



Title	Dicarboxylic acids, oxocarboxylic acids and alpha-dicarbonyls in atmospheric aerosols from Mt. Fuji, Japan: Implication for primary emission versus secondary formation
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1 **Dicarboxylic acids, oxocarboxylic acids and α -dicarbonyls in atmospheric aerosols from**
2 **Mt. Fuji, Japan: Implication for primary emission versus secondary formation**

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21 **Abstract**

22 Aerosol samples were collected at the summit of Mt. Fuji in July-August 2009 and
23 analyzed for diacids and related compounds together with major ions to decipher the sources
24 and formation process of organic aerosols in the free troposphere. Molecular distributions of
25 diacids showed the predominance of oxalic acid (C₂) followed by succinic (C₄) and malonic
26 (C₃) acids. The average concentration of total diacids is ten times higher in whole-day
27 samples than night-only samples due to the uplift of planetary boundary layer in daytime,
28 suggesting the daytime formation of diacids in the uplifted ground-level air mass along the
29 mountain slope. A strong correlation is found between C₄ and levoglucosan in whole-day and
30 nighttime samples. Liquid water content (LWC) shows strong correlations in nighttime with
31 anthropogenic and biogenic secondary organic aerosol (SOA) tracers (e.g., adipic (0.90,
32 p<0.5) and phthalic acids (0.93, p<0.05) and 3-methyl 2,3,4-trihydroxy-1-butene (0.95,
33 p<0.05), suggesting that aqueous-phase chemistry is important for the formation of water-
34 soluble organic aerosols in the free troposphere. In whole-day samples, LWC is strongly
35 correlated with organic carbon (r=0.97, p<0.05), and isoprene-SOA tracers such as
36 methylthreitol (0.96, p<0.05), methylerythritol (0.97, p<0.05), 2-methylglyceric acid (0.94,
37 p<0.05) and glycolic acid (0.98, p<0.05), suggesting that daytime SOAs are mainly from the
38 oxidation of isoprene emitted from the regional forests on the foothill of Mt. Fuji. A strong
39 correlation between LWC and glycolic acid further suggests that isoprene is the main
40 precursor for the production of oxalic acid via glycolic acid as intermediate. This study
41 supports the heterogeneous formation of diacids in the free troposphere.

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46 **Highlights: Max 85 characters including space per bullet**

47 Molecular distributions of diacids, oxoacids and α -dicarbonyls over Mt. Fuji, Japan.

48 This study represents lower levels of tropospheric organic aerosols in nighttime.

49 Heterogeneous aqueous phase formation of diacids is important in daytime.

50

51 **Key words: Diacids, oxoacids, α -dicarbonyls, acid-catalyzed heterogeneous reaction, Mt.**

52 **Fuji**

53

54 1. Introduction

55 Tropospheric aerosol particles can play essential roles in regional and global climate.
56 They are produced via both natural and anthropogenic processes. Organic constituents in
57 aerosols are recently paid more attention because they are recognized to account a substantial
58 fraction of atmospheric aerosols, up to 50% of particle mass (Seinfeld and Pandis, 1998). In
59 particular, water-soluble organic species can influence the hygroscopic properties of
60 atmospheric aerosols (Boreddy et al., 2014, Kanakidou et al., 2005). Water-soluble organic
61 aerosols may also cause health problems to human (Poschl, 2005)

62 Dicarboxylic acids (diacids) and related compounds are important in the atmosphere.
63 Total diacids account for 5 to 10% of the particulate carbon in the atmosphere (Kunwar and
64 Kawamura, 2014a, b; Kerminen et al., 2000). Oxalic acid and other short chain diacids are
65 produced in the cloud and aerosol by aqueous phase reaction (Warneck, 2003; Carlton et al.,
66 2007). There are various sources of diacids in the atmosphere. Automobile emission, fossil
67 fuel combustion, meat cooking operation, biomass burning, and atmospheric oxidation of
68 biogenic and anthropogenic organic compounds are the main source of diacids in aerosols
69 (Kawamura et al., 1996; Kawamura et al., 2001; Mochida et al., 2003; Legrend et al., 2007;
70 Wang et al., 2013; Deshmukh et al., 2016; Kunwar et al., 2017). Previous studies reported
71 that the presence of dicarboxylic acids in atmospheric particles affect both deliquescence
72 relative humidity and hygroscopicity of the aerosol particles (Cruz and Pandis, 1998; Brooks
73 et al., 2002)

74 Diacids and related compounds have been studied in the urban, marine, and remote
75 areas (Deshmukh et al., 2015, Pokhrel et al., 2015, 2016; Ho et al., 2007; Wang et al., 2010).
76 However, their distributions have been rarely studied in the high mountain regions of the free
77 troposphere (Kawamura et al., 2013), in which aerosols are largely influenced by long-range
78 atmospheric transport. High levels of both primary (POA) and secondary organic aerosols
79 (SOA) with a dominance of diacids were observed at a summit of Mt. Tai located in the
80 North China Plain, where crop-residue burning is very common on the ground level in early
81 summer followed by long-range atmospheric transport (Kawamura et al., 2013).

82 In this study, we performed the observation study on water-soluble organic aerosols at
83 the summit of Mt. Fuji (elevation, 3776 m) in Japan during summer. In nighttime, the summit
84 of Mt. Fuji is present in the free troposphere whereas it is within the planetary boundary
85 layers in daytime. Ground surface aerosols and their precursors can be uplifted along the
86 mountain slope to the summit in daytime, and thus Mt. Fuji represents the free tropospheric
87 air quality of East Asia. Therefore, the summit of Mt. Fuji is considered as an ideal site for

88 the study of organic aerosols interacted between ground level and the free troposphere (Fu et
89 al., 2014). Based on the molecular distributions of diacids, oxoacids, α -dicarbonyls together
90 with major ions, organic and elemental carbon, back trajectory analysis, liquid water content
91 (LWC) and SOA tracers, we discuss the sources and formation mechanisms of diacids and
92 related compounds over Mt. Fuji.

93

94 **2. Experimental**

95 **2.1. Sampling site**

96 Total suspended particle (TSP) samples (n=8) were collected at the summit of Mt.
97 Fuji (35.4° N, 138.7° E) during the summer of 2009. Mt. Fuji is the highest mountain in
98 Japan and is facing the Pacific coast of Honshu Island (Figure 1). Sampling was performed
99 for one month from 27 July to 26 August 2009 when climbing is permitted. Samples were
100 collected using two high-volume samplers (Kimoto AS- 810B) with a flow rate of 1.0 m³ min
101 ⁻¹ using pre-combusted (450 °C for 6 h) quartz fiber filters (20 cm × 25 cm, Pallflex
102 2500QAT-UP). Nighttime samples (n=4, MF07–10) were collected during 23:00–8:00 from
103 27 July to 12 August on a basis of 3 to 4 days. Whole-day samples (n=4, MF12–15) were
104 collected on a basis of 2 to 4 days during 13–26 August. After the sampling, each filter was
105 placed in a pre-combusted (450 °C for 6 hrs) glass jar with a Teflon-lined screw cap and kept
106 in a freezer room at -20 °C before analysis. A field blank was collected by placing a clean
107 filter on the filter cartridge for a few seconds without pumping.

108 **2.2. Chemical analysis**

109 Filter samples were analyzed for water-soluble diacids, oxoacids, and α -dicarbonyls by
110 the method reported previously (Kawamura and Ikushima, 1993; Kunwar and Kawamura,
111 2014b). A filter aliquot with known area was extracted with organic-free pure water.
112 Carboxylic acids and α -dicarbonyls in the extracts were derivatized with 14% BF₃/n-butanol
113 to butyl esters and/or dibutoxy acetals. Those derivatives were determined using capillary gas
114 chromatography (GC; HP 6890). The GC peaks were identified by comparing GC retention
115 times with those of authentic standards, and the peak identifications were confirmed by mass
116 spectral examination using a GC/mass spectrometry (GC/MS) system. Both laboratory and
117 field blanks were analyzed. The concentrations of all species reported here are corrected for
118 blanks. We also performed the recovery test by spiking authentic dicarboxylic acids to quartz
119 filter. The recoveries of spiked diacids were 90% for oxalic acid (C₂) and more than 97% for

120 C₃, C₄, C₅ and C₆ diacids. The standard error of reproducibility in the measurements of major
121 diacids (C₂, C₃, C₄, C₅, and C₆) was ca. 10%.

122 Levoglucosan and isoprene- and monoterpene-SOA tracers were measured by GC/MS
123 after derivatization of the solvent extracts (dichloromethane/methanol 2:1) with N,O-
124 bis(trimethylsilyl)trifluoroacetamide. The methods and the data are reported in Fu et al.
125 (2014).

126 Major cations and anions were measured using an ion chromatograph (761 Compact IC,
127 Metrohm, Switzerland). A detailed method can be found in Kunwar and Kawamura (2014a).

128 2.2. Meteorological Parameter

129 No rainfall events were recorded during the campaign period. Fog and cloud events
130 occurred in nighttime and early in the morning. Figure 2 shows the changes in meteorological
131 parameters such as average sunshine hours, relative humidity and ambient temperature
132 recorded during the sampling period.

133 3. Results and Discussion

134 3.1. Molecular distributions of dicarboxylic acids, oxocarboxylic acids, benzoic acid and 135 α -dicarbonyls

136 Table 1 summarizes the average concentrations of diacids, oxoacids, benzoic acid and
137 α -dicarbonyls with standard deviations in the TSP samples collected from Mt. Fuji. We
138 detected a homologous series of α , ω -dicarboxylic acid (C₂-C₁₂), unsaturated diacids (maleic,
139 M; fumaric, F; methylmaleic, mM; phthalic, Ph; isophthalic, iPh and terephthalic, tPh),
140 multifunctional diacids (hydroxysuccinic acid, hC₄; ketomalonic, kC₃; and ketopimelic, kC₇),
141 ω -oxocarboxylic acids (ω C₂- ω C₉), pyruvic acid (Pyr), and α -dicarbonyls (glyoxal, Gly and
142 methylglyoxal, MeGly) in nighttime and whole-day samples. Benzoic acid was also detected
143 with higher concentrations in whole-day than nighttime samples (Table 1).

144 The total concentrations of diacids ranged from 10 to 84 ng m⁻³ (43±28 ng m⁻³) in
145 nighttime and 180-450 ng m⁻³ (308±103 ng m⁻³) in whole-day samples. Except for one
146 nighttime sample (MF10, August 8-12), oxalic acid (C₂) was found as the most abundant
147 species followed by succinic (C₄) and malonic (C₃) acids. MF10 sample showed a
148 predominance of C₄, followed by C₂ and C₃ (Fig. 3c). During nighttime, glutaric (C₅) or
149 adipic (C₆) acid is most abundant after C₃, while in whole-day samples phthalic acid (Ph) and
150 C₆ are most abundant after C₃ (Figure 3). The average nighttime concentration of C₂ (18.4 ng
151 m⁻³) is an order of magnitude lower than that of whole-day samples (160 ng m⁻³). This result
152 suggests that air masses are totally different between day- and nighttime samples. In daytime,

153 air masses are uplifted from the lowland around Mt. Fuji to the summit whereas the
154 mountaintop is within the free troposphere without the input of local aerosols. This result also
155 suggests more secondary production of diacids in daytime by the oxidation of various organic
156 precursors.

