H., Jimenez, J. L., Weber, R. J., Bahreini, R., Middlebrook, A. M., Russell,
422 L. M., Jolleys, M., Fu, T. M., Allan, J. D., Bower, K. N., Capes, G., Crosier, J., Morgan, W.
423 T., Robinson, N. H., Williams, P. I., Cubison, M. J., DeCarlo, P. F., and Dunlea, E. J.:
424 Exploring the vertical profile of atmospheric organic aerosol: comparing 17 aircraft field
425 campaigns with a global model, *Atmos. Chem. Phys.*, 11, 12673-12696, 2011.
- 426 Henze, D. K., and Seinfeld, J. H.: Global secondary organic aerosol from isoprene oxidation,
427 *Geophys. Res. Lett.*, 33, L09812, 2006.
- 428 Ho, K. F., Cao, J. J., Lee, S. C., Kawamura, K., Zhang, R. J., Chow, J. C., and Watson, J. G.:
429 Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China,
430 *J. Geophys. Res.*, 112, D22S27, 2007.
- 431 Ho, K. F., Lee, S. C., Ho, S. S. H., Kawamura, K., Tachibana, E., Cheng, Y., and Zhu, T.:
432 Dicarboxylic acids, ketocarboxylic acids, alpha-dicarbonyls, fatty acids, and benzoic acid in
433 urban aerosols collected during the 2006 Campaign of Air Quality Research in Beijing
434 (CAREBeijing-2006), *J. Geophys. Res.*, 115, 2010.
- 435 Huang, R. J., Zhang, Y., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y., Daellenbach, K. R.,
436 Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A.,
437 Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis,
438 J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., El Haddad, I., and Prevot, A. S.:
439 High secondary aerosol contribution to particulate pollution during haze events in China,
440 *Nature*, 514, 218-222, 2014.
- 441 Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M., and Offenberg, J. H.:
442 Secondary organic aerosol formation from the oxidation of a series of sesquiterpenes: alpha-
443 cedrene, beta-caryophyllene, alpha-humulene and alpha-farnesene with O-3, OH and NO₃
444 radicals, *Environ. Chem.*, 10, 178-193, 2013.
- 445 Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van
446 Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski,
447 Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K.,
448 Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a
449 review, *Atmos. Chem. Phys.*, 5, 1053-1123, 2005.
- 450 Kawamura, K., and Kaplan, I. R.: Motor Exhaust Emissions as a Primary Source for
451 Dicarboxylic-Acids in Los-Angeles Ambient Air, *Environ. Sci. Technol.*, 21, 105-110, 1987.
- 452 Kawamura, K., and Ikushima, K.: Seasonal-Changes in the Distribution of Dicarboxylic-
453 Acids in the Urban Atmosphere, *Environ. Sci. Technol.*, 27, 2227-2235, 1993.
- 454 Kawamura, K., Kasukabe, H., and Barrie, L. A.: Source and reaction pathways of
455 dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations,
456 *Atmos. Environ.*, 30, 1709-1722, 1996.



