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1 **Alpine snowpit profiles of polar organic compounds from Mt. Tateyama central Japan:**
2 **Atmospheric transport of organic pollutants with Asian dust**

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13 Revised to Atmospheric Environment

14 **Keywords**

15 Diacids, Incloud isoprene oxidation, snowpit, Asian dust, Transboundary pollutions

16

17 **Highlights**

18 1. Bacteria and Incloud isoprene oxidation results in the end product of dicarboxylic acids.

19 2. Organic compounds are attributed to heterogeneous reactions.

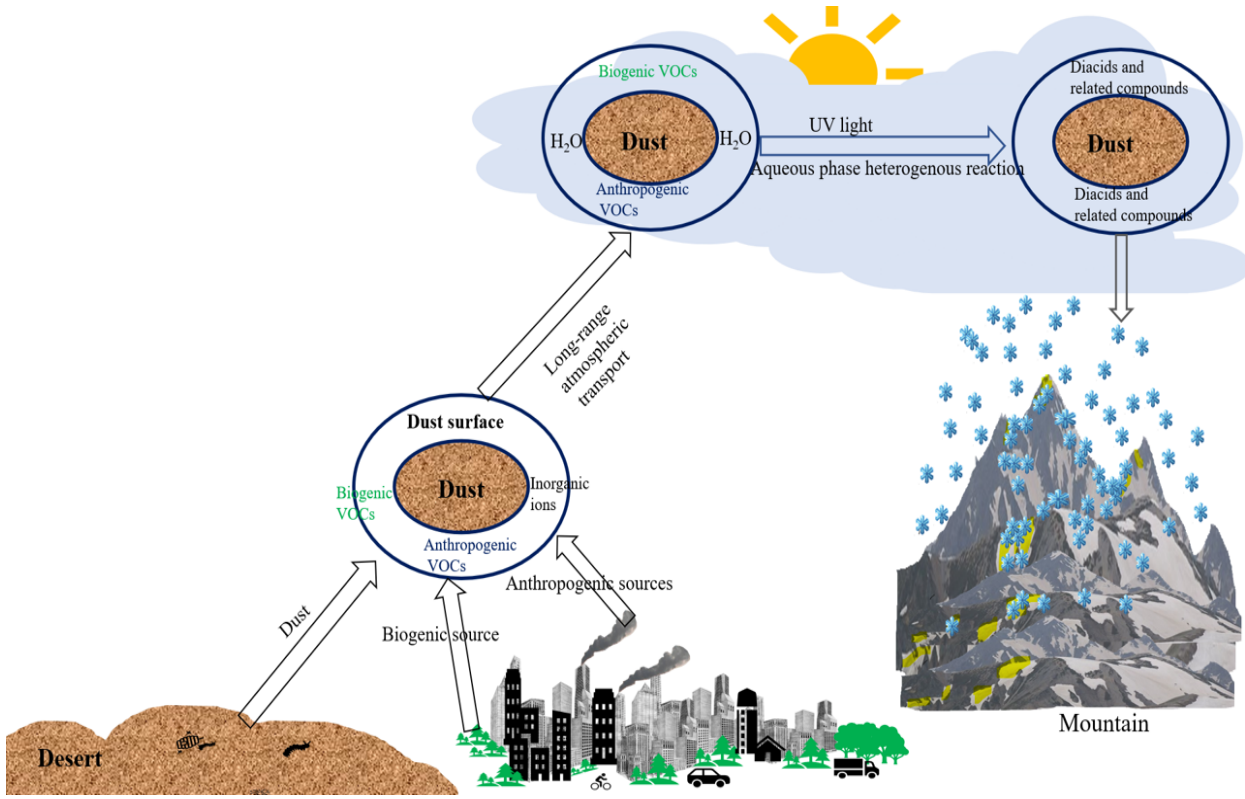
20 3. Atmospheric transport of diacids and oxoacids with Asian dust is important.

21 4. Asian dust is not responsible for the atmospheric photochemical processing of organics.

22 5. Snow metamorphism may play an important role in these organic compounds (fresh organic
23 compounds are well captured).

24

25 Graphical Abstract



26

27

28

29 **Abstract**

30 Snowpit samples (n =10) were collected (19 April 2008) from the snowpit sequences (depth
31 6.60 m) at the Murodo-Daira site (36.58°N, 137.60°E, elevation of 2450 m a.s.l.) of Mt.
32 Tateyama (3015 m a.s.l.), central Japan. The first time, low molecular weight diacids, ω-
33 oxoacids, pyruvic acid, and α-dicarbonyls were measured for this snowpit sequence. Higher
34 concentrations of short-chain diacids (C₂-C₅) are observed in dusty snow than non-dusty snow
35 samples. Longer chain diacids (C₇-C₁₂) are significant in granular and dusty snow samples.
36 Aromatic and aliphatic unsaturated diacids showed higher concentrations in the slightly dusty
37 layer deposited in winter. Except for a clean layer, molecular distributions of diacids are
38 characterized by the predominance of oxalic acid (C₂, ave, 20±22 ng/g-snow) followed by
39 succinic (C₄, 7.2±5.9 ng/g -snow), and malonic acids (C₃, 3.3±2.9 ng/g -snow) for all the snow
40 layers. Lower C₃/C₄ ratios (0.46) suggest that organic aerosols are rather fresh without serious
41 photochemical aging during the long-range transport over central Japan. The higher
42 concentrations of the secondary species in dusty snow than non-dusty samples were mainly
43 attributed to the heterogeneous reaction. The strong correlations of incloud oxidation products
44 of isoprene, aromatic acids, and fatty acids suggest that condensation, oxidation, and photolysis
45 are important reaction mechanisms for the formation of diacids. Chinese Loess (Kosa particles)
46 and Mongolian Gobi desert's dust provided the surface area for polar organic compounds,
47 traveled to several thousand kilometers in the lower troposphere, and snow metamorphism
48 altered the chemical composition of diacids and related compounds.

49 (words: 245)

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51

52 1. Introduction

53 Organic aerosols are characterized by an enrichment of water-soluble dicarboxylic
54 acids (diacids) and related compounds, which includes short-chain diacids (C₂-C₅; S-DCAs)
55 and long-chain diacids (C₆-C₁₂; L-DCAs), ω-oxoacids (ωC₂-ωC₉), pyruvic acid (Pyr), and α-
56 dicarbonyls, i.e., glyoxal and methylglyoxal (Kawamura et al., 1996; Kunwar et al., 2017,
57 2019). These polar organic acids are ubiquitous in the micro scale of the lower troposphere and
58 encompass an important fraction of fine aerosols (Liu et al., 2017, 2018, 2019; Kunwar et al.,
59 2019). These are emitted from human activities and natural sources, i.e., primary emissions and
60 photochemical oxidation of volatile organic compounds (VOCs) (Paulot et al., 2011; Wang et
61 al., 2018). Terrestrial higher plants to marine phytoplanktons emitted huge amounts of biogenic
62 VOCs, which are 10 times larger than anthropogenic VOCs on a global scale (Seinfeld and
63 Pandis, 1998). Biogenic and anthropogenic VOCs are oxidized in the atmosphere to result in
64 secondary organic aerosols (SOA), which are further oxidized to diacids, oxoacids, glyoxal,
65 and methylglyoxal via heterogeneous reactions (Talbot et al., 1995; Lim et al., 2005; Volkamer
66 et al., 2009; Kunwar and Kawamura, 2014a,b; Pokhrel et al., 2019).

67 Carlton et al. (2006, 2007) and Zhu et al. (2015) reported that primary organic aerosols
68 (POA) are emitted from plants, fungal spore, fossil fuel combustion, biomass burning, and soil
69 particles, whereas SOA are photochemically produced by heterogeneous oxidations of biogenic
70 and anthropogenic VOCs (Surratt et al., 2010; Ho et al., 2010; Kundu et al., 2010). POA and
71 SOA control the physicochemical properties of atmospheric particles (Kanakidou et al. 2005;
72 Quinn and Bates, 2011), which are involved with geochemical cycles of carbon in the lower
73 troposphere and stored in ice crystal in cold regions after snowfall (Pokhrel et al., 2015, 2020).

74 However, the studies on organic compounds in snow/ice archives suggested that
75 organic compounds in snow/ice/glaciers are of biological origin (Domine et al., 2011; McNeill
76 et al. 2012; Jacobi et al., 2012; Pokhrel, 2015; Feng et al., 2018). For example, formate and
77 acetate using the ice sheet in Dome C from Antarctica have been reported (Saigne et al., 1987).
78 Similarly, Kawamura et al. (1996a, 2001a,b) reported mono- and/or di-carboxylic acids in rain
79 and snow samples from Los Angeles and Greenland ice core. Formic and acetic acids are
80 reported from the High Mountain site (Paulot et al., 2011; Kawamura et al., 2012) and east
81 Antarctica (de Angelis et al., 2007).

82 However, little is known about diacids, oxoacids, and α-dicarbonyls for different types
83 of snow particles in the outflow regions of East Asia, in which long-range atmospheric
84 transport is significant over the western North Pacific including Japanese Islands
85 (Myriokefalitakis et al., 2011). Here, we report, for the first time, the molecular distribution of

86 homologous series of diacids and related compounds in different types of snow samples
87 collected from snow pit (6.5 m depth) at a high mountain site in central Japan. Besides, we
88 compare the diacids compositions of this snowpit sequence with reference dust collected from
89 the Gobi desert, Tengger, and Chinese loess plain (Fig. 1).

90 **2. Samples and methods**

91 A series of snow pit samples (10) were obtained by cutting the snowpit wall and
92 surfaces (length 0.0-6.5) on 19 April 2008 at the Murodo Daira site (36.58° N, 137.60° E, the
93 elevation of 2450 m a.s.l), central Japan (Table S1 and Fig. 1). The snow samples were placed
94 in a pre-cleaned glass jar (8 L) with a Teflon-lined screw cap using a clean stainless steel scoop,
95 to which mercuric chloride was added to avoid microbial degradation of organic compounds.
96 These samples were transported to Hokkaido University and stored in a dark refrigerator room
97 at 4°C before analysis (Kawamura et al., 2012).

98 Low molecular weight diacids (LMW-DCAs) and related compounds, oxoacids, and α -
99 dicarbonyls were measured using the methods reported elsewhere (Kunwar and Kawamura,
100 2015). The homologous series of LMW-DCAs and related compounds, as well as fatty acids,
101 were determined using butyl ester derivatization methods (Mochida et al., 2003). Briefly, ca.
102 100 mL of snow meltwater were placed in a pear shape flask (300 mL) and the pH of the
103 sample was adjusted to 8.5-9.0 using a 0.05 M KOH solution. The samples were concentrated
104 down to ca. 5 mL using a rotary evaporator under vacuum at 50°C. The concentrates were
105 transferred to a pear-shaped flask (50 mL), concentrated until dryness using a rotary evaporator
106 under vacuum, and then reacted with ~0.25 mL of 14% boron trifluoride (BF₃)/n-butanol at
107 100°C for 1 hour. During this procedure, -COOH groups were converted to butyl esters, and
108 carbonyl groups converted to dibutoxy acetal. The butyl ester and acetal derivatives were
109 determined using capillary gas chromatography (GC; HP 6890). The GC peak identification
110 was performed using a GC/mass spectrometry.