157 During nighttime, average concentrations of C_2 and C_4 are similar ($C_2=18 \text{ ng m}^{-3}$,
158 $C_4=15 \text{ ng m}^{-3}$). This characteristic is different from ambient aerosols from ground levels
159 (Kawamura and Bikkina, 2016). However, the concentration of C_3 is 3.3 times lower than C_2 .
160 In contrast, in whole-day samples, the concentration of C_2 is 2.2 times higher than C_4 and 2.5
161 times higher than C_3 . C_3 is partly derived from the incomplete combustion of fossil fuels and
162 biomass burning but largely produced by photochemical oxidation of C_4 in the atmosphere
163 (Kawamura and Ikushima, 1993). Thus, C_4 become more abundant than C_3 in ambient
164 aerosols from biomass burning, vehicular and biogenic emissions (Fu et al., 2012; Kawamura
165 and Kaplan, 1987; Kundu et al., 2010). In one nighttime sample (MF10), collected on August
166 8 to 12, we found a very high concentration of C_4 followed by C_2 and C_3 (Figure 3c). Similar
167 molecular distribution has been reported in the aerosols collected at Syowa Station in
168 Antarctica during summer (Kawamura et al., 1996), over the Arctic Ocean during late
169 summer (Kawamura et al., 2012) and the central northern North Pacific near the Aleutian
170 trench (Hoque et al., 2015), where photochemical degradation of oxalic acid may occur in
171 aqueous phase of aerosols in the presence of Fe (Kawamura et al., 2010).

172 Based on the laboratory experiment, Pavuluri and Kawamura (2012) reported that
173 oxalic acid decomposes in the presence of Fe under the irradiation of UV light, but it is stable
174 in the absence of Fe. C_3 acid could also decompose in the presence of Fe (III). However, the
175 decomposition rate of its Fe-complex is ca. 20 times lower than that of C_2 (Faust and Zepp,
176 1993). The decomposition of oxalic and malonic acid may be accelerated under foggy
177 conditions with solar irradiation (Kawamura et al., 2012). Kawamura and Kaplan (1987)
178 reported that degradation of malonic acid is more significant than succinic acid in vehicular
179 emissions. C_3 is thermally less stable than C_4 due to reactive hydrogen of methylene-chain
180 adjacent to two carboxyl groups of malonic acid during the combustion process (Kawamura
181 and Ikushima, 1993). Therefore, C_4 can be abundant in the atmosphere. However, C_4 can
182 serve as a precursor of C_3 via photochemical oxidation (Kawamura and Ikushima, 1993).

183 We also detected a series of ω -oxocarboxylic acids (C_2 - C_9) and pyruvic acid. Among
184 the oxoacids, 4-oxobutanoic acid (ωC_4) is the most abundant in nighttime samples followed
185 by 7-oxoheptanoic acid (ωC_7), 3-oxopropanoic acid (ωC_3), and glyoxylic acid (ωC_2) (Table

186 1). This molecular characteristic of oxoacids is in contrast to those of previously studied
187 aerosols from marine, mountainous, urban areas from low- and mid-latitudes, in which ωC_2 is
188 the most abundant oxoacid (Kawamura and Yasui, 2005, Kunwar and Kawamura, 2014b;
189 Kawamura et al., 2013; Kundu et al., 2010; Kunwar et al., 2016a; Pavuluri et al., 2010; Wang
190 et al., 2010). A very high concentration of ωC_2 was reported over Mt. Tai (106 ng m^{-3} ,
191 Kawamura et al., 2013) and Mt. Hue (26 ng m^{-3} , Meng et al., 2014). However, ωC_2 was
192 below the detection limit in most nighttime samples. The predominance of ωC_2 and ωC_4 were
193 frequently reported in Arctic aerosol (Kawamura et al., 1996) and Greenland ice core samples
194 (Kawamura et al., 2001). The higher concentration of ωC_4 in this study during nighttime is
195 due to the biogenic emission from marine unsaturated fatty acids and/or biomass burning by
196 long-range atmospheric transport.

197 In Mt. Fuji aerosols, biogenic, biomass burning and anthropogenic sources may be
198 important. In one nighttime sample (August 8-12), concentration of C_4 is very high,
199 suggesting strong emissions from biogenic, biomass burning and/or vehicular sources. During
200 nighttime, we found strong correlation of both C_4 and ωC_4 with levoglucosan ($r=0.98, 0.96$),
201 2-methyl threitol (2-MT) (0.95, 0.97) and 2-methyl erythritol (2-ME) (0.95, 0.97). The strong
202 correlations of C_4 and ωC_4 with isoprene SOA tracers (2-MT and 2-ME) and levoglucosan
203 suggest that diacids and related compounds are derived from biomass burning and biogenic
204 emission of isoprene. Moreover, ωC_9 also strongly correlate with isoprene-SOA tracers,
205 suggesting the formation from biomass burning and biogenic emission (Table 2). No
206 correlation of biogenic and biomass burning tracers with C_2 is another evident for the mixed
207 sources in Mt. Fuji aerosols. Based on the correlation analysis, we conclude that Mt. Fuji
208 aerosols are influenced from the mixed sources in nighttime.

209 In daytime, there is a large contribution from local biogenic sources in lowlands along
210 the mountain slopes. Thus, concentrations of diacids and related compounds are very high.
211 Back trajectory analyses showed that long-range atmospheric transport is also important. In
212 addition, higher concentration of oxalic acid further confirms that secondary formation is also
213 important. The strong correlations of C_4 with biomass burning tracers (i.e., levoglucosan,
214 $r=0.95$ and dehydroabietic acid, 0.99) during day time suggest that biomass burning (Table 3)
215 is important. Dehydroabietic acid is a biomarker tracer for Gymnosperm (conifer) biomass
216 burning (Simoneit et al., 1999) In whole day samples, ωC_4 showed a strong correlation with
217 oleic acid ($\text{C}_{18:1}$) (0.99) and levoglucosan (0.96) (Table 3). Similarly, ωC_9 shows strong
218 correlations with isoprene-SOA tracers including 2-MT (0.97) and 2-ME (0.95) and oxidation

219 products of α -/ β -pinene including pinic acid (0.97), and 3-hydroxyglutaric acid (3-HGA,
220 0.98). Based on the correlation analysis, we conclude that Mt. Fuji aerosols are largely
221 influenced by the mixed sources, that is, biogenic SOA and biomass burning products.

222 Two α -dicarbonyls (Gly and MeGly) were detected in Mt. Fuji aerosols. Concentrations
223 of glyoxal (Gly) and methylglyoxal (MeGly) are 20 times higher in whole-day than nighttime
224 samples (Figure 3), ranging from 0.00 to 0.25 ng m⁻³ (0.10±0.09 ng m⁻³) and 0.01 to 0.19 ng
225 m⁻³ (0.11±0.06 ng m⁻³) in nighttime and 2.0 to 3.5 ng m⁻³ (2.8±0.60 ng m⁻³) and 0.81 to 4.9 ng
226 m⁻³ (1.9±1.7 ng m⁻³) in whole-day samples. The average concentrations of Gly and MeGly
227 are similar among nighttime samples, while concentration of Gly is 1.4 times higher than
228 MeGly in whole-day samples (Table 1). Being similar to diacids and oxoacids, we found a
229 higher concentration of Gly and MeGly in whole day samples. This result may suggest that
230 anthropogenic (e.g., benzene and toluene) emissions are also important because Gly is often
231 more abundant than MeGly in polluted aerosols collected from China and India (Ho et al.,
232 2007; Pavuluri et al., 2010). However, in the central northern North Pacific influenced by
233 more biogenic source, relative abundance of MeGly is more abundant than Gly (Bikkinia et al.,
234 2014). Mochizuki et al. (2017) reported higher abundance of MeGly in both daytime and
235 nighttime aerosol samples collected in the foothill forest of Mt. Fuji. Figure 4 represents the
236 nighttime and whole day variations of selected diacids, oxoacids and α -dicarbonyls. We
237 found that concentrations of C₄, M, Ph, C₉ and ω C₄ were very high in the nighttime sample
238 (August 8-12). In whole-day sample (August 18-21), higher concentrations of C₂, C₆, M, ω C₂,
239 ω C₉, MeGly, kC₃, Pyr were also obtained.

240 Relative abundance of oxalic acid (C₂%) has been proposed as a tracer to decipher the
241 photochemical aging of organic aerosols because C₂ is produced in the atmosphere by the
242 oxidation of longer chain diacids and other precursor compounds such as aromatic
243 hydrocarbons, isoprene and monoterpenes (Kawamura and Ikushima., 1993; Ervens et al.,
244 2004; Legrand et al., 2007). Laboratory experiment proved that C₂ is formed by the
245 degradation of long-chain diacids such as C₃, C₄, C₆ and C₉ (Enami et al., 2015; Legrand et
246 al., 2007). Figure 5 shows the relative abundances of selected diacids in Σ C₂-C₁₀ diacids and
247 oxoacids to total oxoacids. Relative abundance of C₂ is higher in whole-day (53%) than
248 nighttime samples (48%) (Figure 5a, b). The higher relative abundances of C₂ in whole day
249 samples suggest the more secondary production of oxalic acid during the daytime. Again, the
250 relative abundance of C₄ in nighttime (33%) is higher than the whole day (20%) samples. C₅
251 and C₆, which are tracers for anthropogenic source, showed higher relative abundances (2%

252 and 1%, respectively) during whole-day samples. Long chain diacid such as C_7 is associated
253 with the emission of unsaturated fatty acids from terrestrial higher plants (Kunwar and
254 Kawamura, 2014b). It showed higher abundances in daytime. C_9 is a specific oxidation
255 product of unsaturated fatty acids emitted from micro layers of ocean surfaces for marine
256 emission showed higher abundance during nighttime (Figure 5a). Back trajectories analysis
257 reveals that during nighttime there is an important input of marine air mass in the free
258 troposphere via long-range atmospheric transport (Figure 6a-d).

259 When concentrations of C_2 increased, its relative abundances are generally increased.
260 However, in one sample collected during August 8 to 12, concentrations of C_2 - C_{10} increased,
261 but the relative abundances of oxalic acid decreased. Hence, there may be a degradation of
262 oxalic acid during August 8 to 12 (Please see Figure S1 in supporting information).
263 Contributions of C_2 to C_2 - C_{10} in Mt. Fuji aerosols (48-53%) are lower than those of the aged
264 aerosols from Chichi-jima Island (81%) in the western North Pacific (Mochida et al., 2003b)
265 and Okinawa Island (74%) in the western North Pacific Rim (Kunwar and Kawamura, 2014a).
266 On the other hand, this level is comparable to those reported from the western North Pacific
267 during the period of high biological activity in summer (56%) (Bikkina et al., 2014) and from
268 Tokyo in summer (55%) via photo-oxidation of anthropogenic VOCs (Kawamura and Yasui,
269 2005) and from biogenic sources in a larch forest at the northern slope of Mt. Fuji
270 (Mochizuki et al., 2017). Strong correlations of selected diacids and oxoacids with isoprene-
271 SOA tracers and biomass burning tracer during nighttime and daytime suggest that organic
272 aerosols of Mt. Fuji are originated from both biogenic and anthropogenic sources with an
273 enrichment of oxalic acid but are photochemically less aged.