- 457 Kawamura, K., and Sakaguchi, F.: Molecular distributions of water soluble dicarboxylic acids
458 in marine aerosols over the Pacific Ocean including tropics, *J. Geophys. Res.*, 104, 3501-
459 3509, 1999.
- 460 Kawamura, K., Umemoto, N., Mochida, M., Bertram, T., Howell, S., and Huebert, B. J.:
461 Water-soluble dicarboxylic acids in the tropospheric aerosols collected over east Asia and
462 western North Pacific by ACE-Asia C-130 aircraft, *J. Geophys. Res.*, 108, 2003.
- 463 Kawamura, K., and Yasui, O.: Diurnal changes in the distribution of dicarboxylic acids,
464 ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, *Atmos. Environ.*, 39,
465 1945-1960, 2005.
- 466 Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Lewis, C. W., Bhave, P. V.,
467 and Edney, E. O.: Estimates of the contributions of biogenic and anthropogenic hydrocarbons
468 to secondary organic aerosol at a southeastern US location, *Atmos. Environ.*, 41, 8288-8300,
469 2007.
- 470 Kumar, P. P., Broekhuizen, K., and Abbatt, J. P. D.: Organic acids as cloud condensation
471 nuclei: Laboratory studies of highly soluble and insoluble species, *Atmos. Chem. Phys.*, 3,
472 509-520, 2003.
- 473 Lim, H. J., Carlton, A. G., and Turpin, B. J.: Isoprene forms secondary organic aerosol
474 through cloud processing: Model simulations, *Environ. Sci. Technol.*, 39, 4441-4446, 2005.
- 475 Lim, Y. B., Tan, Y., and Turpin, B. J.: Chemical insights, explicit chemistry, and yields of
476 secondary organic aerosol from OH radical oxidation of methylglyoxal and glyoxal in the
477 aqueous phase, *Atmos. Chem. Phys.*, 13, 8651-8667, 2013.
- 478 Muller, C., Iinuma, Y., Boge, O., and Herrmann, H.: Applications of CE-ESI-MS/MS
479 analysis to structural elucidation of methylenecyclohexane ozonolysis products in the particle
480 phase, *Electrophoresis*, 28, 1364-1370, 2007.
- 481 Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K.,
482 Segers, A., and Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D
483 modeling study, *Atmos. Chem. Phys.*, 11, 5761-5782, 2011.
- 484 Narukawa, M., Kawamura, K., Takeuchi, N., and Nakajima, T.: Distribution of dicarboxylic
485 acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires,
486 *Geophys. Res. Lett.*, 26, 3101-3104, 1999.
- 487 Noziere, B., Kalberer, M., Claeys, M., Allan, J., D'Anna, B., Decesari, S., Finessi, E., Glasius,
488 M., Grgic, I., Hamilton, J. F., Hoffmann, T., Iinuma, Y., Jaoui, M., Kahnt, A., Kampf, C. J.,
489 Kourtchev, I., Maenhaut, W., Marsden, N., Saarikoski, S., Schnelle-Kreis, J., Surratt, J. D.,
490 Szidat, S., Szmigielski, R., and Wisthaler, A.: The molecular identification of organic
491 compounds in the atmosphere: state of the art and challenges, *Chem Rev*, 115, 3919-3983,
492 2015.



- 493 Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simonelt, B. R. T.:
494 Sources of Fine Organic Aerosol .1. Charbroilers and Meat Cooking Operations, Environ.
495 Sci. Technol., 25, 1112-1125, 1991.
- 496 Sempere, R., and Kawamura, K.: Low molecular weight dicarboxylic acids and related polar
497 compounds in the remote marine rain samples collected from western Pacific, Atmos.
498 Environ., 30, 1609-1619, 1996.
- 499 Sorooshian, A., Varutbangkul, V., Brechtel, F. J., Ervens, B., Feingold, G., Bahreini, R.,
500 Murphy, S. M., Holloway, J. S., Atlas, E. L., Buzorius, G., Jonsson, H., Flagan, R. C., and
501 Seinfeld, J. H.: Oxalic acid in clear and cloudy atmospheres: Analysis of data from
502 International Consortium for Atmospheric Research on Transport and Transformation 2004,
503 J. Geophys. Res., 111, D23s45, 2006.
- 504 Sorooshian, A., Lu, M.-L., Brechtel, F. J., Jonsson, H., Feingold, G., Flagan, R. C., and
505 Seinfeld, J. H.: On the source of organic acid aerosol layers above clouds, Environ. Sci.
506 Technol., 41, 4647-4654, 2007a.
- 507 Sorooshian, A., Ng, N. L., Chan, A. W., Feingold, G., Flagan, R. C., and Seinfeld, J. H.:
508 Particulate organic acids and overall water - soluble aerosol composition measurements from
509 the 2006 Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), Journal
510 of Geophysical Research: Atmospheres (1984–2012), 112, 2007b.
- 511 Sorooshian, A., Wang, Z., Coggon, M. M., Jonsson, H. H., and Ervens, B.: Observations of
512 Sharp Oxalate Reductions in Stratocumulus Clouds at Variable Altitudes: Organic Acid and
513 Metal Measurements During the 2011 E-PEACE Campaign, Environ. Sci. Technol., 47,
514 7747-7756, 2013.
- 515 Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A.,
516 Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.:
517 Chemical composition of secondary organic aerosol formed from the photooxidation of
518 isoprene, J. Phys. Chem. A, 110, 9665-9690, 2006.
- 519 Talbot, R. W., Vijgen, A. S., and Harriss, R. C.: Soluble Species in the Arctic Summer
520 Troposphere - Acidic Gases, Aerosols, and Precipitation, J. Geophys. Res., 97, 16531-16543,
521 1992.
- 522 Wang, G., Niu, S., Liu, C., and Wang, L.: Identification of dicarboxylic acids and aldehydes
523 of PM10 and PM2.5 aerosols in Nanjing, China, Atmos. Environ., 36, 1941-1950, 2002.
- 524 Wang, G. H., Kawamura, K., Hatakeyama, S., Takami, A., Li, H., and Wang, W.: Aircraft
525 measurement of organic aerosols over China, Environ. Sci. Technol., 41, 3115-3120, 2007.
- 526 Wang, W., Kourtchev, I., Graham, B., Cafmeyer, J., Maenhaut, W., and Claeys, M.:
527 Characterization of oxygenated derivatives of isoprene related to 2-methyltetrols in