111 Before the analysis of real snowpit samples, a recovery test was conducted. Authentic
112 standard solution (10 μ l) containing free oxalic (C₂), malonic (C₃), succinic (C₄), glutaric (C₅),
113 and adipic (C₆) acids with concentrations of 1.03, 1.12, 1.46, 1.04, and 0.83 nmoles/ μ l,
114 respectively, was spiked to organic-free pure water (100 ml) and analyzed as a real sample.
115 The recoveries were above 89% for C₂ and more than 91% for C₃, C₄, C₅, and C₆. Similarly, C₂
116 is the most volatile organic compound among these diacids and related compounds, thus C₇ to
117 C₁₂ and other compounds have more than 89%. The analytical errors (replicate) were < 6% for
118 each compound whereas laboratory blanks of LMW-diacids were < 4% of the levels of real

119 samples, and these all compounds are corrected for the blanks. The analyses of snow pit
120 samples were completed in 2010.

121 **3. Analysis of reference dust materials**

122 Reference Chinese dust samples were provided by National Institute of Environmental
123 Studies, Japan (e.g., Nishikawa et al., 2000, 2013). The approximate sampling sites are given
124 in Fig. 1. The height of the sites is about 1800 m above sea level. Reference dust materials
125 (Kosa) including Chinese loess deposits from the Tengger (CJ-1, < 250 μm and CJ-2, < 100
126 μm) and Mongolian Gobi deserts (G-D, < 10 μm) were analyzed for LMW dicarboxylic acids.
127 Chinese loess material (CJ-1) was collected in an arid area near Ruining in Gansu Province.
128 Simulated Asian mineral dust material (CJ-2) were collected from the southeast part of the
129 Tengger desert in the Ningxia Hui autonomous region of China. The reference materials were
130 purchased from the National Institute for Environmental Studies. 0.1 g of reference dust
131 samples were extracted with ultra-pure water by the methods as described above for diacids
132 and ions. The detailed information of reference samples is reported elsewhere (Nishikawa et al.,
133 2000, 2013). Five day backward trajectories arriving at Murodo-Daira, Mt. Tateyama of central
134 Japan during the snow accumulation period (2007 October to 2008 April) reach to the
135 sampling sites of reference materials (CJ-1, CJ-2, and G-D) (Fig. 1).

136 **4. Backward Air Mass Trajectory Analysis**

137 Figure 1 represents cluster analysis of 5 days-backward trajectories at Murodo-Daira, Mt.
138 Tateyama in central Japan (2007 October to 2008 April) at 2500 meters above the sea level
139 (a.s.l.). The back trajectory analyses reveal that the source of air masses are influenced by East
140 Asia (e.g., CJ-1, CJ-2, and G-D) via long-range atmospheric transport. Air masses were
141 originated over the same dust region of Northwest China on 31 Dec, 11 Jan, 11 Feb. Besides,
142 15 April showed Northeast China, central Mongolia, and the mainland of Russia and 3 March
143 showed the Siberian region of southeast Russia. However, the air mass origin is very short on
144 19 April represents short-range airmass transport Northeast China and Hokkaido, Japan (Fig.
145 1). Kawamura et al. (2012) has reported a detailed description of sampling method and
146 backward trajectories at Murodo-Daira.

147 **5. Results and Discussion**

148 **5.1. Molecular distributions of dicarboxylic acids and related compounds**

149 Figure 2 shows the molecular distributions of diacids (DCAs), oxoacids and α -dicarbonyls
150 for each snow pit samples from Central Japan. Among 10 samples, we found dust layers that
151 are associated with 4 snowpit samples (sample no. 2, 6, 7, and 9), which are categorized as
152 dusty snowpit samples. The remaining samples do not contain dust layers (sample no. 1, 3, 4, 5,

153 8, 10) and categorized as non-dusty snowpit samples. The molecular distributions of non-dusty
 154 snowpit samples showed a predominance of C₂ (ave. 8.6±4.5 SD ng/g-snow) followed by C₄
 155 (4.2±3 ng/g-snow), C₃ (1.9 ±1.6 ng/g-snow), and phthalic (Ph) acid (1.4±1.1 ng/g-snow).
 156 Similar distributions (C₂>C₄>C₃) were observed in biomass burning aerosols and marine
 157 aerosols (Kundu et al., 2010b; Cong et al., 2015; Hoque et al., 2015, Deshmukh et al., 2017;
 158 Kunwar et al., 2019). The molecular distributions of dusty snowpit samples showed a
 159 predominance of C₂ (12-74 ng/g-snow, ave: 37±28 ng/g-snow), followed by C₄ (3.4-18 ng/g-
 160 snow, 12±7 ng/g-snow) and Ph (0.75-14 ng/g-snow, 7.2±5.9 ng/g-snow). Ph is the third most
 161 abundant diacid in the dusty snowpit samples, suggesting more anthropogenic sources
 162 influenced in the dusty snowpit sample during long-range atmospheric transport. Ph is reported
 163 as a tracer of the anthropogenic sources (Pavuluri et al., 2010).

164 Photochemically aged aerosols in the ambient atmosphere showed that C₃/C₄ ratios are
 165 higher than 2.0 (Kawamura and Bikkina, 2016; Kunwar and Kawamura, 2014a). However, the
 166 concentration ratios of C₃/C₄ in the snowpit samples are less than unity (dusty snowpit: ave.
 167 0.48±0.06 and non-dusty snowpit: ave. 0.40±0.14), which will be discussed in a later section
 168 (section 5.3). This molecular signature infers that the organic species scavenged over the
 169 snowpit site are significantly influenced by biomass/biogenic emission together with
 170 anthropogenic sources without serious photochemical aging.

171 Table S2 shows the average concentrations and concentration ranges of homologous
 172 series of normal saturated (C₂-C₁₂), branched-chain (iC₄-iC₆), unsaturated (M, F, mM, Ph, iPh,
 173 and tPh), keto (kC₃ and kC₇) and hydroxyl (hC₄) diacids, oxocarboxylic acids (ωC₂-ωC₉ and
 174 Pyr), and α-dicarbonyls (Gly and MeGly) in dusty and non-dusty snowpit samples, and
 175 reference Chinese dust samples. The reference dust samples were collected from three regions
 176 from East Asia; Tengger desert (CJ-1), Chinese loess (CJ-2), and Gobi desert (G-D) (Fig. 1).

177 The concentration ranges and average concentrations of C₂, C₃, and C₄ in dusty snowpit
 178 samples are 12-74 ng/g-snow and ave. 37±28 ng/g-snow, 1.7-9.1 ng/g-snow and 5.6±3.2 ng/g-
 179 snow, and 3.4-18 ng/g-snow and 12±7.2 ng/g-snow, respectively, whereas those in non-dusty
 180 snowpit samples are 3-15 ng/g-snow and 8.6±4.5 ng/g-snow, 0.44-4.5 ng/g-snow and 1.9±1.6
 181 ng/g-snow, and 1.4-7.1 ng/g-snow and 1.9 ±1.6 ng/g-snow, respectively (Table S2). The
 182 concentration range of oxalic acid in non-dusty samples are comparable to those reported in
 183 central Greenland ice core (range: 1-20 ng/g-ice) (Kawamura et al., 2001b). Greenland is
 184 influenced by biomass burning activities (Savarino and Legrand 1998). The average
 185 concentration of oxalic acid in non-dusty snowpit samples in this study (8.6±4.5 ng/g-snow) is

186 1.6 times lower than 180-year average of oxalate concentrations from Mt. Everest ice core
187 (13.7 ng/g-ice ng/g-ice) (Kang et al., 2001), 4.0 times higher than Greenland Site-J (0.36-11
188 ng/g-ice, ave. 2.1 ng/g-ice) ice core (Kawamura et al., 2001a) but similar to those (2.0-28 ng/g-
189 ice, ave. 7.2 ± 4.2 ng/g-ice) from Alaskan ice core (Pokhrel, 2015). The concentration range of
190 oxalic acids in non-dusty samples in this study is very similar to those of fresh snow collected
191 on the route from Syowa Station to Dome Fuji Station (range: 2.17-17.4 ng/g-snow),
192 Antarctica (e.g., Matsunaga et al., 1999; and references therein). Alaskan fine aerosol sample
193 (PM_{2.5}) showed somewhat different molecular distribution ($C_2 > C_3 > C_4$) during the biomass
194 burning periods (Deshmukh et al., 2018).

195 The concentrations of C_2 , C_3 , and C_4 in dusty snowpit samples are 4.3, 2.9, and 2.8
196 times higher than non-dusty snowpit samples, respectively. Aromatic diacids such as phthalic
197 (Ph), isophthalic (iPh) and terephthalic (tPh) are more abundant in dust samples by a factor of 5,
198 4 and 7.5 times, respectively. Aromatic diacids (e.g., Ph) are emitted to the atmosphere by
199 anthropogenic activities such as fossil fuel combustion, whereas tPh is emitted by the plastic
200 burning (Kunwar and Kawamura, 2014a; Jung et al., 2010). Hence, more anthropogenic and
201 plastic burning tracers are condensed and adsorbed on the dust surface during long-range
202 atmospheric transport. Dust can provide the surface area for organic and inorganic acids, which
203 can be easily traveled to several thousand kilometers in the atmosphere (Kunwar et al., 2016,
204 2017; Hoque et al., 2020). Glyoxylic (ωC_2), pyruvic (Pyr), glyoxal (Gly), and methylglyoxal
205 (MeGly) are produced in the atmosphere by oxidation of the precursor compounds such as
206 isoprene. Their concentrations in dusty snowpit samples are 3.5, 3.6, 6.6, and 5 times higher
207 than those of non-dusty samples.

208 Figure 3 shows the profiles of selected DCAs in snowpit sequences (samples Nos. 1 to
209 10). Similar profiles were found for C_2 - C_5 (except for C_2 and C_4 at point Nos. 2 and 4,
210 respectively), methylsuccinic (iC₅), maleic (M), fumaric (F), and methylmaleic (mM) acids
211 (Fig. 3a-d). Except for C_6 (not shown in fig.), all these diacids (C_2 - C_5) and related compounds
212 showed higher concentrations with dusty snowpit samples (e.g., sample Nos. 6 and 7). In
213 contrast, C_6 showed higher concentration in clean snow (sample No. 8). We have reanalyzed
214 this sample to check about such a high concentration of C_6 . Reanalysis showed a similar
215 concentration. Hence, we believe that there is a specific source of C_6 .