274 Among oxoacids, the relative abundance of ωC_4 is higher than ωC_2 in nighttime (Figure
275 5c, d). This is in contrast to other studies where higher relative abundance of ωC_2 is reported
276 (Kawamura and Bikkina 2016; Kawamura and Sakaguchi, 1999; Kunwar and Kawamura
277 2016b; Kawamura et al., 2013). In contrast to ωC_2 , relative abundances of ωC_3 , ωC_4 , ωC_7 ,
278 ωC_9 in total oxoacids are higher in nighttime. This result suggests that these ω -oxoacids are
279 produced by the photochemical oxidation of marine-derived unsaturated fatty acids. Relative
280 abundances of pyruvic acid (Pyr) in whole-day aerosols are 3 times higher than nighttime
281 samples, suggesting that photochemical oxidation is important in daytime because Pyr is
282 formed in the atmosphere by the oxidation of biogenic (e.g., isoprene) and anthropogenic
283 aromatic hydrocarbons (Legrand et al., 2007; Kawamura et al., 1996).

284 3.2. Comparison of Mt. Fuji aerosols with previous studies: a global perspective

285 Concentration of oxalic acid (av. 18 ng m^{-3}) during nighttime over Mt. Fuji is several
286 times lower than summertime aerosols reported from Chennai (241 ng m^{-3} , Pavuluri et al.,
287 2010), Delhi (1906 ng m^{-3} , Miyazaki et al., 2009), Raipur, India (778 ng m^{-3} , Deshmukh et al.,
288 2017), Tokyo, Japan (July, 157 ng m^{-3} , Kawamura and Yasui, 2005), 14 Chinese cities (513
289 ng m^{-3} , Ho et al., 2007), Gosan, Jeju Island, Korea (564 ng m^{-3} , Kundu et al., 2010), and
290 Okinawa Island, Japan (96 ng m^{-3} , Kunwar and Kawamura, 2014b). Similarly, concentration
291 of oxalic acid from Mt. Fuji is several times lower than Mt. Tai (1046 ng m^{-3} , Kawamura et
292 al., 2013) and Mt. Hui, China (522 ng m^{-3} , Meng et al., 2014). Again, concentration of oxalic
293 acid in nighttime from Mt. Fuji is ca. 3 times lower than those from the Pacific Ocean
294 (40 ng m^{-3} , Kawamura and Sakaguchi, 1999) and Atlantic Ocean ($45\text{-}50 \text{ ng m}^{-3}$, Fu et al.,
295 2013) and 3.2 times lower than northern slope of Mt. Everest (59.8 ng m^{-3} , Cong et al., 2015).

296 Thus, this study from the summit of Mt. Fuji provides the lowest concentrations of short
297 chain diacids in the atmosphere of East Asia, especially during night when the mountaintop is
298 far above the planetary boundary layer. The low level of oxalic acid over Mt. Fuji could be
299 explained by the removal through both dry and wet depositions, as well as photochemical
300 degradation of oxalic acid in the presence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions in aerosols. Thus, we conclude
301 that nighttime aerosols over Mt. Fuji provide background concentrations of diacids and
302 related compounds in the free troposphere of the Northern Hemisphere.

303 3.3. Nighttime and daytime chemistry

304 During nighttime, C_2 is strongly correlated with C_3 ($r=0.95$). Similarly, C_4 shows good
305 correlations with C_9 (0.96), isoprene-SOA tracers such as 2-MT (0.95), and Ph (0.97),
306 suggesting that C_4 is originated from both biogenic and anthropogenic sources. A strong
307 correlation (0.98) between levoglucosan and C_4 again suggest that these low molecular
308 weight diacids over Mt. Fuji are influenced by biogenic emissions of unsaturated fatty acids,
309 isoprene-oxidation products, plastic- and biomass-burning products during nighttime via
310 long-range atmospheric transport.

311 Recently, laboratory and field studies have shown that aqueous phase photo-oxidations
312 of isoprene and other precursors are the main formation pathway of SOA and small diacids
313 (Carlton et al., 2006; Ervens et al., 2011; Myriokefalitakis et al., 2011). In addition, during
314 atmospheric transport organic compounds (e.g., aromatic hydrocarbons, cyclic olefins and
315 unsaturated fatty acids) emitted from anthropogenic and biogenic sources can degrade to
316 result in Gly, MeGly, Pyr and ωC_2 and finally in oxalic acid via in-cloud oxidation (Carlton

317 et al., 2007; Charbouillot et al., 2012; Ervens et al., 2004; Legrand et al., 2007). The strong
318 correlations of Gly with Pyr (0.99) and ωC_2 (0.95) suggest that include oxidation process is
319 important. However, there is no correlation ($r=0.01$) between C_2 and ωC_2 , suggesting a
320 presence of various sources of oxalic acid over the mountaintop during nighttime.

321 Isoprene and α - β -pinenes and aromatic hydrocarbons can produce both MeGly and
322 Gly (Legrand et al., 2007; Meng et al., 2013). During daytime, emissions of isoprene and
323 α / β -pinenes are significant in the forest (Fu and Kawamura, 2011). MeGly presents strong
324 correlations with 2-ME ($r=0.95$), 3-hydroxy glutaric acid (3-HGA) (0.99) and pinic acid
325 (0.96). Both pinic acid and 3-HGA are SOA tracers formed by the oxidation of α - β -pinenes
326 (Claeys et al., 2007; Fu et al., 2014). We found strong correlations of MeGly with Pyr (0.94,
327 $p<0.05$), glycolic acid (0.94, $p<0.05$), and ωC_2 (0.95, $p<0.05$), suggesting a heterogenous
328 aqueous phase oxidation of short chain diacids. Very strong negative correlation (-1.0)
329 between Gly and ωC_2 was observed in whole-day samples, suggesting a different source or
330 different reaction mechanisms for these species. C_9 diacid, a tracer of biogenic source showed
331 a strong negative correlation (-0.95) with Gly, suggesting that daytime Gly is derived mainly
332 by the oxidation of aromatic hydrocarbons emitted by anthropogenic sources.

333 A strong linear correlation between C_2 and SO_4^{2-} was found for nighttime samples
334 ($r=0.99$), which is consistent with the measurements observed in other mountainous region
335 (Meng et al., 2014) and Chinese cities (Wang et al., 2017), indicating that oxalic acid and
336 sulfate are both formed via a similar formation pathway (Warneck, 2003). However, we did
337 not find such a good correlation between C_2 and SO_4^{2-} ($r=0.40$) in whole-day samples over Mt.
338 Fuji. The correlations of C_2 with MeGly, ωC_2 and Pyr are not strong; this suggest that there
339 are various sources of C_2 for whole-day samples such as biogenic emissions of unsaturated
340 fatty acids, isoprene, monoterpenes and aromatic hydrocarbons.

341 **3.4. Compositional Changes of diacids and related compounds**

342 Succinic (C_4) acid has been suggested to be a precursor of malonic (C_3) acid
343 (Kawamura et al., 1996). The mean ratio of C_3/C_4 in this study is 1.19 in whole-day versus
344 0.58 in nighttime samples. The nighttime C_3/C_4 ratios are higher than that for vehicular
345 aerosols (average 0.35, Kawamura and Kaplan, 1987), but similar to that of urban aerosols
346 from China (0.61 in winter, Ho et al., 2007). Nighttime C_3/C_4 ratios ranged from 0.18–1.16,
347 and decreased down to 0.18 during August 9 to 12, when Ph and M maximized (Fig. 4g, i),
348 suggesting more influences from anthropogenic emission followed by significant oxidation

349 because M is formed by the oxidation of aromatic hydrocarbon. The relatively high C_3/C_4
350 ratio (1.1) was observed during nighttime of August 4–8 when the air masses were delivered
351 from Philippines via the Pacific Ocean to the sampling site.

352 The higher C_3/C_4 ratios may be caused by photochemical production of C_3 from C_4
353 during a long-range atmospheric transport. However, C_3/C_4 ratios in nighttime (0.18–1.16)
354 and whole-day samples (0.42–1.9) are similar to those (0.2–1.5) from Mt. Tai aerosols
355 (Kawamura et al., 2013), and are much lower than those (up to 10) in remote marine aerosols
356 from the North and Central Pacific (Kawamura and Sakaguchi, 1999), where photochemical
357 transformation is serious. The ratio is low in the fossil fuel combustion and biomass burning
358 aerosols due to thermally unstable nature of malonic acid (Kawamura and Kaplan, 1987;
359 Kundu et al., 2010). Aggarwal and Kawamura. (2008) clearly observed increases in C_3/C_4
360 ratios from the source regions to downwind remote site due to photochemical aging. Figure 7
361 shows a comparison of C_3/C_4 ratios of Mt. Fuji aerosols with the different aerosols from the
362 world. The average C_3/C_4 ratios in this study in nighttime and whole-day samples are 0.57
363 and 1.19, respectively.

364 Nighttime C_3/C_4 ratios are very similar to those reported for the biomass-burning
365 influenced aerosols from Amazonia (nighttime=0.59, Kundu et al., 2010), New Delhi
366 (nighttime=0.58 Miyazaki et al., 2009), north slope of Mt. Everest (0.51, Cong et al., 2015),
367 where biomass burning is an important source of organic aerosols. The C_3/C_4 ratios reported
368 in coastal and remote islands such as Gosan (2.7), Okinawa (2.8) and Chichijima (3.8) are
369 much higher than those from Mt. Fuji (Figure 7). Higher ratios were observed in background
370 site of South Africa (3–5) (Limbeck et al., 2001) and in remote marine aerosols from the
371 equatorial central Pacific (up to 10) (Kawamura and Sakaguchi, 1999). The C_3/C_4 ratios in
372 the whole-day samples from Mt. Fuji are very similar to those in the aerosols from
373 summertime Southern 14 Chinese cities (1.12, Ho et al., 2007), summertime Chennai, India
374 (1.3, Pavuluri et al., 2010) and Tanzania (dry season=1.0 and wet season=1.3 for PM_{10} , dry
375 season=0.81 and wet season=0.72 for $PM_{2.5}$, Mkoma and Kawamura, 2013). These
376 comparisons demonstrate that mountaintop aerosols over Mt. Fuji are experienced
377 photochemical aging during the uplift transport of ground level aerosols. However, its levels
378 are less serious than remote marine aerosols in the central equatorial Pacific.

379 Both C_9/Ph and C_9/C_6 ratios can be used to evaluate the source strength of biogenic
380 versus anthropogenic source for dicarboxylic acids and related compounds (Kunwar et al.,

2014b). C₆ and Ph are produced by the oxidation of anthropogenic cyclohexene and aromatic hydrocarbons such as naphthalene (Hatakeyama et al., 1987; Kawamura and Ikushima, 1993). In contrast, C₉ is mainly derived by the oxidation of biogenic unsaturated fatty acids containing a double bond predominantly at C-9 position (Kawamura and Gagosian, 1987; Kunwar et al., 2017). In nighttime, one sample (MF-07) collected during July 27-30 showed very high C₉/C₆ ratios (28) when concentration of Ph is below detection limit and back trajectory analysis revealed that air masses are delivered from both marine and continental areas. Except for MF-07, average C₉/C₆ and C₉/Ph ratios in nighttime are 0.81 and 4.1, respectively, whereas those of whole-day samples are 1.21 and 0.13, respectively. Very high C₉/C₆ ratio (4.1) in whole-day samples is mainly attributed to a strong vegetational activity in the foothill forest of Mt. Fuji in daytime. The average C₉/C₆ value of 4.1 at the mountaintop is higher than those from other mountain areas in summer such as Central Himalaya (2.1) (Hedge and Kawamura, 2012), northern slope of Mt. Fuji (3.1) (Mochizuki et al., 2017) and Mt. Tai (1.4) (Kawamura et al., 2013). These comparisons emphasize that organic aerosols over Mt. Fuji are largely influenced by biogenic emissions in daytime.