528 Amazonian aerosols using trimethylsilylation and gas chromatography/ion trap mass
529 spectrometry, *Rapid Commun. Mass Spectrom.*, 19, 1343-1351, 2005.

530 Yu, J. Z., Huang, X. F., Xu, J. H., and Hu, M.: When aerosol sulfate goes up, so does oxalate:
531 Implication for the formation mechanisms of oxalate, *Environ. Sci. Technol.*, 39, 128-133,
532 2005.

533 Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M.
534 R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K.,
535 DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimojo, A., Hatakeyama,
536 S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S.,
537 Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen,
538 J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated
539 species in organic aerosols in anthropogenically-influenced Northern Hemisphere
540 midlatitudes, *Geophys. Res. Lett.*, 34, L13801, 2007.

541 Zhang, Y.-L., Liu, J.-W., Salazar, G. A., Li, J., Zotter, P., Zhang, G., Shen, R.-r., Schäfer, K.,
542 Schnelle-Kreis, J., Prévôt, A. S. H., and Szidat, S.: Micro-scale (μg) radiocarbon analysis of
543 water-soluble organic carbon in aerosol samples, *Atmos. Environ.*, 97, 1-5, 2014.

544 Zhang, Y.-L., and Cao, F.: Fine particulate matter (PM_{2.5}) in China at a city level, *Scientific*
545 *Reports*, 5, 14884, 2015.

546 Zhang, Y. L., Huang, R. J., El Haddad, I., Ho, K. F., Cao, J. J., Han, Y., Zotter, P., Bozzetti,
547 C., Daellenbach, K. R., and Canonaco, F.: Fossil vs. non-fossil sources of fine carbonaceous
548 aerosols in four Chinese cities during the extreme winter haze episode of 2013, *Atmos. Chem.*
549 *Phys.*, 15, 1299-1312, 2015a.

550 Zhang, Y. L., Schnelle-Kreis, J., Abbaszade, G., Zimmermann, R., Zotter, P., Shen, R. R.,
551 Schafer, K., Shao, L., Prevot, A. S., and Szidat, S.: Source Apportionment of Elemental
552 Carbon in Beijing, China: Insights from Radiocarbon and Organic Marker Measurements,
553 *Environ. Sci. Technol.*, 49, 8408-8415, 2015b.

554



555 **Table 1.** Average concentrations (ng m^{-3}) and concentration ranges (ng m^{-3}) for straight chain
 556 diacids ($\text{C}_2\text{--C}_{11}$), branched chain diacids ($\text{iC}_4\text{--iC}_6$), unsaturated diacids (M, F and mM),
 557 multifunctional diacids (hC_4 , kC_3 and kC_7), oxoacids ($\omega\text{C}_2\text{--}\omega\text{C}_4$, ωC_9 , and Pyr), and α -
 558 dicarbonyls (Gly and MeGly) of aerosol samples collected by aircraft campaigns over China.