216 Figure 3c showed straight forward concentration trends of branched-chain saturated
217 diacids (iC₄, iC₅, and iC₆). Among the branch chain diacids, methyl succinic acid (iC₅) is the
218 dominant (1.25 ± 0.95 and 0.28 ± 0.24 ng/g-snow) branched-chain diacid in dusty and non-dusty
219 snowpit samples. Concentration trends of branched-chain diacids are flat in sample Nos. 1 to 5

220 (0.0-0.50 m in depth). Branched-chain diacids are emitted by anaerobic bacteria (e.g., Allison,
 221 1978). Thus, iso C₄-C₆ diacids could be involved with bacterial activities in the ocean surfaces,
 222 atmospheric aerosols, and soil dust. Interestingly, we also found a good correlation of iso
 223 diacids (iC₄, iC₅ and iC₆) with C₂ (R²=0.96), C₃ (0.94), C₄ (0.98), C₅ (0.98), and suberic (C₈)
 224 acid (0.89), suggesting that short-chain (C₂-C₅) and long-chain diacids (C₈) are produced by
 225 bacterial activities before snow formation phase and incloud oxidation.

226 Figures 3d and 3e present the concentrations of aliphatic unsaturated and aromatic
 227 diacids in the snow sequence, respectively. They showed higher concentrations in slightly
 228 dusty snow sample (No. 7), being different from short-chain diacids such as C₂ and C₃, which
 229 showed maxima in the dust layer (No. 6). Aromatic diacids are associated with coal and plastic
 230 burning, whereas aliphatic unsaturated diacids are formed by the degradation of aromatic
 231 hydrocarbons. A considerable amount of coal is burned for heating purposes during winter in
 232 East Asia, especially in China. Thus, the higher concentrations of diacids in a slightly dusty
 233 snowpit layer (No. 7) should be involved with condensation and adsorption of coal burning-
 234 derived aerosols on dust surface and transported from the Asian continent over Mt. Tateyama
 235 in winter (Table S1).

236 Figure 4b-c shows the profiles of concentrations of long-chain diacids (C₇-C₁₂),
 237 oxoacids, pyruvic acid, and α -dicarbonyls. Among long-chain diacids, C₉ shows the highest
 238 concentration. Except for C₆, long-chain diacids (e.g., C₇-C₉) showed higher concentrations in
 239 surface granular (No. 3) and dusty snowpit samples during Asian dust events, whereas C₁₀ to
 240 C₁₂ diacids showed the highest concentration in dusty snow pit layer (Fig. 4c), followed by the
 241 second (except for C₁₁) and third peak in the clean snow (No. 8) and surface granular snow
 242 (No.3) samples. Minimum concentrations were observed in surface fresh snow (No. 1), clean
 243 snow (No. 8) samples (except for C₁₀), and/or bottom of the snowpit (No. 10). The oxidation
 244 products of low molecular weight unsaturated fatty acids (e.g., C_{14:1}, C_{16:1}, C_{18:1}, C_{18:2}, C_{18:3},
 245 C_{18:1 ω 7}, and C_{18:1 ω 9}) derived from phytoplankton and bacterial activities and high molecular
 246 weight unsaturated fatty acids (e.g., C_{20:4}, C_{20:5}, C_{22:1}, C_{22:6}, and C_{24:1}) are pimelic (C₇), suberic
 247 (C₈), azelaic (C₉) sebacic (C₁₀), undecanedioic (C₁₁), and dodecandioic (C₁₂) acids (C₇-C₁₂).
 248 For example, C₉ and C₁₁ can be produced by the photooxidation of unsaturated fatty acids
 249 (UFAs) such as oleic acid (C_{18:1}) and vaccenic acid (C_{18:1 ω 7}), which are primarily emitted from
 250 marine microbial activities and can be found in the sea surface microlayers (Winterhalter et al.,
 251 2009). Azelaic acid (C₉) shows the highest concentration in granular snow (sample No. 3)
 252 followed by dusty snow layer (No. 6) and lower concentrations in fresh (No. 1), clean (No. 5),
 253 and bottom of sequence snow samples (No. 10). C₉ is a specific photochemical oxidation

254 product of biogenic UFAs (e.g., C_{18:1}) (Kawamura and Gagosian, 1987) and can be further
255 oxidized to C₆, C₇, and C₈ and short chain diacids (C₂-C₅) (Legrand et al., 2007; Pavuluri et al.,
256 2015).

257 **5.2. Molecular composition and concentration trends of oxoacids, pyruvic acid, and α -** 258 **dicarbonyls**

259 Among oxoacids, glyoxylic (ω C₂) acid is the dominant species (dusty snowpits: ave.
260 9.7 ± 6.3 ng/g-snow, and non-dusty snowpits: 2.7 ± 2.3 ng/g-snow), followed by 4-oxobutanoic
261 (ω C₄) acid (2.6 ± 1.6 ng/g-snow and 0.82 ± 0.51 ng/g-snow) and 3-oxopropanoic (ω C₃) acid
262 (1.3 ± 0.84 ng/g-snow, and 0.32 ± 0.12 ng/g-snow) in both dusty and non-dusty snow pit
263 samples (Table S2). Oxoacids (ω C₂ > ω C₄ > ω C₃) showed molecular characteristics similar to
264 those of diacids (C₂ > C₄ > C₃). Predominance of ω C₂ and ω C₄ were reported from Antarctic
265 aerosol samples (Kawamura et al., 1996b) and predominance of ω C₂ is reported frequently
266 from the observation studies conducted at many sites in the world, where atmospheric
267 oxidation of precursor compounds is an important factor (Kunwar et al., 2016, 2017, 2019,
268 references therein). We detected high concentrations of ω C₂ in the snowpit sequence, which
269 can be derived from the oxidation of glyoxal (Gly), methylglyoxal (MeGly), maleic (M),
270 methylmaleic (mM) and fumaric (F) acids, aromatic hydrocarbon, and unsaturated fatty acids.
271 On the other hand, ω C₃ and ω C₄ are oxidation products of unsaturated fatty acids and longer
272 chain ω -oxoacids (e.g. ω C₅- ω C₉) rather than anthropogenic sources (Kawamura et al., 2001a,b;
273 Pokhrel, 2015). ω C₂- ω C₄ show similar concentration trends to each other (Fig. 3d). These
274 results suggest that they were co-transported and formed from similar sources during long-
275 range atmospheric transport.

276 The concentrations trends of ω -oxoheptanoic (ω C₇), ω -oxooctanoic (ω C₈), and ω -
277 oxononanoic (ω C₉) acids are similar to each other (Fig. 4e) with maxima during Asian dust
278 periods (Nos. 6, 7, and 9). On the other hand, the lower concentrations were observed in
279 sample No. 5 (snow with ice plate) followed by No. 3 (surface granular snow) and/or No. 1
280 (surface fresh snow) (Table S1 and S2). They may be derived from both anthropogenic and
281 marine biogenic sources during long-range atmospheric transport. The higher concentrations of
282 oxoacids in the dusty snowpit samples suggest that ω -oxoacids are emitted from biogenic
283 sources which could be injected from the Asian dust source regions with more microbial
284 activities via long-range atmospheric transport (Wang et al., 2017).

285 Includ oxidation of isoprene (Carlton et al., 2006, 2007), aromatic hydrocarbons
286 and/or biomass burning products (Pavuluri et al., 2010) can contribute pyruvic (Pyr) acid.

287 Recent studies showed that third-generation products of isoprene are methylglyoxal (MeGly)
288 and glyoxal (Gly). MeGly and intermediate compounds, e.g., malic acid (hC₄) can be further
289 oxidized to result in Pyr (Carlton et al., 2006, 2007). The higher concentrations of Pyr can be
290 observed in sample Nos. 2 (dusty and granular), 6 (dusty snow layer), and 7 (slightly dusty
291 snowpit layer).

292 Concentration trends of two α -dicarbonyls are similar to each other (Fig. 4f). The
293 photochemical oxidation of aromatic hydrocarbons such as benzene, toluene, xylene and p-
294 xylene, and alkenes produces Gly (Rogge et al., 1991, 1998; Volkamer et al., 2001, 2006). The
295 third-generation products of isoprene, i.e., Gly and MeGly, are present in the aerosol phase
296 (Hallquist et al., 2009). Gly and MeGly also have anthropogenic sources and can produce an
297 end product of s-DCAs, i.e., C₂ via in-cloud aqueous phase reaction (Legrand and De Angelis,
298 1995; Warneck, 2003, Surrat et al., 2007) (discussed in a later section).

299 **5.3. Relative abundances in dusty and non-dusty snowpit samples: A signal of less** 300 **photochemical aging during long-range atmospheric transport**

301 Figure 5 provides the information of the average relative abundance (%) of individual
302 diacids in total diacids. The average relative abundance of C₂ (48%) in the dusty snowpit
303 samples is higher than that of non-dusty samples (40%). In contrast, relative abundances C₄
304 and long-chain diacids (C₅-C₆) are higher in non-dusty snowpit samples. This result may
305 suggest that the formation of short chain diacids are more significant in dusty snowpit samples
306 from its precursors diacids. Very high relative abundance of C₂ (>80%) is the indication of gas
307 to particle-phase conversion (Kawamura et al., 2012) as well as significant photochemical
308 processing of long-chain diacids and aqueous phase oxidation of biogenic and anthropogenic
309 volatile organic carbons (VOCs) via Gly, MeGly, Pyr and ω C₂ (Legrand et al., 2007; Ervens et
310 al., 2004). An increased relative abundance of C₂ (60–70%) has been reported in the marine
311 aerosols from the Pacific during long-range atmospheric transport (Kawamura and Sakaguchi,
312 1999). The relative abundances of C₂ from this study (dusty snowpit: 48% and non-dusty
313 snowpit: 40%) are less than those reported in marine aerosols from the western Pacific (65%)
314 (Wang et al., 2006) and the central equatorial Pacific (>70%) (Kawamura and Sakaguchi,
315 1999), suggesting that diacids in the snowpit samples are less aged compared to marine
316 aerosols. The average relative abundance of ω C₂ to total oxoacids (ω C₂- ω C₉) is higher (62%)
317 in the dusty snowpit sample than non-dusty samples (56%). Accordingly, those of ω C₄ (dusty
318 snowpit: 18% and non-dusty snowpit: 22%) and ω C₅ (2%, and 4.2%) are higher in non-dusty
319 samples (Fig. 5a,b).