Field observations and model simulation suggested that the concentration ratio of particulate Gly/MeGly is about 1:5 when biogenic sources are predominant whereas it is about 1:1 when anthropogenic sources are predominant (Meng et al., 2014; Fu et al., 2008 Volkamer et al., 2007; Zhao et al., 2006). The global production ratios of Gly and MeGly are about 1:1 for anthropogenic sources and 1:5 for biogenic sources and uptake coefficients of Gly and MeGly by particles are similar (Fu et al., 2008). In nighttime, the average Gly/MeGly ratio is 1:1, which is very similar to the anthropogenic sources. Although biogenic emission is significant in daytime, the average Gly/MeGly ratio is 1:0.67. One reason for the higher ratio is the life time of MeGly (1.6 h), which is shorter than Gly (2.9 h). Very low Gly/MeGly ratios were observed in the Mt. Tai atmosphere in daytime (1:5.1) and nighttime (1:4.8), which are associated with biogenic sources (Meng et al., 2018). This comparison again demonstrates the importance of biogenic sources on Mt. Fuji aerosols.

The contribution of oxalic acid to OC (C₂-C/OC ratio) in this study ranged from 0.43 to 5.8% (ave., 3.5±2.3%) in nighttime and 2.2 to 5.1% (3.4±1.2%) in whole-day samples. Interestingly, C₄-C/OC ratio (3.8±3.4%) in nighttime is higher than those of oxalic acid (ave., 3.5±2.3%), which suggests a large production of succinic (C₄) acid in the free troposphere. Average total diacid-C/OC is higher during nighttime (10±8%) than whole-day (8.1±3.9%) samples. The average total diacid-C/OC in this study (9.1%) is higher than those reported for

414 aerosols from Sapporo (4.8%) (Aggarwal and Kawamura 2008), New Delhi (1.0%)
415 (Miyazaki et al., 2009), Chennai (5.9%) (Pavuluri et al., 2010), and summertime Okinawa
416 (3.4%) (Kunwar and Kawamura, 2014b). However, this ratio is lower than those from the
417 Indian Ocean (13.5%) (Fu et al., 2013), California Coast (14.5-22.9%) (Fu et al., 2013), and
418 the Atlantic Ocean (14.5-16.5%) (Fu et al., 2013). The diacids-C/OC (av. 9.1%) from this
419 study is higher than the mountain aerosols from Mt. Tai (diacid-C/TC, 2.4%,) (Kawamura et
420 al., 2013) and Mt Hui (6.5%) (Meng et al., 2014).

421 **3.5. Source apportionment of diacids and related compounds**

422 To decipher the source region of air masses, we performed backward trajectory analysis
423 (BTA). Figure 6 shows the results of BTA for nighttime and whole-day samples. Results of
424 BTA predict that most of the air masses delivered during nighttime are originated from
425 marine regions and the Asian continent, whereas during daytime most of the air masses are
426 originated from East Asia.

427 Isoprene (2-methyl-1,3-butadiene, C_5H_8) is emitted from deciduous forest in daytime.
428 Due to the presence of a double bond, it is highly reactive to oxidants such as OH, O_3 , and
429 NO_3 and degrades to result in secondary organic aerosols (SOA) (Carlton et al., 2006, 2009;
430 Claeys et al., 2004). Isoprene emission is dependent on light and temperature (Tambunana et
431 al., 2006), whereas monoterpene emission is not (Fu and Kawamura, 2011 and reference
432 therein). During daytime, the valley breeze can transport large amounts of ground surface
433 biogenic and anthropogenic VOCs together with SO_2 and NO_x .

434 In nighttime, mountain breeze dominates the winds over the foothill of Mt. Fuji, and
435 thus the upward transport of aerosols from the ground surface is negligible. Thus, the
436 tropospheric aerosols over the summit of Mt. Fuji are mainly derived by long-range
437 atmospheric transport from different source regions in which marine and biomass burning-
438 derived organic aerosols are present.

439 Both isoprene- and monoterpene-SOA tracers can be oxidized to oxalic acid (Jaoui et al.
440 et al., 2005; Kleindienst et al., 2007; Koch et al., 2000; Legrand et al., 2007; Meng et al., 2014;
441 Pacifico et al., 2011). Thus, it is meaningful to calculate the ratios of C_2 to isoprene- and
442 monoterpenes-SOA tracers. Although isoprene emission is higher in daytime, we found
443 higher $C_2/2$ -MT and $C_2/2$ -ME ratios in nighttime (Figure 8). The higher nighttime ratios
444 suggest that the formation of diacids and related compounds is significant in the free
445 troposphere. Emission of isoprene is light dependent while that of monoterpenes is light
446 independent (Fu and Kawamura, 2011 and references therein). However, the higher ratio in

447 nighttime aerosols suggest that isoprene is emitted in daytime and accumulated in the free
448 troposphere as its oxidized forms and is finally degraded to result in C₂ in the presence of
449 oxidants. This study suggests that large amount of SOA remains in the troposphere, which
450 can further oxidize to small chain diacids and related compounds. Heald et al. (2005) reported
451 that large amounts SOA are present in the free troposphere.

452 3.6. Sources and formation of sulphate and nitrate in mountain aerosols

453 Ohara et al. (2007) reported an emission inventory for Asia (Regional Emission
454 inventory in Asia) for the period 1980–2020 with estimated emission ratios of NO_x to SO_x
455 of 1:1.9 from power plants, 1:2 from industry, 1:3.7 from domestic coal burning (mean NO_x
456 to SO₂ = 1:1.3). [NO₃⁻]/[SO₄²⁻] ratios provide the information on relative contribution of
457 different anthropogenic activities. The ratio of greater than 1 indicates more contribution of
458 NO₃⁻ emitted from automobile sources such as vehicular emissions, whereas ratio less than 1
459 indicates the contribution of SO₄²⁻ emitted from stationary sources such as industrial activities
460 (Arimoto et al., 1996). Sulphur can be emitted from both marine and non-marine sources.
461 Keene et al. (1986) and Hawley et al. (1988) suggest that long term oceanic salinity is stable
462 enough to estimate the sea salt sulphate (ss) and non-sea salt sulphate (nss) based on the mass
463 concentrations of the reference species sodium in seawater. nss-SO₄²⁻ can be calculated as
464 $[nss-SO_4^{2-}] = [SO_4^{2-}] - (0.25 \times [Na])$. The mean [NO₃⁻]/[nssSO₄²⁻] ratios in nighttime and
465 whole-day samples from Mt. Fuji are 0.19±0.16 and 0.13±0.16, respectively. Similar ratios
466 during nighttime and whole-day samples suggest that stationary source emissions contribute
467 significantly in the study site.

468 Due to the high abundances of SO₄²⁻ and NO₃⁻, aerosols show acidic nature. SO₄²⁻
469 and NO₃⁻ ions are produced by the oxidation of gaseous precursors (SO₂ and NO_x) in the
470 atmosphere and are neutralized by mineral aerosols (Ca²⁺ and Mg²⁺ and NH₄⁺) (Han et al.,
471 2007). Ca²⁺ is primarily emitted from soil and dust and largely presents in coarse mode
472 particles. The strong correlation between SO₄²⁻ with Ca²⁺ (r=0.97) in nighttime suggest that
473 aerosols are neutralized by alkaline species such as Ca²⁺. Ca²⁺ can adsorb SO₂ in the presence
474 of water and make a thin film of SO₄²⁻ around its surface. Hence, heterogeneous aqueous
475 phase reaction is very important in nighttime samples. Both NH₄⁺ and SO₄²⁻ exist in fine
476 mode (Kulshrestha et al., 1995, Kunwar and Kawamura, 2014). The strong correlation (0.97)
477 between nss-SO₄²⁻ and NH₄⁺ suggests that NH₄⁺ plays a major role to neutralize the acidic
478 species during daytime or they are derived from similar sources.

479 The acid neutralization capacity of different cations can also be estimated by
480 calculating neutralization factors (NF) with respect to particular cation. The calculation of NF

481 is based upon the facts that NO_3^- and SO_4^{2-} are the major acidifying anions and Ca^{2+} , NH_4^+ ,
482 Mg^{2+} and K^+ are major acid-neutralizing cations in aerosols. The neutralization factor can be
483 calculated as:

484 $\text{NF}(\text{Ca}^{2+}) = [\text{Ca}^{2+}]/[\text{SO}_4^{2-}] + 2[\text{NO}_3^-] \dots \dots \dots (2)$

485 $\text{NF}(\text{Mg}^{2+}) = [\text{Mg}^{2+}]/[\text{SO}_4^{2-}] + 2[\text{NO}_3^-] \dots \dots \dots (3)$

486 $\text{NF}(\text{NH}_4^+) = [\text{NH}_4^+]/2[\text{SO}_4^{2-}] + [\text{NO}_3^-] \dots \dots \dots (4)$

487 We observed that Ca^{2+} , Mg^{2+} and NH_4^+ are the major neutralizing components with
488 average neutralization factors of 0.067 ± 0.01 , 0.02 ± 0.03 and 0.15 ± 0.12 in nighttime, and
489 0.09 ± 0.09 , 0.05 ± 0.09 and 0.09 ± 0.05 in whole-day samples. These results suggest that,
490 during nighttime NH_4^+ plays the major role in neutralizing aerosols, whereas Ca^{2+} and NH_4^+
491 act as major neutralizing species in daytime.

492 **3.7. Influences of liquid water content and relative humidity for the formation of diacids**
493 **and related compounds**

494 He et al. (2013) and Liu et al. (2012) reported various factors that influence SOA
495 formation in clouds. These studies suggested that liquid water content (LWC) is an important
496 factor that drives the incloud production of SOA. In this context, it is important to investigate
497 whether the aerosol LWC could be a principal factor in mountaintop SOA. Here, we
498 estimated the LWC using ISORROPIA-II model for both nighttime and whole-day aerosol
499 samples (Nenes et al., 1998; Deshmukh et al., 2016). We also investigated the relationships
500 between aerosol LWC and measured chemical constituents (e.g., OC, total diacids, and
501 isoprene-SOA tracers) to evaluate the role of LWC in the formation of diacids and related
502 compounds.

503 Deshmukh et al. (2017) found that LWC well correlated with oxalic acid in summer
504 aerosols from India, indicating that aqueous phase formation of C_2 is important. During
505 nighttime, LWC shows strong correlations with anthropogenic tracers such as C_6 and Ph,
506 suggesting that aqueous phase chemistry is also important for the formation of C_6 and Ph.
507 Similarly, we found a very strong correlation of LWC with 3-methyl 2, 3, 4 trihydroxy-1-
508 butene (0.98), which is a SOA tracer produced by the oxidation of isoprene (Fu et al., 2011).
509 The strong correlations of LWC with C_6 , Ph, and 3-methyl 2,3,4-trihydroxy-1-butene, suggest
510 that heterogeneous aqueous phase oxidation is important for the formation of anthropogenic
511 and biogenic SOAs in nighttime because C_6 and Ph are produced by the oxidation of cyclic
512 aliphatic and polycyclic aromatic hydrocarbons while 3-methyl 2, 3, 4 trihydroxy-1-butene is
513 a SOA tracer of isoprene.