	2003 Summer (inland China)		2004 Spring (inland China)		2002/2003 Winter (coastal China)	
	Range	Mean (SD) ^a	Range	Mean (SD)	Range	Mean (SD)
Oxalic, C_2	36.4-401	183 (111)	76.5-918	286 (216)	13.3-425	92.6 (94.5)
Malonic, C_3	6.3-131	54 (35)	12.2-216	57.5 (47.6)	1.4-79	15 (17.9)
Succinic, C_4	9.4-277	117 (68.2)	16-319	69.1 (69.9)	2.3-87.9	21.4 (19.8)
Glutaric, C_5	20.7-289	159 (79.1)	6.5-73.8	18.1 (16.3)	0.9-26.1	9.7 (7.3)
Adipic, C_6	52.3-135	93.9 (23.2)	5.7-69	19.4 (18.1)	3.7-34.5	13.4 (8.1)
Pimelic, C_7	0-2.5	0.8 (0.7)	n.d.-8.1	1.7 (2)	0.3-7.5	1.9 (1.7)
Suberic, C_8	n.d. ^b	n.d.	n.d.-2.7	0.2 (0.7)	n.d.-11	3.2 (2.9)
Azelaic, C_9	2-13.5	5.6 (3)	2.4-18.2	6.3 (4.3)	2.9-20.6	8.5 (4.8)
Sebacic, C_{10}	0.3-3.6	1.3 (1.0)	n.d.-8.4	3.6 (2.5)	0-6.9	1.1 (1.8)
Undecanedioic, C_{11}	0.8-4.3	2.1 (0.9)	n.d.-4.3	1.5 (1.3)	n.d.	n.d.
Methylmalonic, iC_4	1.2-5.9	3.7 (1.7)	1.1-12.5	4.9 (3)	0-3.9	0.9 (0.9)
Methylsuccinic, iC_5	0.6-10.8	4.4 (3.1)	1.3-27.5	5.9 (6.1)	0.7-23.2	5.9 (5.8)
Methylglutaric, iC_6	n.d.-1.3	0.4 (0.4)	0.4-5.9	1.2 (1.3)	n.d.-2.8	0.7 (0.8)
Maleic, M	1.8-12.5	6.5 (3.6)	3.3-22.3	9.4 (5)	1.6-11.1	5.7 (2.9)
Fumaric, F	0.1-3.9	1.7 (1.1)	0.5-8.4	3.0 (2.1)	0.1-6.2	1.5 (1.5)
Methylmaleic, mM	2.3-15.1	6.3 (3.6)	2.2-18.0	7.4 (3.8)	1.3-8.2	4 (2)
Hydroxysuccinic, hC_4	1.7-12.5	5.3 (3.4)	n.d.-9.3	1.9 (2.2)	n.d.-13.7	1.9 (3.2)
Ketomalonic, kC_3	0.4-9.2	4.2 (2.5)	n.d.-22.8	5.6 (5.3)	n.d.-26	5.1 (5.6)
Ketopimelic, kC_7	0.4-8.2	3.0 (2.3)	n.d.-18.7	4.0 (4.5)	n.d.-3.9	0.6 (0.9)
Total diacids	139-1230	653 (290)	148-1780	507 (402)	40.4-757	193 (164)
n.s. $\text{C}_2\text{--C}_{11}$	128-1160	615(272)	128-1630	464 (371)	31.3-678	167 (149)
Pyruvic acid, Pyr	n.d.-9.6	2.9 (3.0)	0.1-11.4	2.1 (2.8)	0.7-36.5	10 (8.6)
Glyoxylic, ωC_2	8.1-89.6	37.7 (25.2)	8.3-146	46.0 (38.0)	6.7-129	30.6 (28.9)
3-oxopropanoic, ωC_3	0.1-9.7	3.3 (2.4)	0.1-1.1	0.5 (0.3)	n.d.-1.9	0.5 (0.5)
4-oxobutanoic, ωC_4	0-23.1	8.0 (7.0)	6.8-38.9	14.9 (8.5)	0.6-35.5	7.5 (8.6)
9-oxononoic, ωC_9	3.4-36.2	11.6 (8.9)	0.3-20.5	5.8 (5.2)	0.2-5.5	1.8 (1.4)
Total Keto acid	18.7-131	63.5 (36.0)	23.7-178	69.3 (48.5)	12.2-176	50.0 (36.9)
Glyoxal, Gly	0.7-14.8	4.0 (3.6)	0.2-9.5	2.3 (2.5)	0.6-23	4.3 (5.1)
Methylglyoxal, MeGly	0.6-28.2	10.8 (7.7)	0.8-27.3	7.4 (8.3)	2.5-24.3	7.6 (5.6)
Total dicarbonyls	1.3-42.9	14.8 (11.1)	1.7-36.8	9.8 (10.7)	3.1-47.3	11.8 (10.5)
Total	170-1390	731 (329)	174-1990	586 (457)	68.5-980	255 (209)
Gly/MeGly	0.1-1.2	0.4 (0.2)	0.04-1.0	0.4 (0.3)	0.2-0.9	0.5 (0.2)
M/F	1.7-13.9	4.9 (2.9)	1.1-13.8	4.5 (3.1)	1.6-27.4	6.8 (6.2)
$\omega\text{C}_2/\text{C}_2$	0.1-0.2	0.2 (0.03)	0.1-0.3	0.2 (0.04)	0.2-0.8	0.4 (0.1)
C_2/C_4	0.6-6.7	2.0 (1.6)	2.9-5.9	4.6 (0.9)	2.8-13.5	4.6 (2.3)
C_3/C_4	0.2-1.9	0.5 (0.42)	0.7-1.1	0.9 (0.1)	0.4-1.7	0.7 (0.3)
C_5/C_9	5.2-64.6	31.3 (15.6)	1.6-4.3	2.8 (0.7)	0.1-2.7	1.1 (0.6)
C_6/C_9	10.0-41.0	19.8 (7.21)	1.3-4.6	2.8 (0.9)	0.5-2.8	1.6 (0.6)