320 The malonic to succinic acid (C_3/C_4) ratios have been used to evaluate the extent of
321 photochemical aging of air masses. Low values of C_3/C_4 ratios (0.25–0.44; ave. 0.35) were
322 reported for vehicular emissions as compared to aged atmospheric aerosols (0.6–2.9; ave. 1.6)
323 (Kawamura and Ikushima, 1993). Malonic acid is thermally less stable than succinic acid in
324 vehicular exhaust emissions. Lower C_3/C_4 ratios were reported in the polluted area where the
325 primary source is significant (Kawamura and Ikushima, 1993; Deshmukh et al., 2018; Jung et
326 al., 2010), while higher ratios were reported for aerosols collected from remote marine and
327 remote Island (Wang et al., 2009; Fu et al., 2013; Kunwar et al., 2017). Higher C_3/C_4 ratios
328 (0.6–5.8) has been reported from marine aerosols during round the world cruise due to the
329 severe photochemical aging of air masses (Fu et al., 2013). Similarly, higher C_3/C_4 ratios were
330 reported in the daytime (ave. 0.81) than nighttime (0.59) samples collected from Rondonia
331 (Brazil) (Kundu et al., 2010b) due to more photochemistry in the daytime. The average C_3/C_4
332 ratios from Gobi Desert (G-D), Chinese Loess (CJ-1), and Tengger dust (CJ-2) are 0.64, 0.30,
333 and 0.46, respectively. These ratios are almost similar to this study of dusty (range: 0.50–0.51,
334 ave. 0.50 ± 0.00) and non-dust snowpit samples (0.23–0.63, ave. 0.41 ± 0.14). Hence, C_3/C_4 ratios
335 from this study indicate that dust is not responsible for the atmospheric photochemical
336 processing of C_4 to C_3 . The dominant presence of succinic (C_4) over C_3 has been reported in
337 the Antarctic aerosols (Kawamura et al., 1996b), spring snowpack samples from the Arctic
338 (Narukawa et al., 2002), and winter aerosols from Tokyo (Sempéré and Kawamura, 1994). It
339 should be noted that a higher relative abundance of C_4 is common in the cold environment
340 where photochemical oxidation is less severe (Sempere and Kawamura, 2003). The average
341 C_3/C_4 ratio of this study is 0.46 further suggests that snow particles are influenced from urban
342 aerosols with a strong influence of fossil fuel combustion without severe photochemical
343 processing from transboundary air pollution of east Asia. Fresh aerosols have to be captured
344 and deposited within the snow particles. Snow metamorphism (e.g., nos. 1 and 3) plays an
345 important role in these diacids, i.e., fresh organic compounds are confined.

346 In addition, unsaturated aliphatic diacids, i.e., maleic acid (M, cis configuration) and
347 fumaric (F, trans configuration), are formed by the degradation of aromatic hydrocarbons such
348 as toluene and benzene in the presence of oxidants. Under the intense solar radiation, M is
349 further isomerized to its trans isomer (F), through photochemical processes. Hence, M/F ratio
350 can be used to better understand photoisomerization. Lower M/F ratio is deciphered to the
351 higher photochemical aging. The M/F ratios range from 1.9–4.2 (3.0 ± 0.8) of this study, being
352 similar to the M/F ratios reported in the aerosols collected from remote Himalaya (1.55–8.16,
353 ave. 4.44) (Cong et al., 2015) and urban site such as New Delhi (2.0–3.6) (Miyazaki et al.,

2009), Beijing (2.3) and Mongolia (2.0) (Jung et al., 2010). The average M/F ratio from this study is 11.5 times higher than those reported in marine aerosols collected from the North Pacific (0.26). Further, the M/F ratio of this snow samples is comparable to biomass burning aerosols from Mt. Tai, China (2.0), Rondonia, Amazonia (2.8) and Mongolia (2.0) (Kunwar and Kawamura, 2014a; Jung et al., 2010; Kundu et al., 2010b). This finding also suggests that polar organic compounds are well deposited in the seasonal climatic snow line of Mt. Tateyama. The C₃/C₄ and M/F ratios suggest that Mt. Tateyama (Fig. 1) is the receptor site of fresh aerosols at least in the winter season (end of October to April 19, 2007) of Central Japan (Table S1).

5.4. Sources and formation mechanisms of diacids in the snow samples

Phthalic acid (Ph) and terephthalic (tPh) acids are emitted to the atmosphere from polynuclear aromatic hydrocarbons (PAHs). These aromatic diacids are further degraded to mM, F, Gly and MeGly. These compounds further degrade to ωC₂ and finally result in oxalic acid (C₂). Hence, it is better to see the correlations between these compounds with Ph and tPh. Ph and benzoic acids show strong correlations with C₂ in the dusty (R²= 1.00 and 1.00) and non-dusty (0.88 and 0.84) snowpit samples (Fig. S1). Further, strong correlations of Ph and benzoic acid with unsaturated aliphatic diacids such as mM in the dusty (1.00 and 0.97, respectively) and non-dusty (0.75 and 0.94) snowpit samples, F in the dusty (0.90, and 0.79) and non-dusty (0.85 and 0.94) snowpit samples. Very strong correlations of Ph and benzoic acid are observed with other descendent such as M, Gly, and MeGly in both dusty (range: 0.78 to 0.99 and 0.79 to 0.98) and non-dusty (0.42 to 0.88 and 0.84 to 0.94) snowpit samples. Similar correlations of tPh were observed with mM, C₂, ωC₂, F, M, Gly, MeGly in the dusty (0.73-0.99 and) and non-dusty (0.40-0.83) snowpit samples. This result suggests that short-chain diacids are produced by the photooxidation of aromatic hydrocarbons.

Further, both aromatic and aliphatic unsaturated diacids showed strong correlations with short-chain diacids C₂-C₅ (R²= 0.72 to 0.99). Intermediate compounds (e.g., hC₄, kC₃, and kC₇) also showed strong correlations with C₂ (0.70, 0.77, and 0.91, respectively), C₃ (0.92, 0.82, and 0.96), C₄ (0.83, 0.85, and 0.99), and C₅ (0.82, 0.88, and 0.98). The strong correlations of C₂-C₅ diacids with unsaturated aliphatic, branched-chain and multifunctional diacids, together with tracers of plastic burning products such as Ph and tPh, suggest a contribution of anthropogenic sources including plastic burning followed by severe photochemical oxidation of PAHs and deposition to alpine snows in central Japan via long-range atmospheric transport.

Coal-burning emits sulfur dioxide (SO₂). When SO₂ reacts with water, it forms sulfuric acid (H₂SO₄) and deposits as sulfate (SO₄²⁻). We found strong correlations of nss-SO₄²⁻ with

388 short chain diacids C₂-C₅ (0.53-0.79), branched saturated diacids, i.e., iC₅-iC₆ (0.73-0.74),
 389 aliphatic unsaturated diacids (0.60-0.77), aromatic diacids (0.80-0.81) and oxoacids such as
 390 ωC₂ (0.91), ωC₃ (0.53), ωC₈ (0.69), ωC₉ (0.80), benzoic acid (0.76) and MeGly (0.92) in non-
 391 dusty snowpit samples, suggesting that diacids and related compounds are linked to
 392 anthropogenic activities. ss-SO₄²⁻ is the indicator of marine source, which also showed
 393 significant correlations with oxoacids ωC₉ (0.63), ωC₈ (0.53), ωC₇ (0.57), and ωC₂ (0.65),
 394 suggesting the unsaturated fatty acids (UFAs) acids from marine source influence the non-
 395 dusty snowpit samples. UFAs acids are precursors compounds for oxoacids. These results
 396 suggest that this sampling site during the non-dust period is influenced by both marine and
 397 continental sources.

398 Malonic (C₃) is hardly produced by the oxidation of aromatic structures having
 399 conjugated double bonds. It is likely produced by the oxidation of succinic acid (C₄) via an
 400 intermediate compound (i.e., malic acid). C₄ can be produced from gaseous aliphatic
 401 carboxylic acids, n-alkanes, aldehydes, and mid-chain ketocarboxylic acids (Kawamura and
 402 Ikushima, 1993; Kunwar et al., 2017, 2019). Strong correlations of C₄ with hC₄ (R²=0.91), C₃
 403 (0.88) and C₂ (0.79) in non-dusty snowpit samples and very strong correlations of C₄ with hC₄
 404 (0.99), C₃ (0.99) and C₂ (0.97) observed in dusty snowpit samples suggest that shorter-chain
 405 diacids are formed by the oxidation of longer-chain diacids.

406 nss-Ca²⁺ is a tracer of dust (Kunwar and Kawamura, 2014a). Interestingly, we found
 407 very strong correlations of nss-Ca²⁺ with C₂, (R²= 0.98) C₃ (0.99), C₄ (0.99), and C₅ (1.00), C₇
 408 (0.74), C₈ (0.81), C₁₀ (0.99), C₁₂ (0.99), iC₄-iC₅ (range: 0.92–0.99), aliphatic and aromatic
 409 acids (0.97-1.00), multifunctional diacids such as hC₄ (0.99), kC₃ (0.99), kC₇ (0.97), ω-
 410 oxoacids from ωC₂ to ωC₉ (0.92-0.99), and α-dicarbonyls such as Gly (0.98), and MeGly
 411 (0.99). The strong correlations of nss-Ca²⁺ with diacids and related compounds suggest that
 412 dust particles provided the surface for the oxidative reaction. Interestingly, nss-Ca²⁺ doesn't
 413 show any correlation with C₉ (R²= 0.28). The strong correlations of nss-Ca²⁺ with C₈, C₁₀, and
 414 C₁₂ suggest that bacterial activities from the dust are the source of long-chain diacids (Grosjean
 415 et al., 1978). Bacterial emission and unsaturated fatty acids from marine and terrestrial plants
 416 could be the precursors for C₈, C₁₀, and C₁₂ diacids. A strong correlation (0.94) is observed
 417 between MSA⁻ and nss-Ca²⁺, suggesting that dust is the source of MSA⁻. The higher
 418 concentrations of MSA⁻ and the secondary species in dusty snowpit samples than non-dusty
 419 samples were mainly attributed to the heterogeneous reaction and mixing of dust with polluted
 420 aerosol.

421 **5.4. Incloud oxidation for the formation of diacid and related compounds**

422 Isoprene accounts for more than half of non-methane volatile organics globally and has
423 been proposed as the source for the production of oxalic acid in-cloud process (Warneck, 2003,
424 Lim et al., 2005). Isoprene oxidation in gas phase yields glycolaldehyde, glyoxal, and
425 methylglyoxal, which can further dissolve in water and react with OH radicals to form oxalic
426 acid via glycolic, glyoxylic, pyruvic, and acetic acids (Pokhrel, 2015, references therein). The
427 aqueous-phase chemical mechanism proposed by Lim et al. 2005 is very similar to the cloud
428 photochemistry model reported by Ervens et al. (2004) except for the fate of methylglyoxal.
429 The incloud oxidation model proposed by Ervens et al. (2004) is the reaction between
430 methylglyoxal and OH, which yields pyruvic acid that is further oxidized to acetaldehyde and
431 finally CO₂ without forming low-volatility organic acids. However, methylglyoxal oxidation
432 yields pyruvic, acetic, glyoxylic, and finally oxalic acids (Lim et al., 2005). We found very
433 strong correlations (R^2) of C₂ with its precursor compounds (except for sample no. 6) such as
434 ω C₂ (dusty snowpit samples: 0.95 and non-dusty samples: 0.84), Gly (1.00 and 0.28), Pyr (0.70
435 and 0.16), and MeGly (0.99 and 0.82) (Fig. S1). However, C₂ does not show any correlations
436 with formic (0.00) and acetic (0.01) acids, but shows a strong correlation (0.70) with suberic
437 (C₈) acid in dusty snowpit samples (Fig. S2). Hence, hydrated glyoxylic acid is the major
438 pathway for the formation of oxalic acid in the cloud. Field observation from this sampling site
439 is similar to the in-cloud oxidation model of isoprene proposed by Ervens et al. (2004). For the
440 correlation analysis of dust samples, we did not include sample no. 6, which showed very high
441 concentrations of these diacids and related compounds (i.e., Fig. S1, S2, and S3).