514 Kleindienst et al. (2009) reported the SOA formation during the reaction of isoprene +
515 OH in the absence of NO_x and showed the presence of the three isoprene tracer compounds,
516 2-methyl glyceric acid (2-MGA), 2-methylthreitol, and 2-methylerythritol. The isoprene SOA
517 tracer compounds have previously been reported in laboratory irradiations of isoprene (Edney
518 et al., 2005) and from field samples, particularly in areas having strong isoprene emissions
519 (Claeys et al., 2004). While low levels of SOA were detected from isoprene/NO_x irradiations,
520 the tracers were found to increase dramatically along with an increased formation of SOA
521 following the addition of SO₂ with the likely formation of acidic sulfate aerosol in the system
522 (Edney et al., 2005; Surratt et al., 2007; Jaoui et al., 2008). During daytime, LWC is strongly
523 correlated with OC (0.97), 2-MT (0.96), 2-ME (0.97), 2-methyl glyceric acid (0.94) and
524 glycolic acid ($r=0.98$). The higher concentration of SO₄²⁻ in whole-day samples further
525 supports that acid catalyzed heterogeneous aqueous phase reaction is important in daytime for
526 the formation of diacids and related compounds from isoprene. A strong correlation between
527 LWC and glycolic acid further suggests that isoprene is main precursor via glycolic acid for
528 the formation of oxalic acid. However, daytime LWC shows strong negative correlation with
529 Gly (-0.97). Thus, we hypothesize that major pathway for the production of oxalic acid in
530 daytime is acid catalyzed heterogeneous aqueous reaction via glycolic acid.

531 **4. Conclusions**

532 We studied dicarboxylic acids and related compounds in the tropospheric aerosols from
533 the top of Mt. Fuji (3776 m asl), which is faced to the Pacific coast of Honshu Island in Japan.
534 The molecular distributions of diacids showed the predominance of oxalic acid followed by
535 succinic and malonic acids. The relative abundance of C₂ (53%) in daytime samples is higher
536 than that of whole-day samples (48%), whereas the relative abundance C₄ is higher in
537 nighttime (33%) than whole-day samples (20%).

538 Averaged ratio of total diacids-C/OC is higher in nighttime (10.2) than whole-day
539 samples (8.1). The higher ratios suggest that nighttime aerosols are more aged during long-
540 range transport. The averaged total diacids-C/OC in this study (9.1%) is higher than those
541 reported in urban aerosols. However, this value is lower than those of aerosols collected in
542 the remote marine aerosols. Thus, Mt. Fuji aerosols are photochemical more aged than the
543 ground-level continental aerosols but less aged than the remote marine aerosols. For whole-
544 day samples, strong correlations of C₄ with levoglucosan, dehydroabietic acid and isoprene-
545 SOA tracers suggest that diacids have mixed sources over Mt. Fuji. During nighttime, C₄
546 shows good correlations with C₉, isoprene-SOA tracers such as 2-methylthreitol (0.95) and 2-
547 methylerythritol (0.95) and also Ph (0.97), suggesting the C₄ is involved with both biogenic

548 and anthropogenic sources. Concentration ratios of diacids/isoprene-SOA tracers are higher
549 in nighttime than whole-day samples, whereas the ratios of diacids/monoterpenes-SOA
550 tracers showed the opposite trend.

551 This study from Mt. Fuji provides background concentrations of short chain diacids in
552 the free troposphere of East Asia, especially in nighttime when the mountaintop is far above
553 the planetary boundary layer. Strong correlations of LWC with OC ($r=0.97$), 2-MT (0.96), 2-
554 ME (0.97), 2-methylglyceric acid (0.94) and glycolic acid (0.98) together with higher
555 concentration of SO_4^{2-} in daytime support that acid catalyzed heterogeneous aqueous phase
556 reaction is important for the formation of diacids and related compounds from isoprene.
557 During nighttime, LWC shows strong correlations with anthropogenic (e.g., C_6 and Ph) and
558 biogenic SOA tracers (e.g., 3-methyl 2,3,4-trihydroxy-1-butene), suggesting that aqueous
559 phase chemistry is important for the formation of C_6 and Ph and biogenic SOA.

560

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845 Figure captions:

846 Figure 1. Geographical location of Mt. Fuji, Japan.

847 Figure 2. Meteorological parameters (a) average sunshine (hr), (b) relative humidity (%), and
848 (c) temperature (°C) recorded during study period over Mt. Fuji.

849 Figure 3. Molecular distributions of straight chain diacids (C₂-C₁₂), branched chain diacids
850 (iC₄-iC₆), unsaturated diacids (M, mM, F, Ph, iPh, and tPh), multifunctional diacids (hC₄,
851 kC₃ and kC₇), oxoacids (ω C₂- ω C₉, and pyruvic), and α -dicarbonyls (Gly and MeGly) in
852 aerosols collected from Mt. Fuji for (a) average nighttime, (b) average whole day and (c)
853 August 8/8-12 samples. The error bars represent the standard deviation.

854 Figure 4. Nighttime and whole day variations of (a) oxalic acid (C₂), (b) malonic acid (C₃),
855 (c) succinic acid (C₄), (d) glutaric acid (C₅), (e) adipic acid (C₆), (f) azelaic acid (C₉), (g)
856 malic (M), (h) fumaric (F), (i) phthalic acid (Ph) and (j) ketomalonic acid (kC₃), (k)
857 ketopimelic acid (kC₇), (l) hydroxysuccinic acid (hC₄), (m) glyoxylic acid (ω C₂), (n) 9-
858 nonanoic acid (ω C₉), (o) 4-oxobutanoic acid (ω C₄), (p) pyruvic acid (Pyr), (q)
859 methylglyoxal (MeGly), and (r) glyoxal (Gly) in aerosols collected from Mt. Fuji, Japan.

860 Figure 5. Relative abundances (%) of individual diacid during (a) night-time and (b) whole
861 day, and individual oxoacid during (c) night-time and, (d) whole day samples in aerosols
862 collected from Mt. Fuji, the highest peak of Japan. Please refer to Table 1 for diacid and
863 oxoacid identities.

864 Figure 6. Five-day backward trajectory analysis for (a) 7/27-7/30, (b) 7/30-8/4, (c) 8/4-8/8,
865 (d) 8/4-8/12 (e) 8/12-8/15 (f) 8/15- 8/18 (g) 8/18- 8/21 and (h) 8/18- 8/21. Backward
866 trajectories at 3800m above sea level were drawn with the NOAA HYSPLIT model.

867 Figure 7. Comparison of C₃/C₄ ratio in aerosols collected from Mt. Fuji with the different
868 locations of the World.

869 Figure 8. Nighttime and whole-day variations in concentration ratios of oxalic acid to
870 isoprene and monoterpene SOA tracers (a) C₂/2-methylthreitol, (b) C₂/2-
871 methylerythreitol, (c) C₂/pinic acid, (d) pinonic acid, (e) C₂/3HGA and (f) C₂/C_{18:1} in
872 aerosols collected from Mt. Fuji, Japan.

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876 Table 1. Concentrations (ng m⁻³) of diacids, oxoacids, and α -dicarbonyls in the TSP samples collected from Mt.

877 Fuji, Japan

Species	Nighttime		Whole-day	
	Min-Max	AV \pm STD	Min-Max	AV \pm STD
		Diacids		
Oxalic, C ₂	4.4-30	18 \pm 9.0	103-206	160 \pm 37
Malonic, C ₃	1.4-8.0	5.5 \pm 2.5	33-63	54 \pm 12
Succinic, C ₄	3.5-37	15 \pm 14	24-136	63 \pm 44
Glutaric, C ₅	0.17-1.4	0.79 \pm 0.48	3.7-7.6	5.9 \pm 1.6
Adipic, C ₆	0.01-0.76	0.46 \pm 0.32	2.2-4.0	2.9 \pm 0.72
Pimelic, C ₇	0.00-0.12	0.06 \pm 0.05	0.51-0.76	0.65 \pm 0.10
Suberic, C ₈	0.09-0.41	0.21 \pm 0.13	0.16-0.64	0.33 \pm 0.20
Azelaic, C ₉	0.26-0.71	0.44 \pm 0.19	0.35-1.0	0.80 \pm 0.28
Sebacic, C ₁₀	0.03-0.13	0.10 \pm 0.04	0.05-0.38	0.15 \pm 0.13
Methylmalonic, iC ₄	0.10-0.22	0.16 \pm 0.05	0.98-2.4	1.6 \pm 0.51
Methylsuccinic, iC ₅	0.06-0.21	0.15 \pm 0.06	1.03-2.1	1.7 \pm 0.43
Methylglutaric, iC ₆	0.00-0.18	0.08 \pm 0.06	0.48-0.95	0.64 \pm 0.19
Maleic, M	0.03-1.21	0.50 \pm 0.44	1.4-3.5	2.6 \pm 0.89
Methylmaleic, mM	0.07-0.87	0.31 \pm 0.32	1.0-2.7	2.0 \pm 0.63
Fumaric, F	0.02-0.35	0.17 \pm 0.12	0.51-0.98	0.68 \pm 0.19
Phthalic, Ph	0.00-0.78	0.33 \pm 0.30	4.4-9.7	6.5 \pm 1.9
Isophthalic, iPh	0.00-0.04	0.03 \pm 0.02	1.2-1.9	1.5 \pm 0.27
Terephthalic, tPh	0.01-0.56	0.22 \pm 0.21	0.72-1.9	1.2 \pm 0.47
Hydroxysuccinic, hC ₄	0.00-0.03	0.02 \pm 0.01	0.17-0.56	0.34 \pm 0.14
Ketomalonic, kC ₃	0.00-0.20	0.10 \pm 0.09	0.80-2.1	1.4 \pm 0.48
Ketopimelic, kC ₇	0.00-0.22	0.11 \pm 0.08	0.79-1.6	1.0 \pm 0.32
Total diacids	10-83	43\pm28	179-450	308\pm102
		Oxoacids		
Pyruvic acid	0.00-0.52	0.23 \pm 0.19	5.3-9.3	6.7 \pm 1.6
Glyoxylic, ω C ₂	0.00-1.0	0.26 \pm 0.45	11-17	14 \pm 2.4
3-oxopropanoic, ω C ₃	0.08-0.42	0.28 \pm 0.14	0.19-2.4	1.6 \pm 0.84
4-oxobutanoic, ω C ₄	0.10-3.3	1.2 \pm 1.3	3.21-6.18	4.7 \pm 1.4
7-oxoheptanoic, ω C ₇	0.12-0.75	0.46 \pm 0.22	0.86-4.58	3.0 \pm 1.4
8-oxooctanoic, ω C ₈	0.05-0.31	0.22 \pm 0.10	1.27-2.01	1.7 \pm 0.31
9-oxononoic, ω C ₉	0.02-0.22	0.09 \pm 0.08	0.36-3.0	1.2 \pm 1.0
Total oxoacids	0.37-6.6	2.7 \pm 2.4	22-44	33\pm 22
Benzoic	0.08-2.0	0.70 \pm 0.80	1.4-4.7	3.0 \pm 1.3
		α -Dicarbonyls		
Glyoxal, Gly	0.00-0.25	0.10 \pm 0.09	2.0-3.5	2.8 \pm 0.60
Methylglyoxal, MeGly	0.01-0.19	0.11 \pm 0.06	0.81-4.9	1.9 \pm 1.7
Total α-dicarbonyls	0.01-0.44	0.21\pm0.15	2.83-8.39	4.7\pm2.3