559 ^aSD denotes standard deviation (1σ); ^bn.d. denotes not detected.



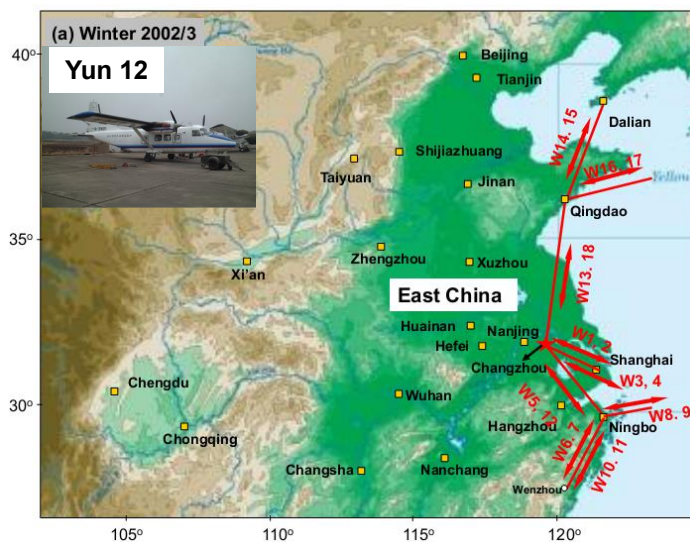
560 **Table 2.** Correlation coefficients (r^2) among oxalic acid (C_2), pyruvic acid (Pyr), glyoxylic acid
561 (ωC_2), glyoxal (Gly) and methylglyoxal (MeGly) detected in aerosol samples from aircraft
562 campaigns during summer 2003, spring 2004 and winter 2002/2003 over China. See Table 1
563 for abbreviations.

Summer 2003					
	C_2	Pyr	ωC_2	Gly	MeGly
C_2	1.00				
Pyr	0.89	1.00			
ωC_2	0.97	0.95	1.00		
Gly	0.75	0.86	0.85	1.00	
MeGly	0.91	0.97	0.97	0.90	1.00

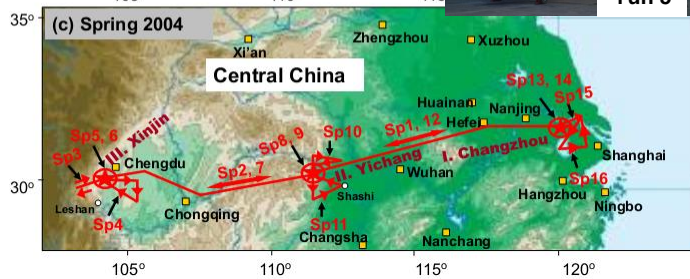
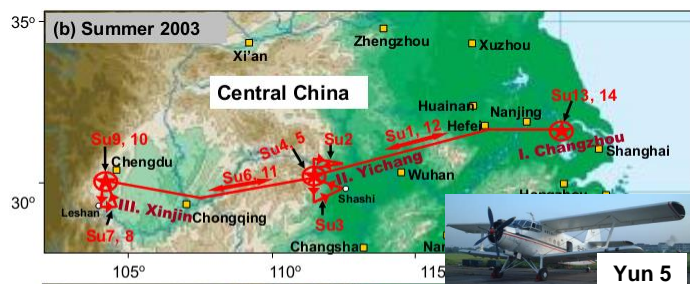
Spring 2004					
	C_2	Pyr	ωC_2	Gly	MeGly
C_2	1.00				
Pyr	0.95	1.00			
ωC_2	0.97	0.93	1.00		
Gly	0.96	0.95	0.97	1.00	
MeGly	0.93	0.92	0.94	0.93	1.00