442 Aromatic hydrocarbons (benzene and toluene) are the main suppliers of anthropogenic
443 emissions. Among these, toluene is one of the most ample species in the atmosphere. The
444 average concentrations of toluene were reported to be 2–39 ppb in urban, 0.05–0.8 ppb in rural,
445 and 0.01–0.25 ppb in remote areas (Finlayson-Pitts and Pitts, 2000). Aromatic hydrocarbons
446 are oxidized in the presence of OH, forming glyoxal and methylglyoxal. They have thus
447 formed Gly and MeGly, which are further oxidized by the OH radicals or decayed by
448 photolysis. Due to their highly effective Henry's law constants (i.e., including hydration of the
449 aldehydes), significant amounts of both glyoxal and methylglyoxal are dissolved in cloud water.
450 Additional oxidation products include ring retaining products (e.g., benzaldehyde, benzoic
451 acids), which can also partition into the aerosol surface, thus contributing to secondary organic
452 aerosol mass (Odum et al., 1996). Interestingly, phthalic acid (Ph) showed a strong correlation
453 with Gly (dusty snowpit samples: 0.99 and non-dusty samples: 0.42) and MeGly (1.00 and
454 0.81). In addition, Ph showed strong correlations with mM (1.00 and 0.75), F (0.99 and 0.85),

455 M (1.00 and 0.79), and C₂ (1.00 and 0.88). Benzoic acid also showed strong correlation with
456 mM (0.99 and 0.94), F (0.99 and 0.94), M (0.99 and 0.94), Gly (1.00 and 0.94), MeGly (0.99
457 and 0.94), and C₂ (1.00 and 0.84) (Fig. S3).

458 The occurrence of normal short-chain diacids (C₂-C₅), Pyr, Gly, MeGly and long-chain
459 diacids (C₈, C₁₁, C₁₂), oxoacids, aromatic diacids, and their precursors compounds together
460 with correlation analysis (Fig. S2 and S3) suggest that dust and non-dust samples emitted in the
461 source region and mixed with the polluted air during the long-range atmospheric transport.
462 Snow essentially comes from cloud water. Hence, incloud oxidation of isoprene, aromatic
463 acids, fatty acids, and bacterial metabolisms activities are an important source for diacids in
464 snowpit samples. Hence, heterogeneous oxidation reactions within the cloud condensation,
465 oxidation, and photolysis are the main reactions that took place in the cloud before reaching the
466 sampling site.

467 **5.5. Concentration ratios in dusty and non-dusty snowpit samples: A link to more** 468 **anthropogenic activities in dusty snowpit samples**

469 Ph is produced by incomplete combustion of PAHs such as naphthalene, whereas the
470 incomplete combustion of cyclic olefins (e.g., cyclic hexene) produces C₆. In contrast, C₉ is a
471 specific oxidation product of biogenic unsaturated fatty acids having a double bond at C₉
472 position. Hence, Ph/C₉ and C₆/C₉ ratios have been used as tracers to better distinguish
473 anthropogenic versus biogenic emissions (Pavuluri et al., 2010). The Ph/C₉ (dust: 8.0 and non-
474 dust: 2.3) and C₆/C₉ (2.0 and 1.3) ratios are higher in dusty snowpit samples, suggesting that
475 dust provided the surface area to adsorb anthropogenic organic compounds during the long-
476 range atmospheric transport (Kunwar and Kawamura, 2014a,b). The biogenic volatile organic
477 compounds (BVOCs) such as isoprene may be oxidized in the atmosphere to form less volatile
478 compounds that may condense and contribute to SOA formation (Kunwar et al., 2014a).
479 Biogenic emissions contribute more production of MeGly than Gly, giving higher of
480 MeGly/Gly ratios. We found that MeGly/Gly (0.39 and 0.52) ratios are higher in non-dusty
481 snowpit samples, further suggesting less biogenic influence in dusty snowpit samples.

482 C₂ is formed by the oxidation of long-chain diacids such as C₉. Hence, C₂/C₉ ratios can
483 decipher the formation of low molecular diacids from long-chain diacids. C₂/C₉ (42 and 14)
484 ratios are higher in dusty snowpit samples, suggesting that an intensive degradation of longer-
485 chain diacids occurs on the dust surface during long-range atmospheric transport because dust
486 provides a favorable area for the chemical reaction. The elevation of 2450 m a.s.l. of this
487 sampling site lies below the climatic snow line (Mt. Tateyama: 36.58° N), which is similar to
488 the elevation of climatic snow line (ground temperature below 0°C) of Eastern Siberia (2300-

489 2800 m), Kamchatka interior (2000-2800 m), northern slopes of Alps (2500-2800 m), and
 490 Rocky Mountains (2100-3350 m) in the Northern Hemisphere (<https://nsidc.org> and
 491 <https://www.quora.com>). Thus, snowfalls in Mt. Tateyama well captured these polar organic
 492 compounds, demonstrating that the heterogeneous aqueous reactions occur before the snow
 493 formation phase in the troposphere during the cold months from November-April via a long-
 494 range atmospheric transport of Asian Dust at high altitude over central Japan.

495 **6. Summary and Conclusions**

496 We study, for the first time, water-soluble dicarboxylic acids and related compounds in
 497 snow pit samples collected from the Alpine mountain site in central Japan (elevation, 2450 m
 498 a.s.l.). The molecular distributions of diacids are characterized by the predominance of oxalic
 499 acid (C₂) followed by succinic acid (C₄) and phthalic (Ph) in dusty snowpit samples
 500 (C₂>C₄>Ph), whereas malonic (C₃) acid is predominant after C₄ in the non-dusty snowpit
 501 samples (C₂>C₄>C₃). Glyoxylic (ω C₂) acid is the most abundant oxoacid followed by 4-
 502 oxobutanoic (ω C₄) and 3-oxopropanoic (ω C₃) acid for dusty and non-dusty snowpit samples.
 503 The molecular characteristics are consistent between oxoacids (ω C₂> ω C₄) and diacids (C₂>C₄),
 504 suggesting that organic compounds in snowpit sequences have a similar photochemical process
 505 and/or similar source. The C₃/C₄ ratios of Gobi desert (0.30), Chinese Loess (0.30), and
 506 Tengger dust (0.46) are close to this study of non-dusty (range: 0.22 to 0.63, ave. 0.41±0.14),
 507 dusty (0.50 to 0.51, ave. 0.50±0.007), and total samples (n=10) of snowpit (0.23-0.63, ave.
 508 0.45 ±0.12), indicating the influence of fresh aerosols prior to the formation of snow particles.

509 The relative abundance of C₂ (48%) to total diacids is higher in dusty snowpit samples,
 510 suggesting that the aerosols are subjected to more photochemical oxidation for dusty samples.
 511 We found very strong correlations (R²) of C₂ with its precursors such as ω C₂ (dusty snowpit
 512 samples: 0.95 and non-dusty snowpit samples: 0.84), Gly (1.00 and 0.28), MeGly (0.99 and
 513 0.82), Pyr (0.70 and 0.16) and suberic acid (0.70 and 0.50). Hence, hydrated glyoxylic acid is
 514 the major pathway for the formation of oxalic acid via heterogenous incloud oxidation. The
 515 C₆/C₉ (dusty snowpit samples: 2.0, non-dusty snowpit samples: 1.27), Ph/C₉ (8.0 and 2.3), and
 516 C₂/C₉ (41.6, 14.0) ratios are higher in dusty snowpit layers, suggesting the mixing of polluted
 517 air masses with the dusty aerosols followed by snow scavenging.

518 We found very strong correlations of nss-Ca²⁺ with short-chain diacids, i.e., C₂, C₃, C₄,
 519 and C₅ (range: 0.98-1.00), long-chain diacids, e.g., C₇ (0.74), C₈ (0.81), C₁₀ (0.99), C₁₂ (0.99),
 520 iC₄-iC₅ (0.92-0.99), aliphatic and aromatic acids (0.97-1.00), multifunctional diacids such as
 521 hC₄ (0.99), kC₃ (0.99) and kC₇ (0.97), ω -oxoacids from ω C₂ to ω C₉ (0.92-0.99), Gly (0.98),

522 and MeGly (0.99), suggesting that dusts provide the surface for the oxidative reaction. Snow
 523 particles essentially come from cloud water (>2000m). Hence, the strong correlations of
 524 incloud oxidation product of isoprene, aromatic acids, and fatty acids suggest heterogeneous
 525 aqueous phase reaction together with adsorption, condensation and photolysis and/or in situ
 526 oxidation processes are an important source for diacids and related compounds and they are
 527 involved in cloud condensation nuclei and well deposited in the sampling site of Mt. Tateyama
 528 (2450m a.s.l.), sea coast in central Japan. It further helps to evaluate air quality in the free
 529 troposphere during cold months of central Japan (November-April), showing the atmospheric
 530 transport and formation processes of organic compounds in dusty and non-dusty snow layers,
 531 and diacids photochemistry during snow metamorphism.

532

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536 (Total words: 6,489)