878 Note: Ave. means average and SD means standard deviation. Limit of detection (LOD) is 0.001 ng m⁻³

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882 Table 2. Nighttime correlation analysis of the selected diacids, oxoacids, α -dicarbonyls, fatty acids, isoprene-SOA tracers, monoterpenes-SOA tracers and levoglucosan (Levo) in aerosols over

883 Mt. Fuji

Species	C ₂	C ₃	C ₄	C ₆	C ₉	Ph	BzA	Pyr	α C ₂	α C ₄	α C ₉	Gly	MeGly	C _{18:1}	levo	DHAA	2-MT	2-ME	3-HGA	Pinic	
C ₂	1																				
C ₃	0.95*	1																			
C ₄	0.26	0.53	1																		
C ₆	0.81	0.93	0.76	1																	
C ₉	0.42	0.64	0.96*	0.87	1																
Ph	0.46	0.70	0.97*	0.88	0.97*	1															
BzA	0.79	0.68	0.07	0.66	0.34	0.24	1														
Pyr	0.40	0.65	0.93	0.75	0.85	0.95*	0.00	1													
α C ₂	0.01	0.31	0.95*	0.54	0.84	0.88	-0.22	0.90	1												
α C ₄	0.23	0.50	0.99**	0.72	0.94*	0.96*	0.00	0.95*	0.97*	1											
α C ₉	0.20	0.49	0.97*	0.67	0.89	0.95*	-0.09	0.97*	0.98*	0.99**	1										
Gly	0.27	0.53	0.90	0.63	0.78	0.89	-0.17	0.99*	0.95*	0.93	0.97*	1									
MeGly	0.60	0.80	0.83	0.81	0.78	0.89	0.14	0.96*	0.75	0.83	0.90	0.90	1								
C _{18:1}	0.07	-0.08	-0.29	0.04	-0.05	-0.25	0.67	-0.55	-0.47	-0.36	-0.50	-0.70	-0.55	1							
Levo	0.12	0.39	0.98*	0.68	0.95*	0.92	0.06	0.83	0.94*	0.96*	0.90	0.80	0.68	-0.15	1						
DHAA	-0.92	-0.91	-0.27	-0.69	-0.32	-0.45	-0.48	-0.51	-0.10	-0.26	-0.30	-0.40	-0.72	0.31	-0.08	1					
2-MT	0.03	0.32	0.95*	0.54	0.83	0.88	-0.23	0.91	0.99**	0.97*	0.98*	0.90	0.77	-0.50	0.93	-0.13	1				
2-ME	0.03	0.33	0.95*	0.54	0.83	0.88	-0.23	0.92	0.99**	0.97*	0.98*	0.90	0.78	-0.51	0.93	-0.13	1.0**	1			
3-HGA	0.51	0.59	0.63	0.82	0.82	0.69	0.75	0.41	0.39	0.55	0.45	0.30	0.38	0.53	0.68	-0.20	0.38	0.37	1		
Pinic	0.57	0.30	-0.64	0.01	-0.47	-0.46	0.60	-0.49	-0.81	-0.67	-0.68	-0.60	-0.24	0.36	-0.72	-0.47	-0.80	-0.79	-0.09	1	

884 Note: DHAA: 3-dihydroxy abietic acid, 2-MT: 2-methylthreitol, 2-ME: 2-methylerythritol, 3-HGA= 3-hydroxyglutaric acid

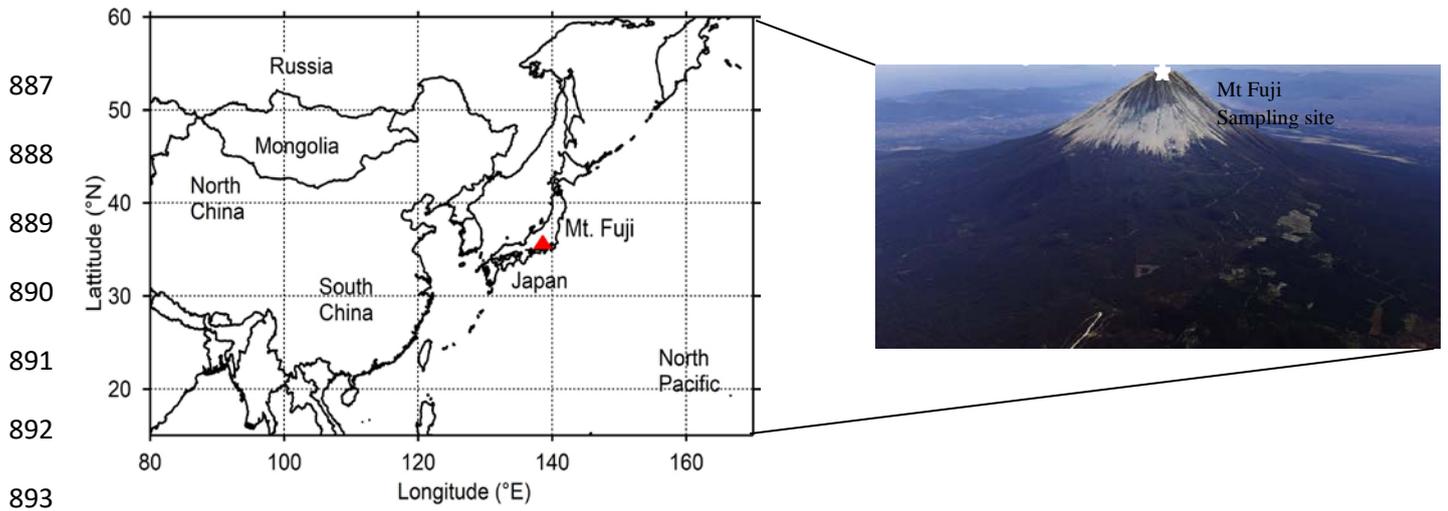
885 Table 3. Whole-day correlation analysis of the selected diacids, oxoacids, α -dicarbonyls, fatty acids, isoprene-SOA tracers, monoterpenes-SOA tracers and levoglucosan (Levo) in

886 aerosols over Mt. Fuji

Species	C ₂	C ₃	C ₄	C ₆	C ₉	Ph	BzA	Pyr	α C ₂	α C ₄	α C ₉	Gly	MeGly	C _{18:1}	Levo	DHAA	2-MT	2-ME	3-HGA	Pinic	
C ₂	1																				
C ₃	0.89	1																			
C ₄	0.38	0.36	1																		
C ₆	0.89	0.58	0.35	1																	
C ₉	0.34	-0.06	0.60	0.66	1																
Ph	0.89	0.64	0.03	0.95*	0.37	1															
BzA	0.07	-0.31	-0.58	0.40	0.29	0.83	1														
Pyr	0.49	0.09	-0.28	0.76	0.46	0.83	0.90	1													
α C ₂	0.58	0.19	0.58	0.84	0.96*	0.60	0.33	0.59	1												
α C ₄	0.68	0.42	0.82	0.80	0.87	0.53	-0.03	0.32	0.93	1											
α C ₉	0.73	0.34	0.05	0.94	0.62	0.92	0.70	0.95*	0.783	0.61	1										
Gly	-0.58	-0.19	-0.58	-0.85	-0.95*	-0.61	-0.32	-0.59	-1.0**	-0.92	-0.78	1									
MeGly	0.72	0.35	-0.06	0.91	0.53	0.94*	0.73	0.95*	0.70	0.52	0.99**	-0.70	1								
C _{18:1}	0.64	0.41	0.86	0.75	0.86	0.46	-0.11	0.24	0.90	0.99**	0.54	-0.90	0.44	1							
Levo	0.54	0.36	0.95*	0.61	0.81	0.29	-0.28	0.05	0.81	0.96*	0.36	-0.81	0.26	0.90	1						
DHAA	0.26	0.24	0.99**	0.25	0.61	-0.09	-0.59	-0.34	0.54	0.77	-0.03	-0.55	-0.13	0.82	0.92	1					
2-MT	0.72	0.32	0.24	0.95*	0.77	0.87	0.60	0.86	0.89	0.75	0.97*	-0.89	0.95*	0.70	0.54	0.17	1				
2-ME	0.74	0.35	0.33	0.96*	0.80	0.85	0.52	0.80	0.94	0.81	0.95*	-0.93	0.91	0.77	0.63	0.26	0.99**	1			
3-HGA	0.64	0.25	-0.12	0.87	0.53	0.91	0.80	0.98*	0.68	0.46	0.98*	-0.68	0.99**	0.39	0.20	-0.20	0.93	0.89	1		
Pinic	0.55	0.12	-0.04	0.85	0.67	0.83	0.81	0.96*	0.77	0.53	0.97*	-0.77	0.96*	0.47	0.29	-0.09	0.95*	0.92	0.98*	1	

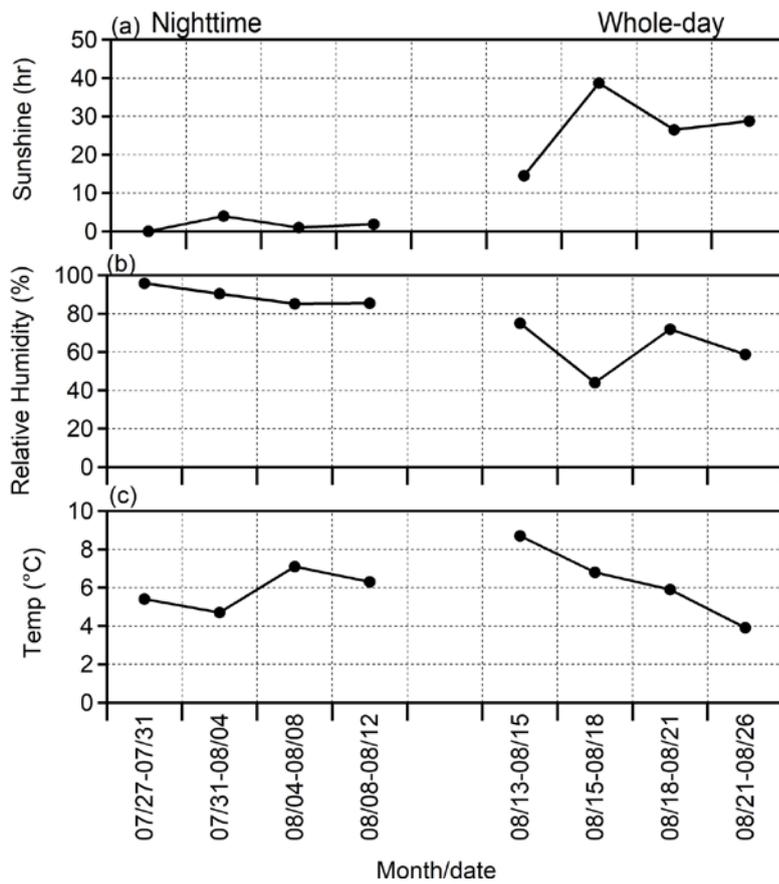
** Correlation is significant at the 0.01 level (2tailed)

* Correlation is significant at the 0.05 level (2tailed)