Winter 2002/2003					
	C_2	Pyr	ωC_2	Gly	MeGly
C_2	1.00				
Pyr	0.70	1.00			
ωC_2	0.98	0.70	1.00		
Gly	0.92	0.69	0.90	1.00	
MeGly	0.85	0.63	0.83	0.94	1.00

564



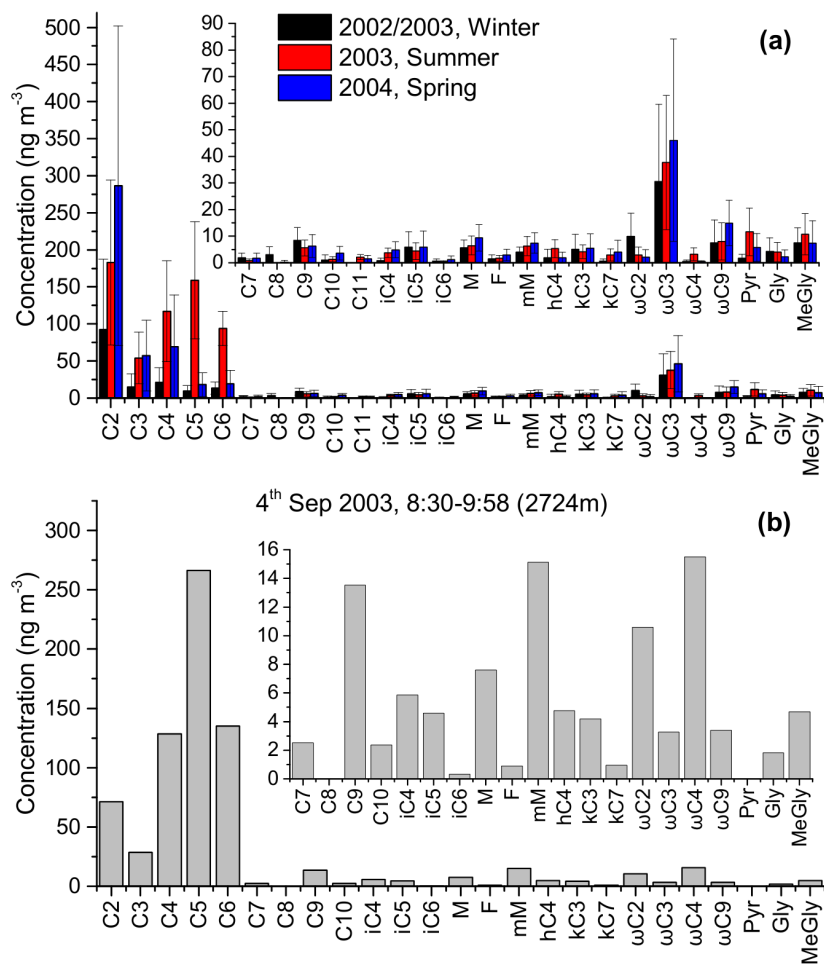
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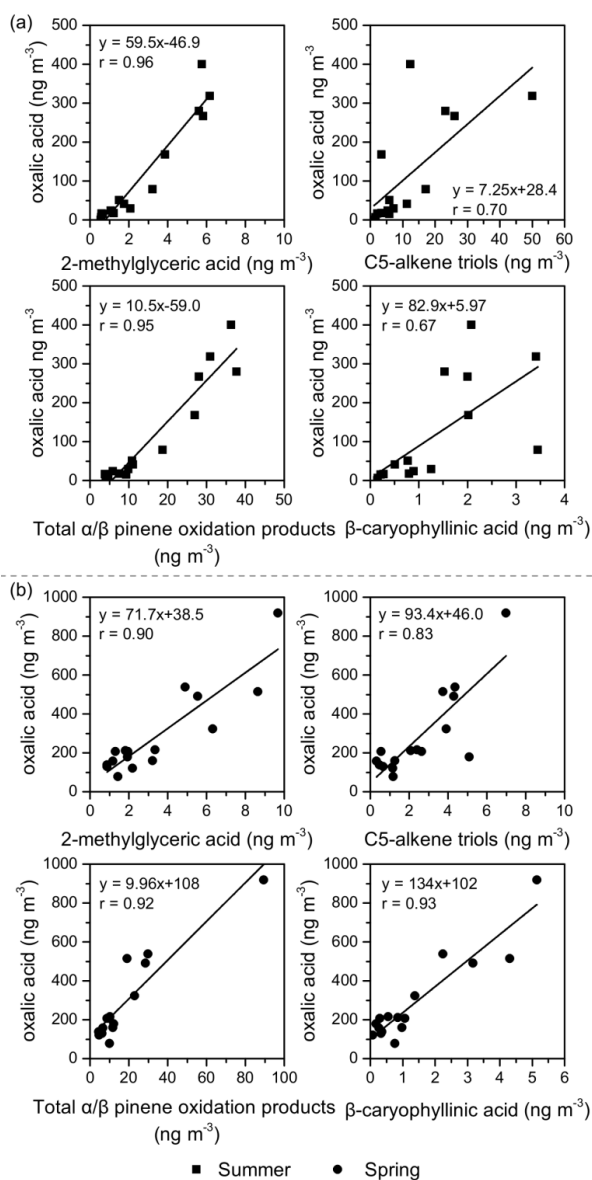
567 **Figure 1.** Tracks of research flights during aircraft measurements over China during (a) winter
568 2002, (b) summer 2003 and (c) spring 2004. The detailed sampling information with flight No.
569 is listed in the Supplementary Table S1. The maps with the flight tracks were drawn by the
570 software of PowerPoint 2010, <https://products.office.com/>.