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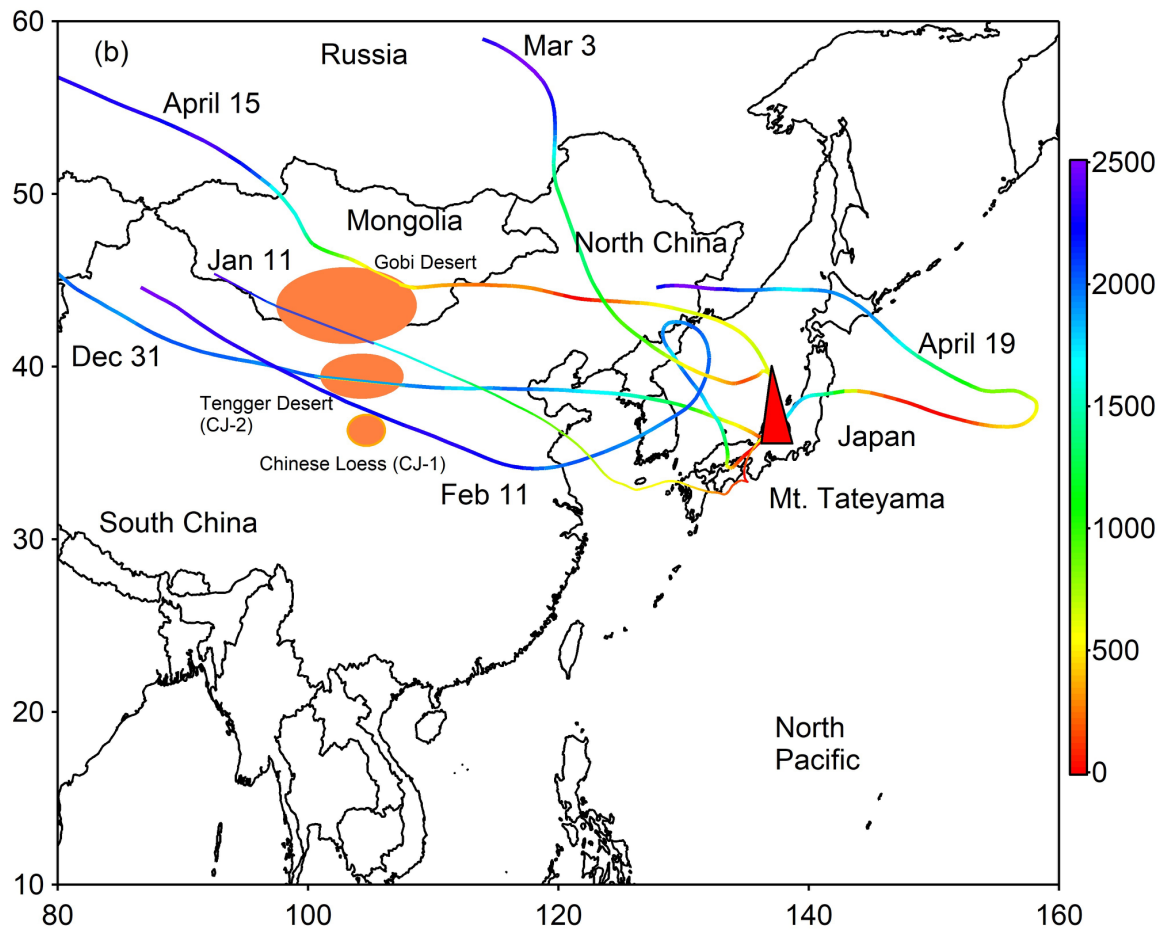
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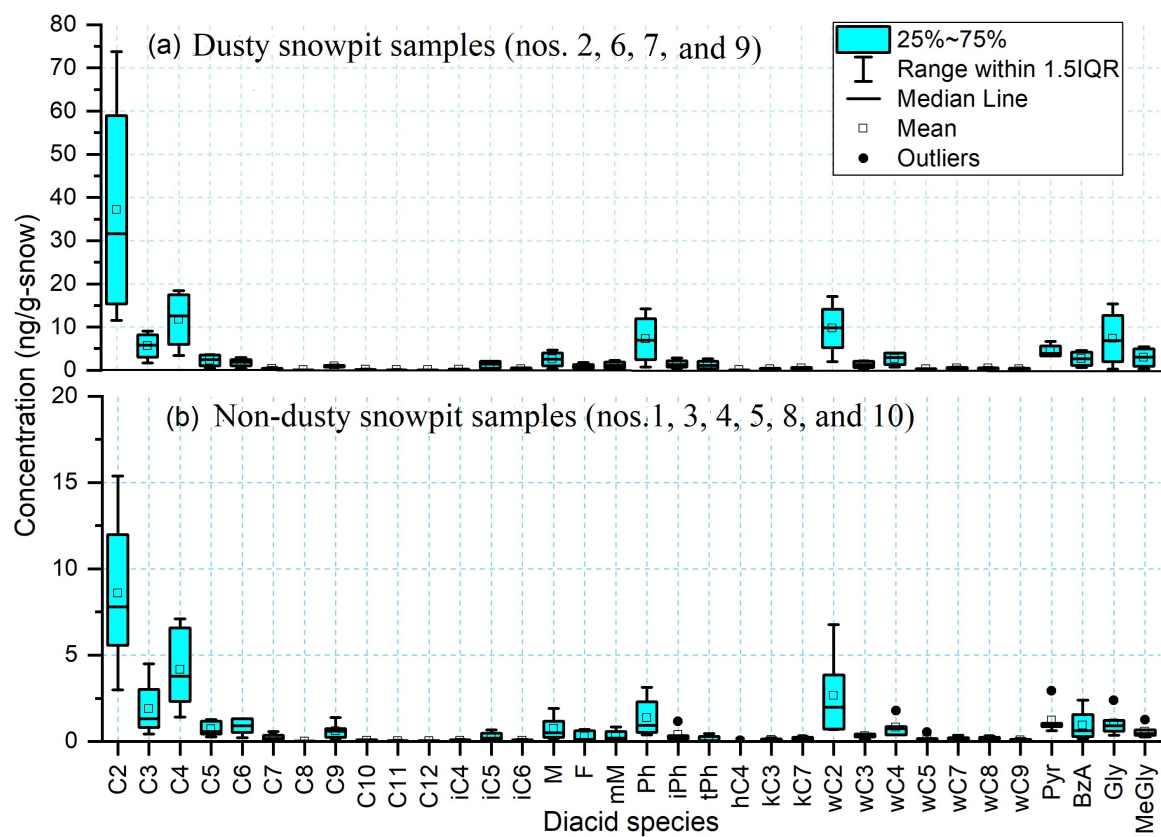
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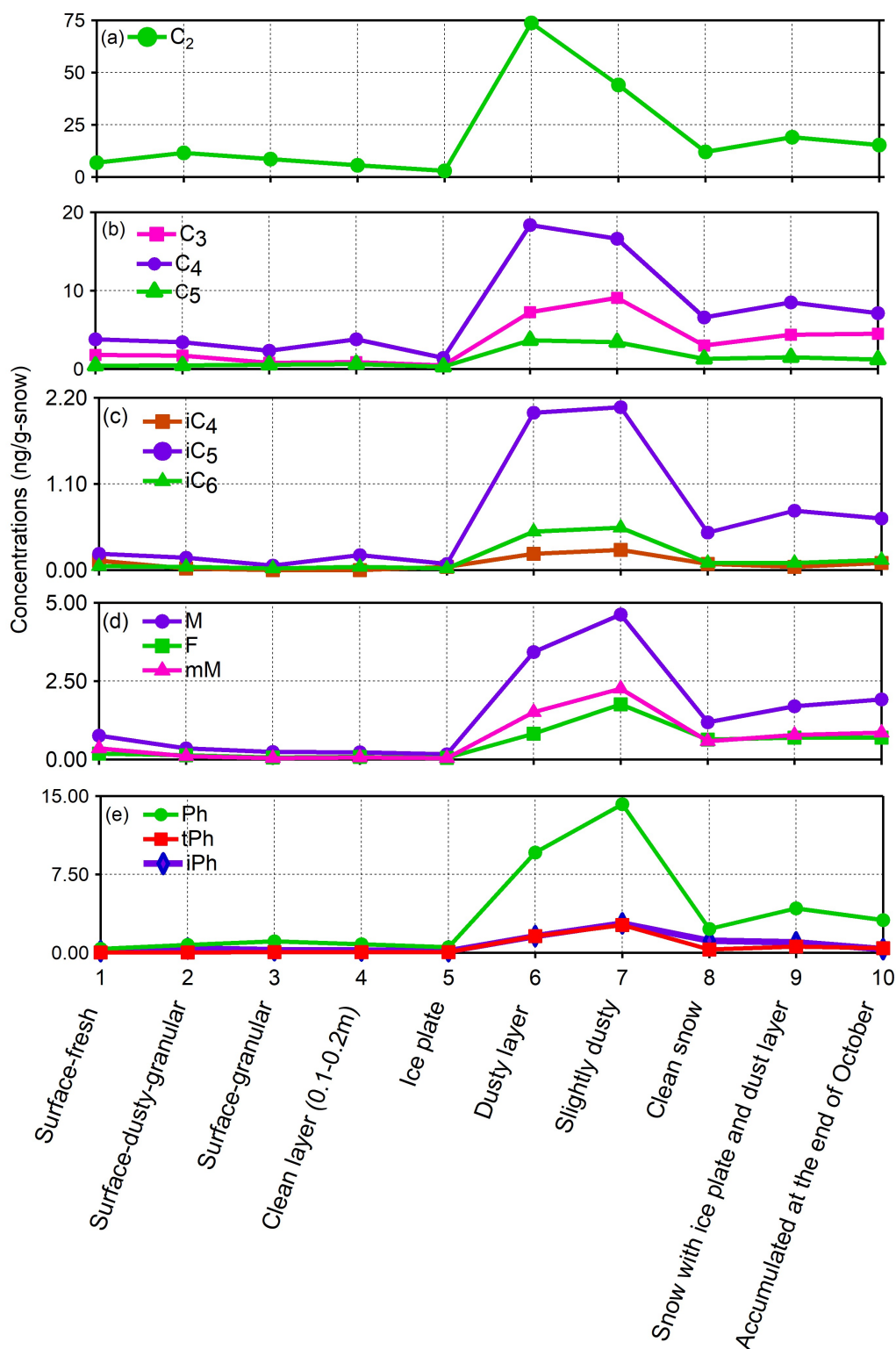
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 770 Figure 1. (a) Map showing the geographical region of Murodo-Daira, Mt. Tateyama of Central
 771 Japan, 6.5 m long snowpit samples were excavated (19 April, 2008) at elevation of 2450 m
 772 a.s.l. and (b) map showing 5 days (2500 m a.s.l. above sea level in meter) backward trajectory
 773 analysis of Murodo-Daira, Mt. Tateyama of Central Japan during the snow accumulation
 774 period (2007 October to 2008 April).
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777 Figure 2. Average molecular distributions of diacids, oxoacids, and α -dicarbonyls in (a) dusty
 778 snowpit samples and (b) non-dusty snowpit samples collected from snowpit sequences (6.5 m) at
 779 the Murodo-Daira site, Mt. Tateyama in Central Japan.