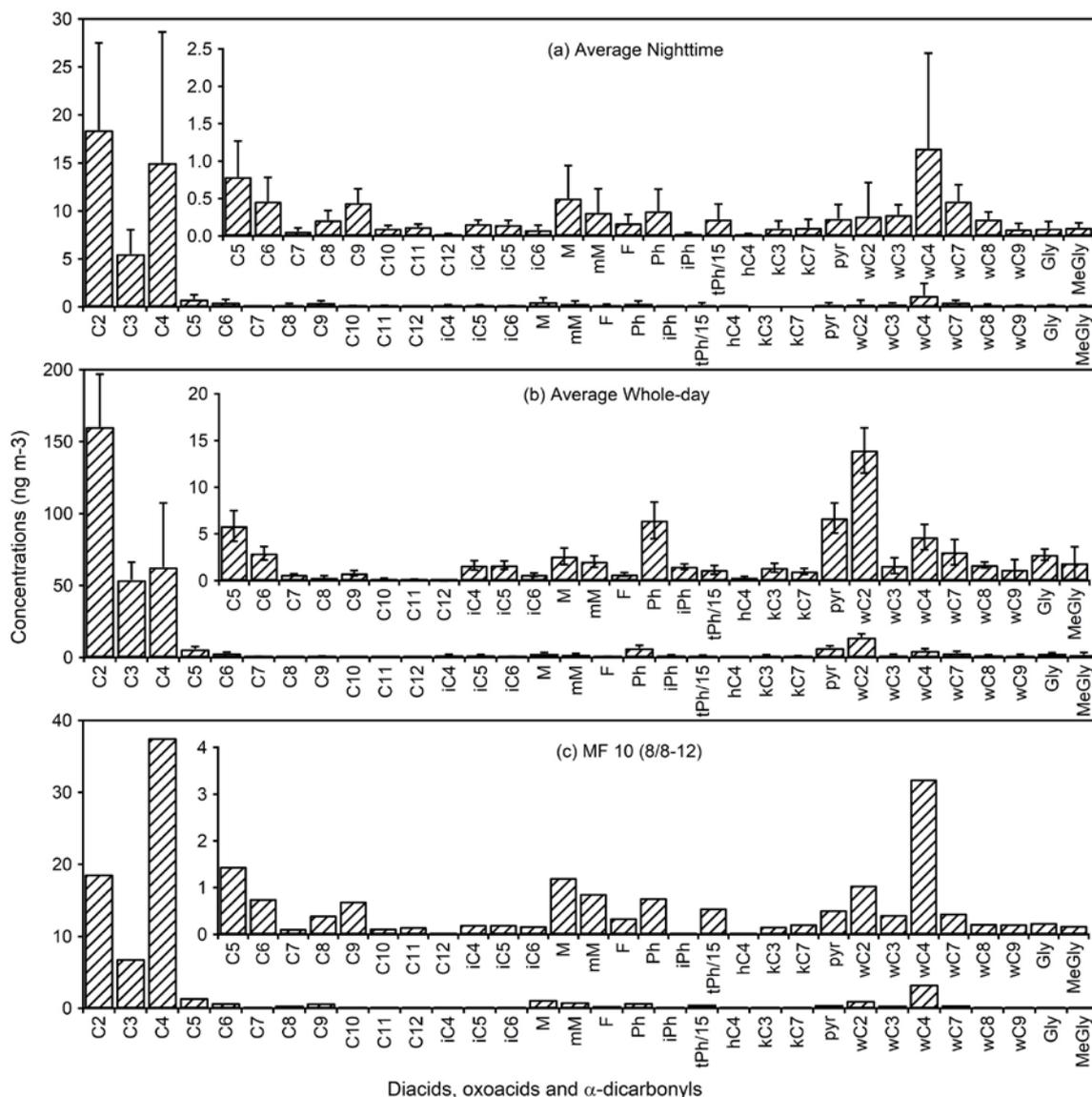
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894 Figure 1. Geographical location of Mt. Fuji, Japan.

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897 Figure 2. Meteorological parameters (a) average sunshine (hr), (b) relative humidity (%), and
898 (c) temperature (°C) recorded during study period over Mt. Fuji.

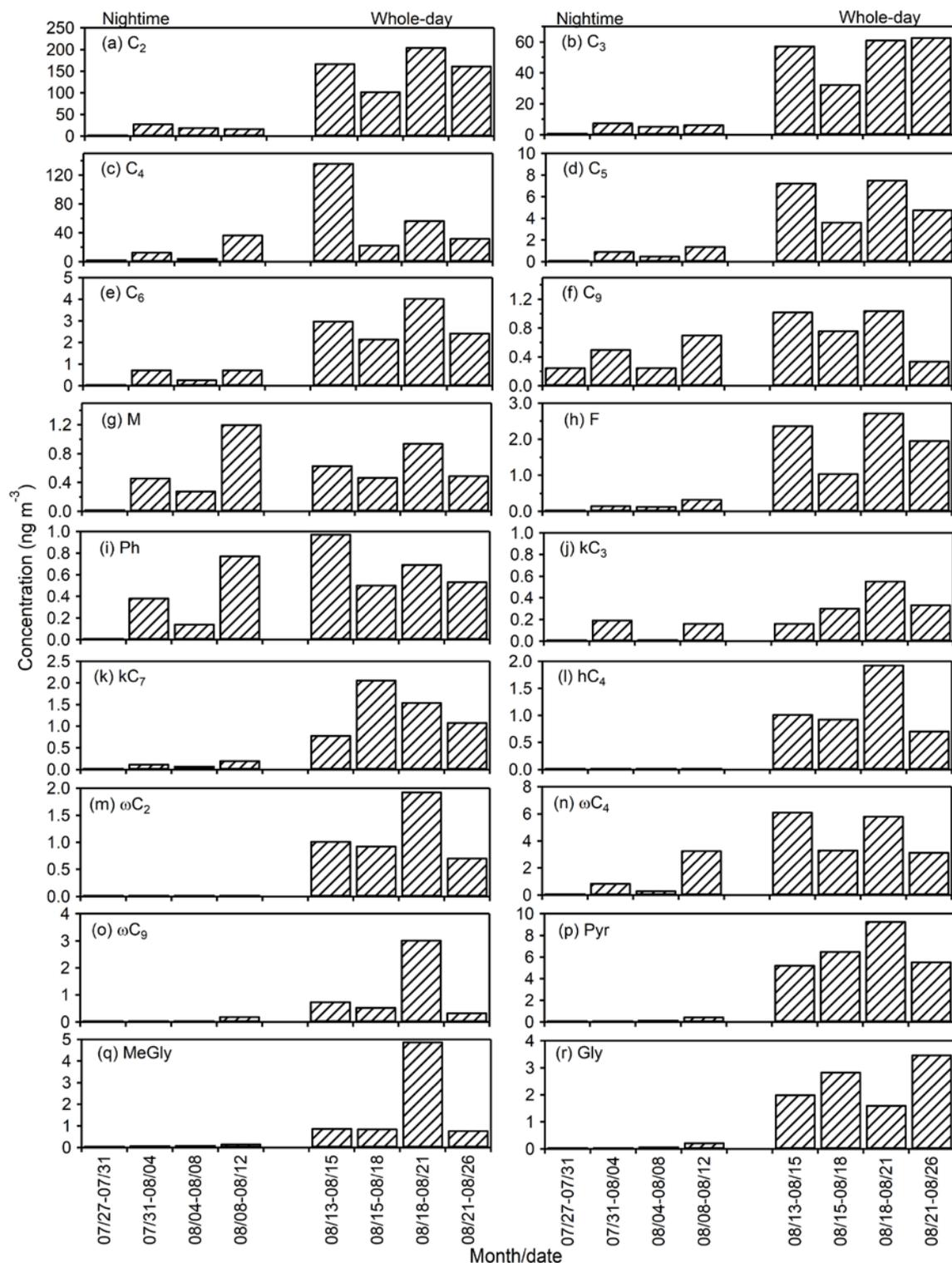


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900 Figure 3. Average molecular distributions of straight chain diacids (C₂-C₁₂), branched chain
 901 diacids (iC₄-iC₆), unsaturated diacids (M, mM, F, Ph, iPh, and tPh), multifunctional diacids
 902 (hC₄, kC₃ and kC₇), oxoacids (ω C₂- ω C₉, and pyruvic), and α -dicarbonyls (Gly and MeGly)
 903 in aerosols collected from Mt. Fuji during (a) nighttime (27 July to 12 August), (b) whole-day
 904 (August 13-26), and (c) nighttime (August 8-12). The error bars represent the standard
 905 deviation.

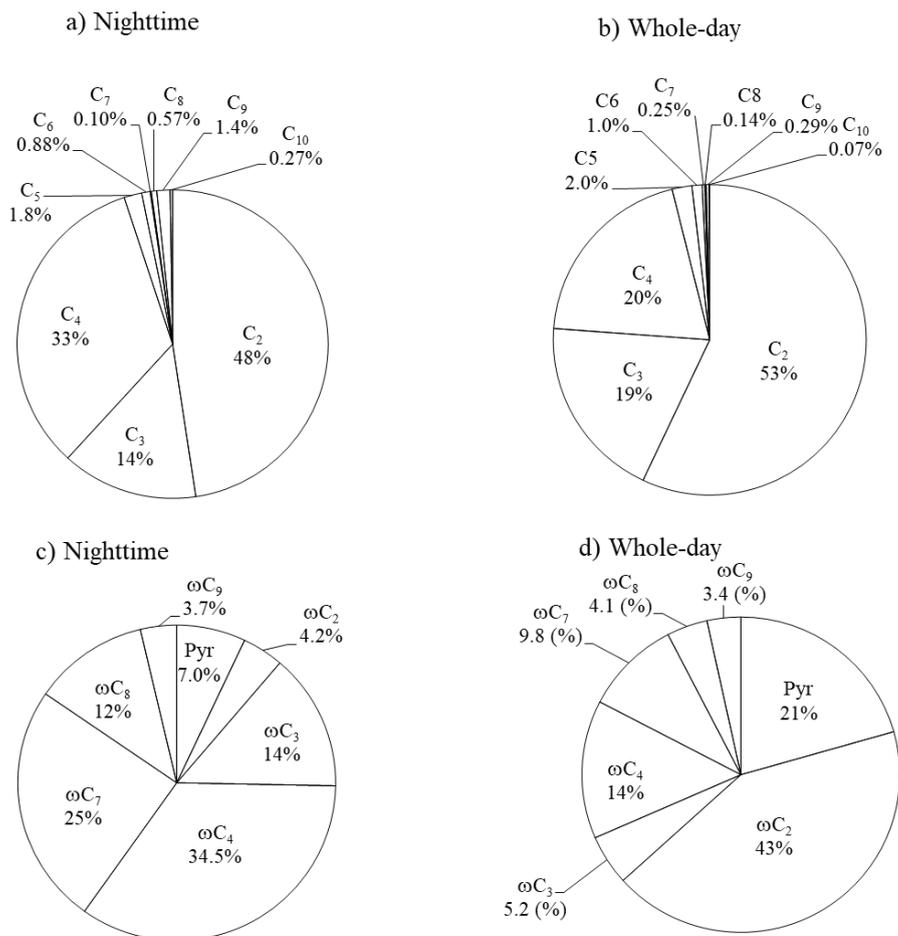
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909 Figure 4. Nighttime and whole day variations of (a) oxalic acid (C_2), (b) malonic acid (C_3),
 910 (c) succinic acid (C_4), (d) glutaric acid (C_5), (e) adipic acid (C_6), (f) azelaic acid (C_9), (g)
 911 malic (M), (h) fumaric (F), (i) phthalic acid (Ph) and (j) ketomalonic acid (kC_3), (k)
 912 ketopimelic acid (kC_7), (l) hydroxysuccinic acid (hC_4), (m) glyoxylic acid (ωC_2), (n) 9-
 913 nonanoic acid (ωC_9), (o) 4-oxobutanoic acid (ωC_4), (p) pyruvic acid (Pyr), (q) methylglyoxal
 914 (MeGly), and (r) glyoxal (Gly) in aerosols collected from Mt. Fuji, Japan.