571



572

573 **Figure 2.** Molecular distributions of straight chain diacids (C₂–C₁₁), branched chain diacids
 574 (iC₄–iC₆), unsaturated diacids (M, F and mM), multifunctional diacids (hC₄, kC₃ and kC₇),
 575 ketoacids (ω C₂– ω C₄, ω C₉, and Pyr), and α -dicarbonyls (Gly and MeGly) in aircraft
 576 measurement over China; (a) averaged concentrations with bars of standard deviation during
 577 winter 2002/2003, summer 2003 and spring 2004; (b) molecular distributions of the measured
 578 compounds in the sample collected on 4th Sep 2003. See Table 1 for abbreviations.

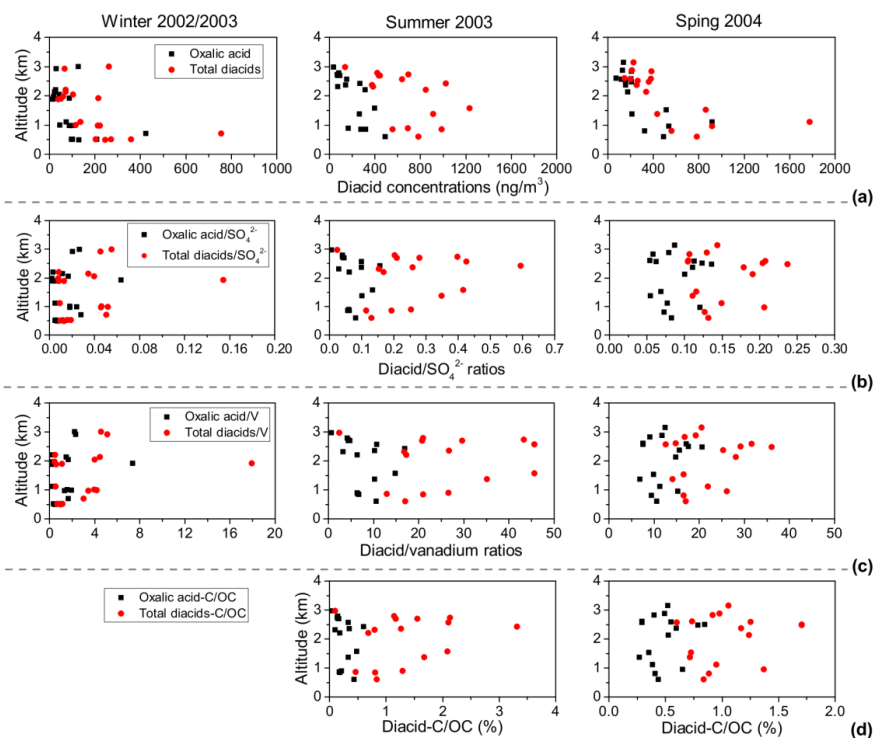


579

580 **Figure 3.** Linear relationship of the concentrations of oxalic acid with the detected tracer
 581 compounds for secondary organic aerosols (SOA) such as isoprene SOA tracers such as 2-
 582 methylglyceric acid and C5-alkene triols (sub-total of cis-2-methyl-1,3,4-trihydroxy-1-butene,