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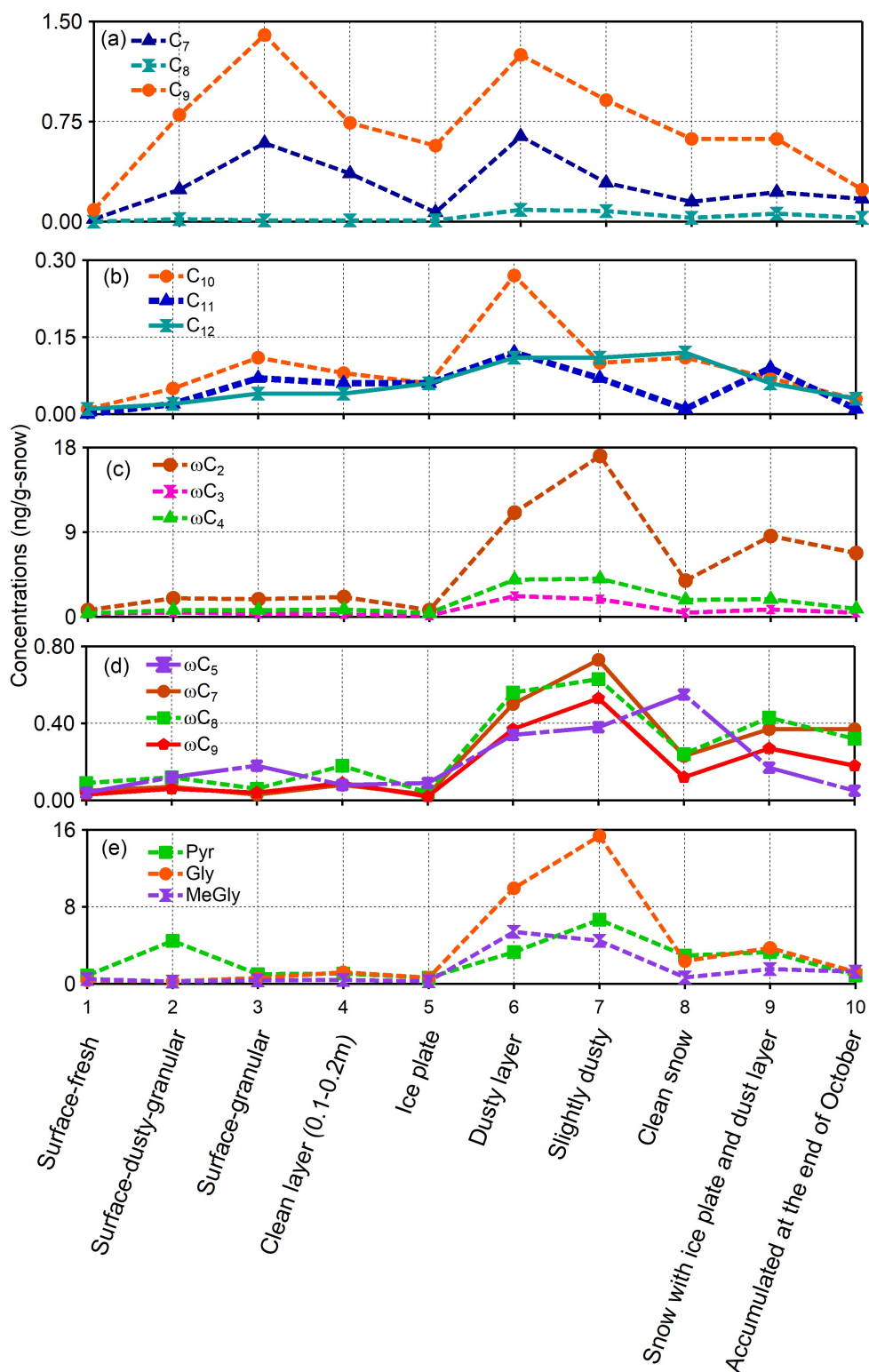
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783 Figure 3. Concentration changes of (a, b) short-chain low molecular weight diacids (s-

784 DCAs) of (a) C₂ (b) C₃, C₄, and C₅, (c) branched-chain saturated diacids (iC₄, iC₅, and785 iC₆), and (d, e) unsaturated diacids (M, F, mM, Ph, tPh, and iPh) in the snowpit

786 sequences (6.5 m) collected from the Murodo-Daira site, Mt. Tateyama in Central Japan.

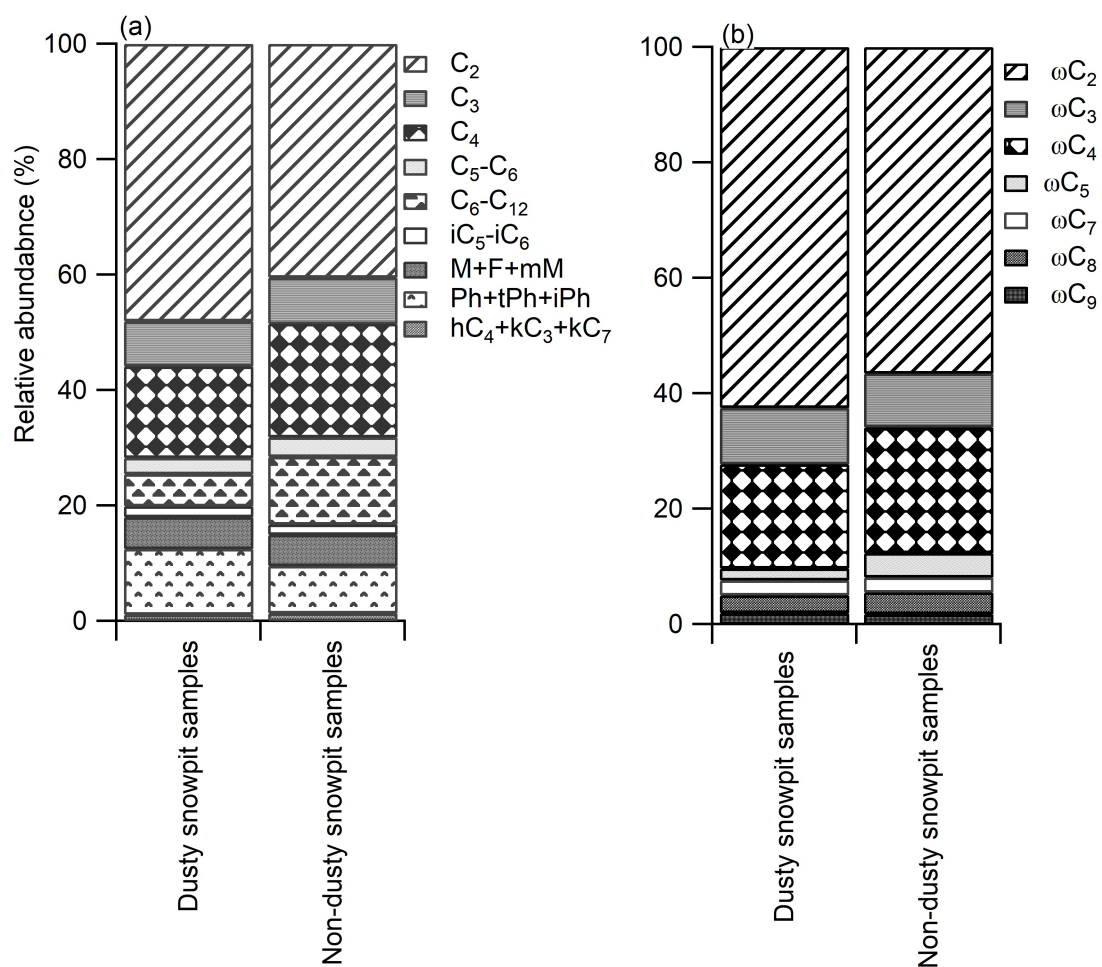
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789 Figure 4. Concentration changes of long-chain low molecular weight diacids, (a, b) C₇-C₁₂,
 790 (c, d) oxoacids (ωC₂ - ωC₉), (e) pyruvic acid (Pyr) and α-dicarbonyls (Gly and MeGly) in
 791 snowpit sequences (6.5 m) collected from the Murodo-Daira site, Mt. Tateyama in Central
 792 Japan.

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794
 795 Figure 5. Relative abundances of (a) diacids and (b) oxoacids in dusty and non-dusty snowpit
 796 samples from snowpit sequences (6.5 m) collected from the Murodo-Daira site, Mt. Tateyama
 797 in Central Japan.
 798

Table S1. Descriptions of surface snow samples (Nos. 1-3) collected around a pit site and snowpack samples (Nos. 4-10) collected from a pit (6.6 m in depth) at Murodo-Daira, Mt. Tateyama, Japan (Kawamura et al., 2012).

Sample ID	Depth (m) from the surface	Description
No. 1	Surface	Fresh snow (collected at 10:15 am)
No. 2	Surface	Dusty and granular snow (fresh snow seemed not accumulated due to a strong wind around the site). Dust may be deposited over the snowfield during Asian dust events that were observed on April 14-16, 2008 by lidar over Toyama.
No. 3	Surface	Granular snow (obtained at 15:15 pm). Surface snow melted due to the warmer temperature and stronger radiation in the afternoon and granular snow was collected.
No. 4	0.1-0.2	Clean snow layer
No. 5	0.5	Snow with ice plate (ca. 2 cm thickness). The only ice layer was collected.
No. 6	0.90-1.1	Dusty snow layer. Asian dust event on March 3, 2008 may be the source of the dirty layer due to a lidar observation in Toyama.
No. 7	1.2-1.3	Dust layer possibly deposited on February 11, 2008.
No. 8	3.5-3.6	Clean snow layer
No. 9	3.7-3.8	Snow with ice plate and dusts. Dust may have deposited on January 11, 2008.
No. 10	6.4-6.5	Snow accumulated at the end of October 2007

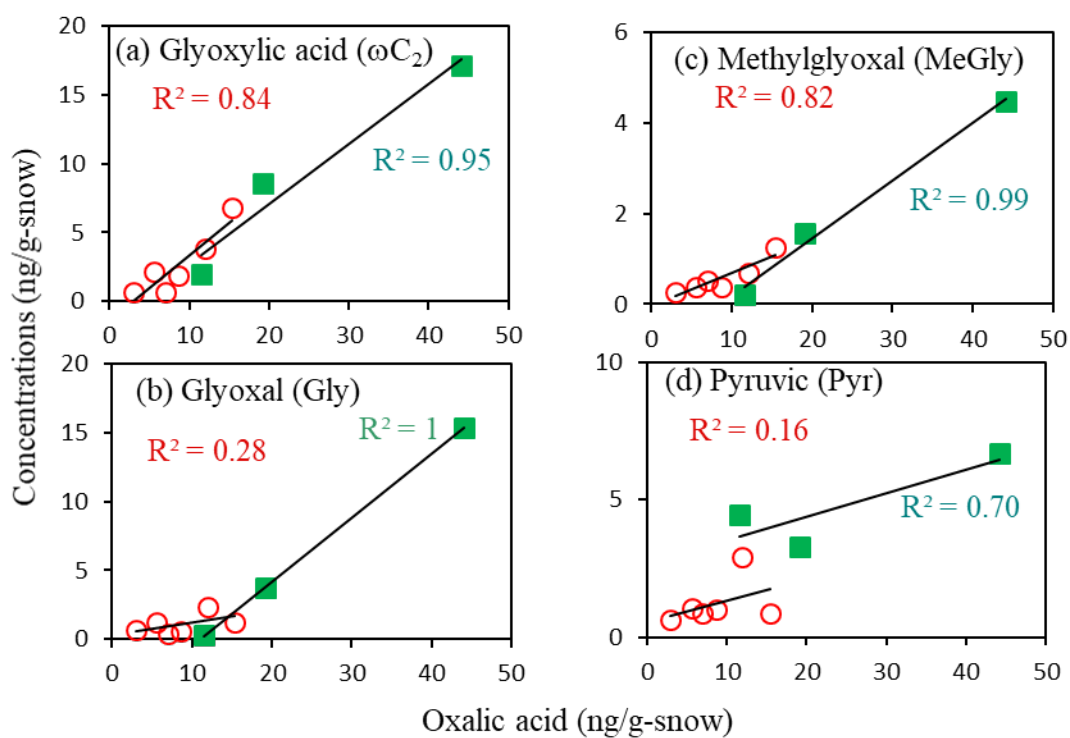
Sampling was conducted from 10:15 to 15:15 on April 19, 2008.