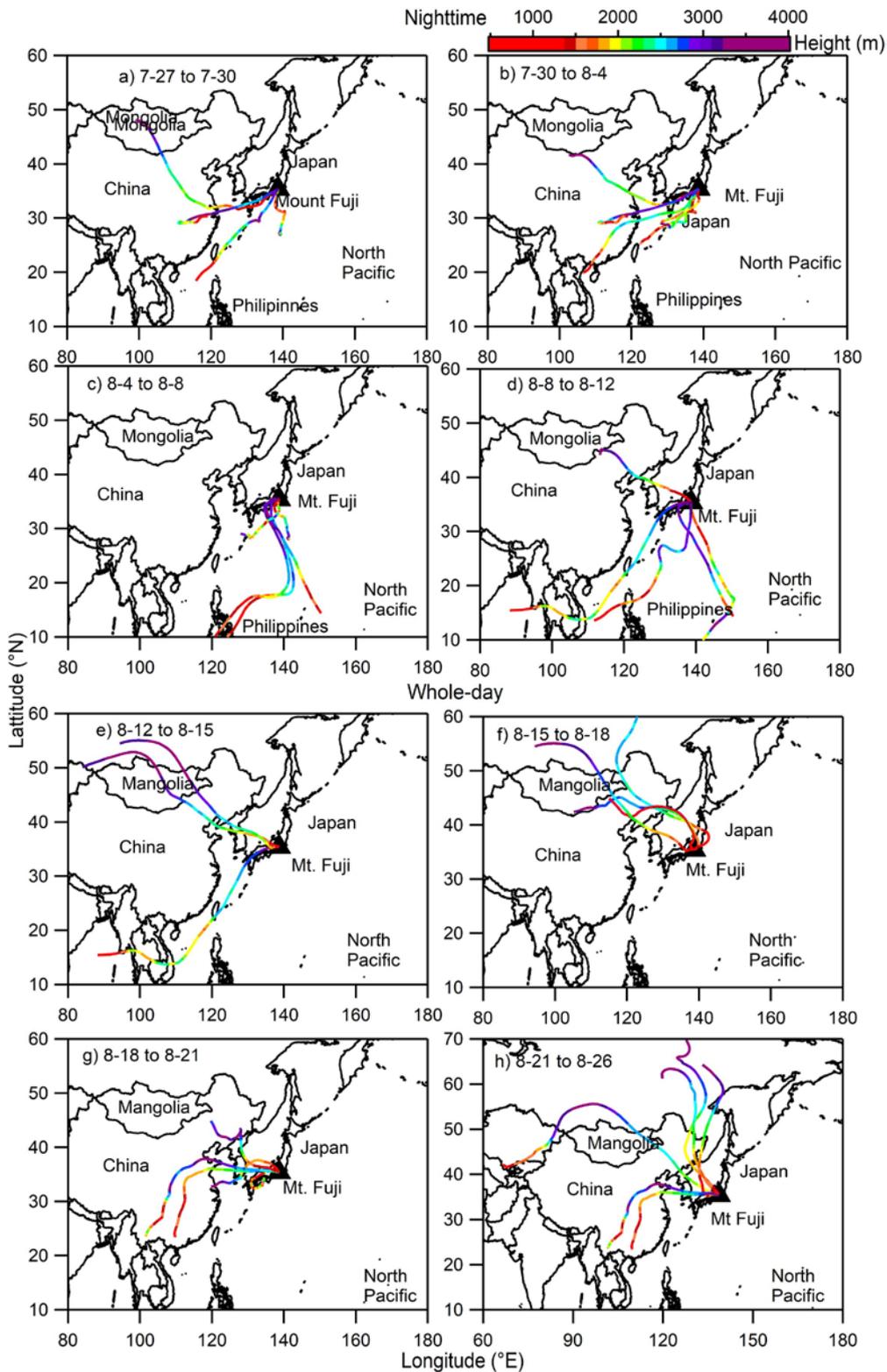


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917 Figure 5. Relative abundances (%) of individual diacid during (a) night-time and (b) whole-
 918 day, and individual oxoacid during (c) night-time and, (d) whole-day samples in aerosols
 919 collected from Mt. Fuji, the highest peak of Japan. Please refer to Table 1 for diacid and
 920 oxoacid identities.

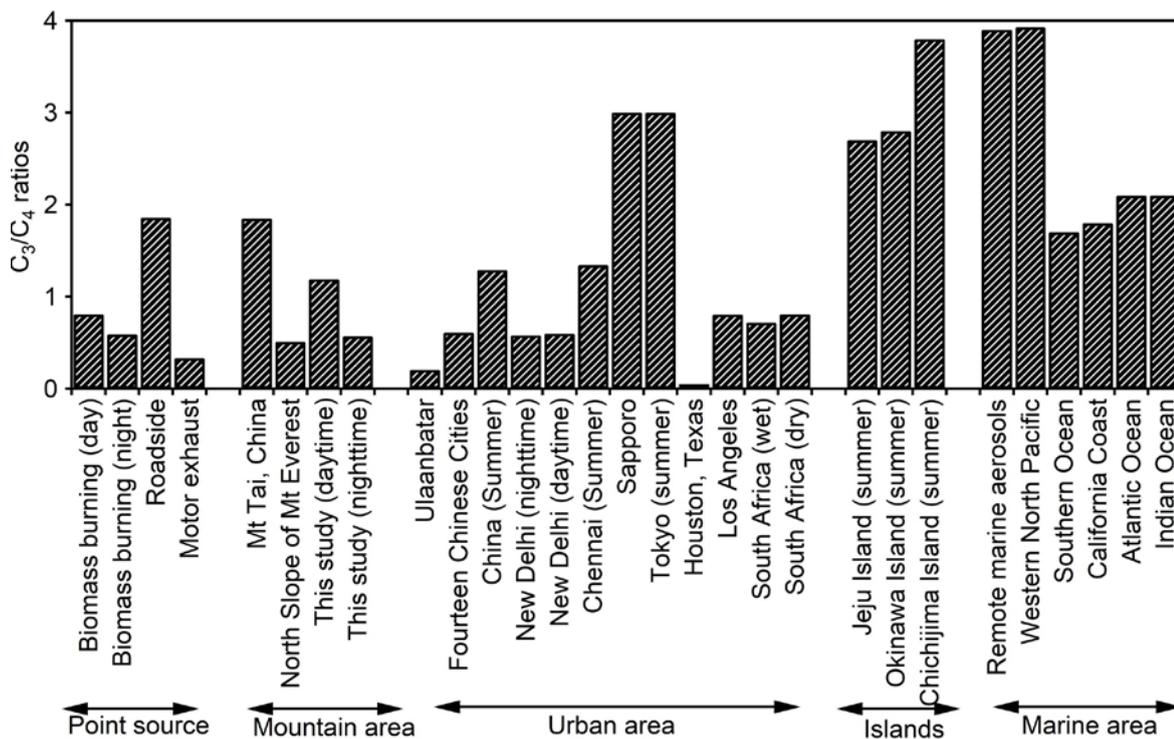
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923 Figure 6. Five-day backward trajectory analysis for (a) July 27-30, (b) July 30- August 4, (c)
 924 August 4-8, (d) August 4-12, (e) August 12-15, (f) August 15- 18, (g) August 18- 21, and (h)
 925 August 18-21. Backward trajectories at 3800m above sea level were drawn with the NOAA
 926 HYSPLIT model.

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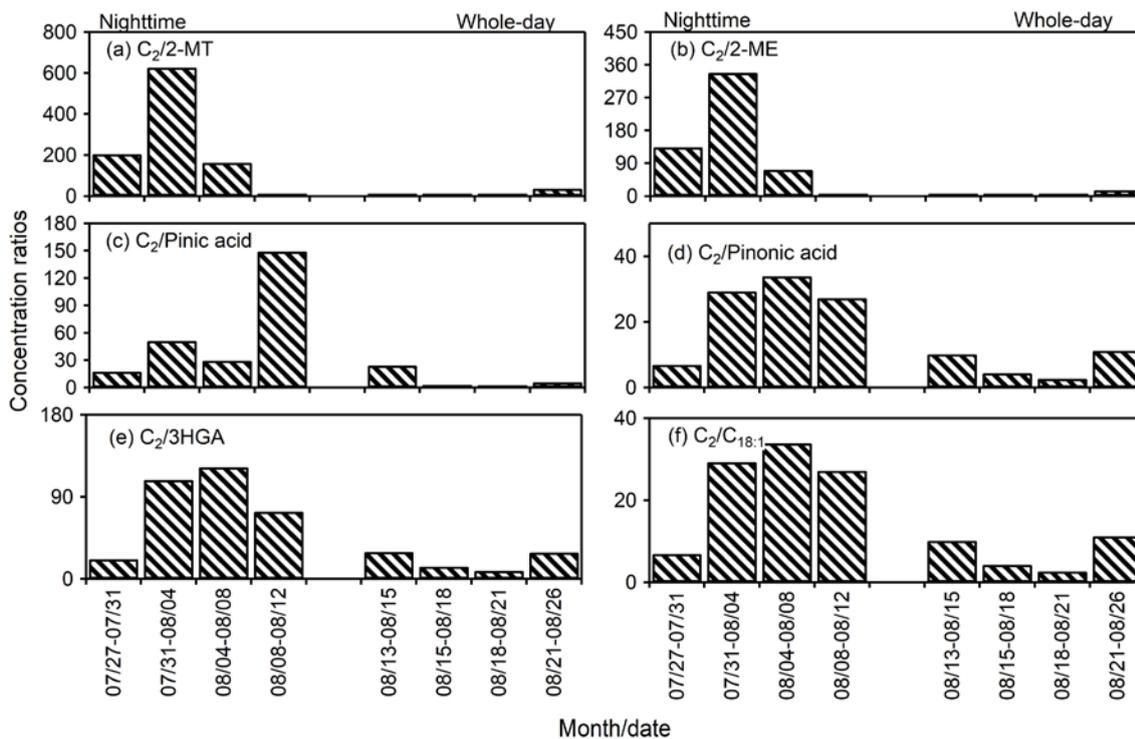
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929 Figure 7. Comparison of C_3/C_4 ratio in aerosols collected from Mt. Fuji with the different
 930 locations in the world.

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935 Figure 8. Nighttime and whole-day variations in concentration ratios of oxalic acid to
 936 isoprene and monoterpene SOA tracers (a) C₂/2-methylthreitol (2-MT), (b) C₂/2-
 937 methylerythreitol (2-ME), (c) C₂/pinic acid, (d) C₂/pinonic acid, (e) C₂/3HGA and (f) C₂/C_{18:1}
 938 in aerosols collected from Mt. Fuji, Japan.

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