 583 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene), α/β -pinene
 584 SOA tracers (subtotal of 3-hydroxyglutaric acid, pinonic acid, pinic acid, 3-methyl-1,2,3-
 585 butanetricarboxylic acid), and β -caryophyllene SOA tracer (i.e., β -caryophyllinic acid) from
 586 aircraft measurements over China during (a) summer and (b) spring.

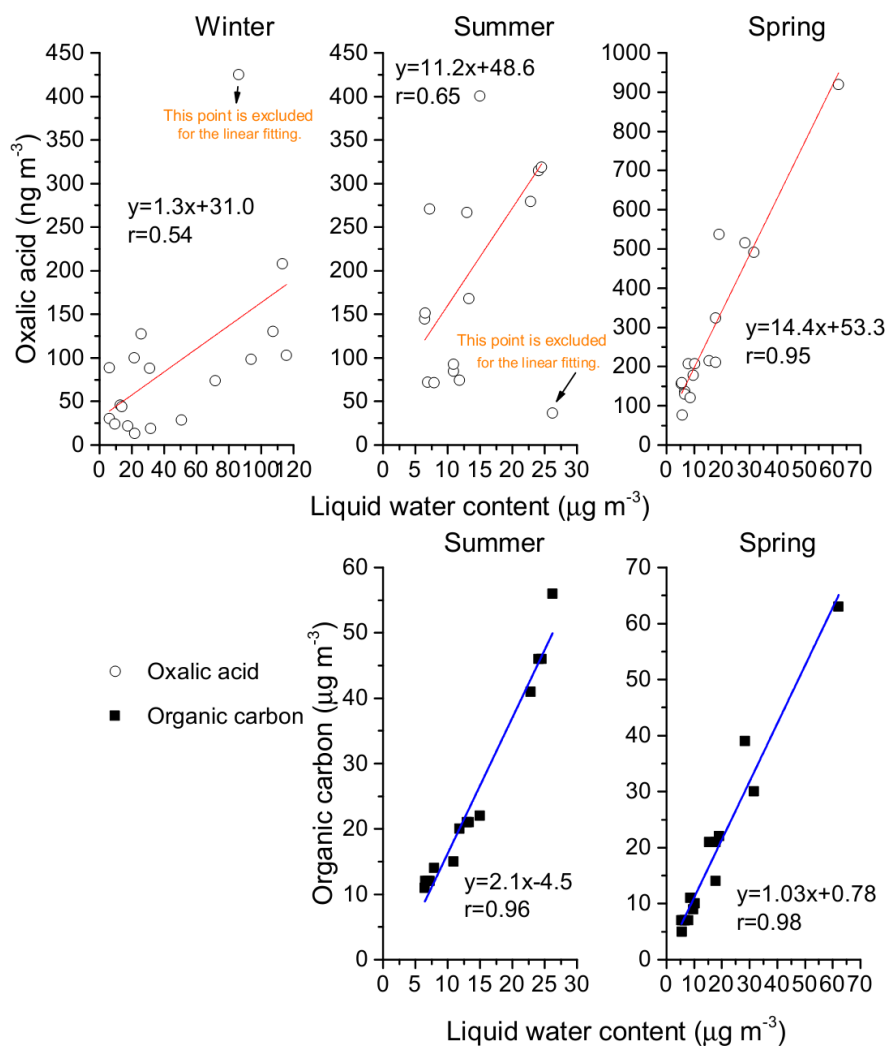


587



588

589 **Figure 4.** Vertical profiles of (a) concentrations of oxalic acid and total diacids, and their
590 relative abundance to (b) sulfate (SO_4^{2-}), (c) vanadium (V), and (d) organic carbon (OC, %) in
591 aerosol samples collected during winter 2002 (left), summer 2003 (middle) and spring 2004
592 (right) aircraft campaigns over China.



593

594 **Figure 5.** The linear fitting of the predicted liquid water content with organic carbon (OC) and
595 oxalic acid aerosols during winter, summer, and spring aircraft measurements over China.