Surface snow samples were collected near the pit site, but the locations were not exactly the same.

801 **Table S2.** Concentrations of dicarboxylic acids, ω -oxocarboxylic acids, pyruvic acid, and α -
 802 dicarbonyls in snow pit samples from the high mountain region of Central Japan in 2008 at
 803 Murodo-Daira, Mt. Tateyama.

Concentration (ng/g-snow)		Dust samples (n=4)		Nondust samples (n=6)		Chinese Loess	Tengger dust	Gobi Desert
Compounds	C _n , Abbr.	Min-Max	Ave±Std	Min-Max	Ave±Std	(CJ-1)	(CJ-2)	(G-D)
Oxalic	C ₂	12-74	37±28	3-15	8.6±4.5	5090	36672	38589
Malonic	C ₃	1.7-9.1	5.6±3.2	0.44-4.5	1.9±1.6	202	1855	1957
Succinic	C ₄	3.4-18	12±7	1.4-7.1	4.2±2.3	657	4040	3039
Glutaric	C ₅	0.46-3.6	2.3±1.5	0.28-1.3	0.72±0.42	111	660	776
Adipic	C ₆	0.34-2.9	1.8±1.1	0.21-1.3	0.78±0.46	70	567	3327
Pimeric	C ₇	0.22-0.64	0.35±0.2	0.02-0.59	0.23±0.21	66	714	1160
Suberic	C ₈	0.02-0.09	0.06±0.03	0-0.03	0.02±0.01	0	0	1185
Azelaic	C ₉	0.62-1.2	0.89±0.26	0.09-1.4	0.61±0.46	182	4557	3888
Sebacic	C ₁₀	0.05-0.27	0.12±0.1	0.01-0.11	0.06±0.04	36	2396	2592
Monodecanoic	C ₁₁	0.02-0.12	0.08±0.04	0-0.07	0.04±0.03	0	226	6990
Dodecanoic	C ₁₂	0.02-0.11	0.08±0.04	0.01-0.06	0.03±0.02	0	0	0
Branched saturated diacids								
Methylmalonic	iC ₄	0.02-0.26	0.13±0.12	0-0.12	0.06±0.05	0	0	0
Methylsuccinic	iC ₅	0.16-2.08	1.25±0.95	0.06-0.66	0.28±0.24	91	248	144
Methylglutaric	iC ₆	0.04-0.54	0.29±0.26	0.02-0.13	0.06±0.04	0	36	0
Unsaturated diacids								
Maleic	C ₄ , M	0.35-4.6	2.5±1.9	0.17-1.92	0.75±0.7	122	280	597
Fumric	C ₄ , F	0.14-1.8	0.86±0.67	0.05-0.7	0.29±0.3	352	169	386
Methylmaleic	C ₅ , mM	0.1-2.26	1.16±0.93	0.04-0.85	0.32±0.34	32	384	267
Phthalic	C ₈ , Ph	0.75-14	7.2±5.9	0.39-3.1	1.4±1.1	875	4133	1424
Isophthalic	C ₈ , iPh	0.41-2.8	1.5±1	0.15-1.2	0.38±0.39	0	0	1918
Terephthalic	C ₈ , tPh	0.03-2.7	1.2±1.2	0.02-0.45	0.16±0.18	0	125	170
Hydroxylated diacids								
Hydroxysuccinic	hC ₄	0-0.1	0.05±0.04	0-0.07	0.01±0.03	20	52	45
Ketodiacids								
Ketomalonic	kC ₃	0.14-0.46	0.3±0.14	0.01-0.23	0.11±0.09	0	65	174
Ketopimelic	kC ₇	0.1-0.62	0.42±0.24	0.06-0.3	0.16±0.1	0	0	40
Total DCAs	0	6.4-328	62±102	5.5-31	17±10	14320	108866	132171
ω -oxocarboxylic acids								
Glyoxylic	ω C ₂	1.97-17	9.7±6.3	0.7-6.8	2.7±2.32	347	2061	4412
3-Oxopropanoic	ω C ₃	0.48-2.2	1.3±0.84	0.12-0.44	0.32±0.12	36	245	569
4-Oxobutanoic	ω C ₄	0.73-4	2.6±1.6	0.39-1.8	0.82±0.51	27	424	543
5-Oxopentanoic	ω C ₅	0.12-0.38	0.25±0.13	0.04-0.55	0.17±0.2	35	60	243
7-oxoheptanoic	ω C ₇	0.07-0.73	0.42±0.27	0.03-0.37	0.13±0.14	21	345	337
8-Oxooctanoic	ω C ₈	0.12-0.63	0.43±0.23	0.04-0.32	0.16±0.11	0	58	110
9-Oxononoic	ω C ₉	0.06-0.53	0.31±0.2	0.02-0.18	0.08±0.06	22	34	853
Total w-oxoacids		1.4-26	8.6±8.3	1.3-10	4.4±3.4			
Pyruvic	C ₃ , Pyr	0.63-6.7	2.51±2	0.63-2.9	1.2±0.85	178	975	1549
α -dicarbonyls								
Glyoxal	C ₂ , Gly	0.27-15	3.6±5.1	0.37-2.4	1.1±0.73	81	546	667
Methylglyoxal	C ₃ , MeGly	0.22-5.4	1.5±1.9	0.27-1.3	0.58±0.36	45	300	541
Total α -dicarbonyls	0	0.49-20.4	10.2±9.1	0.64-3.7	1.68±1.09	126	846	1208

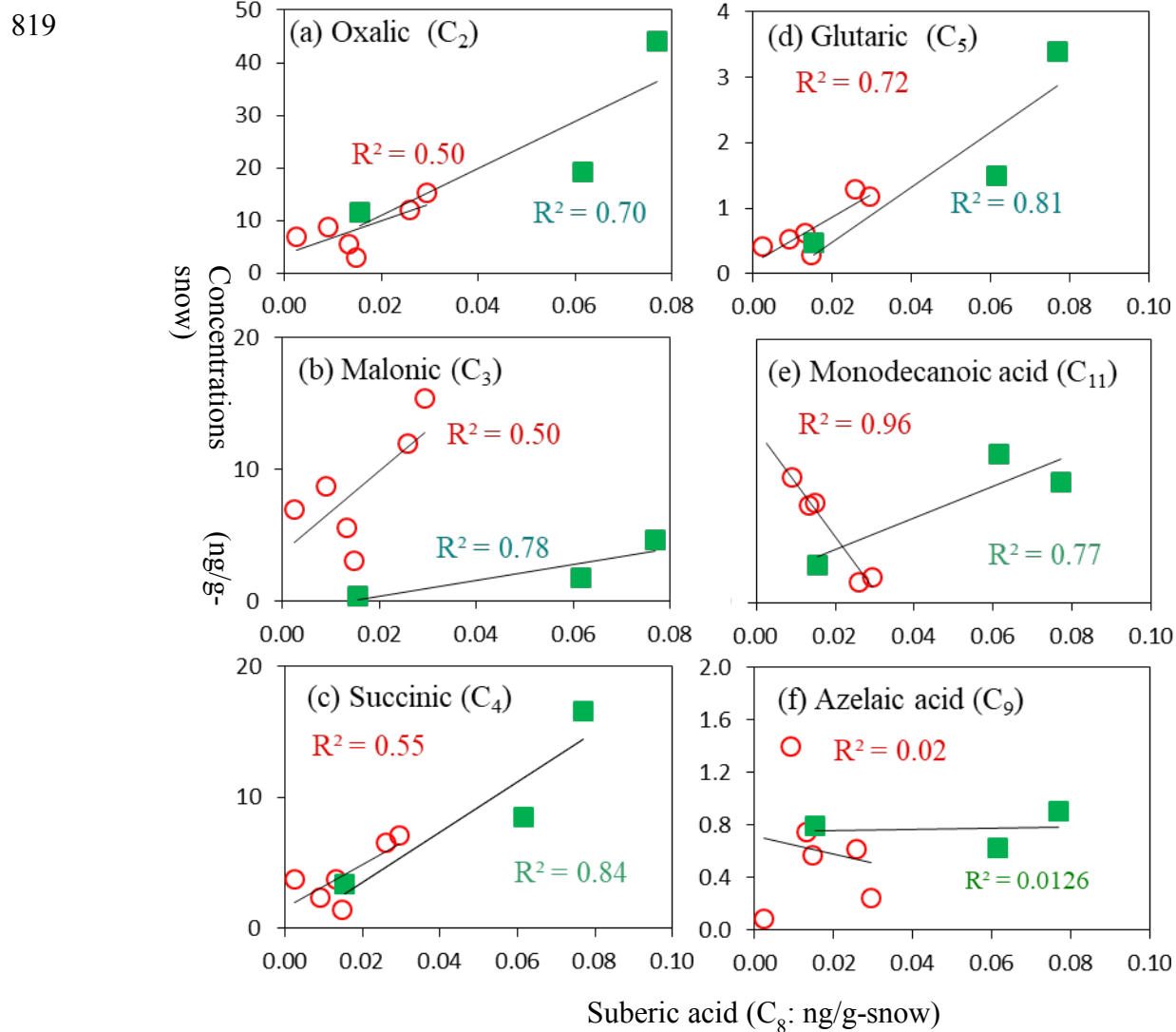
806 **Figure S1:** Correlation plots of oxalic acid with (a) glyoxylic acid (ωC_2), (b) glyoxal (Gly), (c)
 807 methylglyoxal (MeGly), and (d) pyruvic acid (Pyr) in snowpit samples collected from the
 808 Murodo-Daira site, Mt. Tateyama in Central Japan. Red open circle and green closed square
 809 indicate non-dusty and dusty snowpit (excluding no.6) samples, respectively.
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813 **Figure S2:** Correlation plots (red and green colors indicate the non dusty and dusty
 814 samples, respectively) of suberic acid with (a) oxalic (C_2), (b) malonic (C_3), (c) succinic
 815 (C_4) (d) glutaric (C_5), (e) undecanedioic acid (C_{11} : sample no. 1 has zero concentration),
 816 and (f) azelaic acid (C_9) in snowpit samples (excluding no.6) collected from the Murodo-
 817 Daira site, Mt. Tateyama in Central Japan.
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820 **Figure S3.** Correlation plots of phthalic and benzoic acids (red and green colors indicate the non dusty and dusty
 821 samples, respectively) with (a) methylmaleic (mM), (b) fumaric (F), (c) maleic (M), (d) glyoxal (Gly), (e)
 822 methylglyoxal, and (f) oxalic acid with phthalic acid, and (g) methylmaleic (mM), (h) fumaric (F), (i) maleic (M),
 823 (j) glyoxal (Gly), (k) methylglyoxal, and (l) oxalic acid in snowpit samples (excluding no.6) collected from the
 824 Murodo-Daira site, Mt. Tateyama in Central Japan.

