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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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12

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.

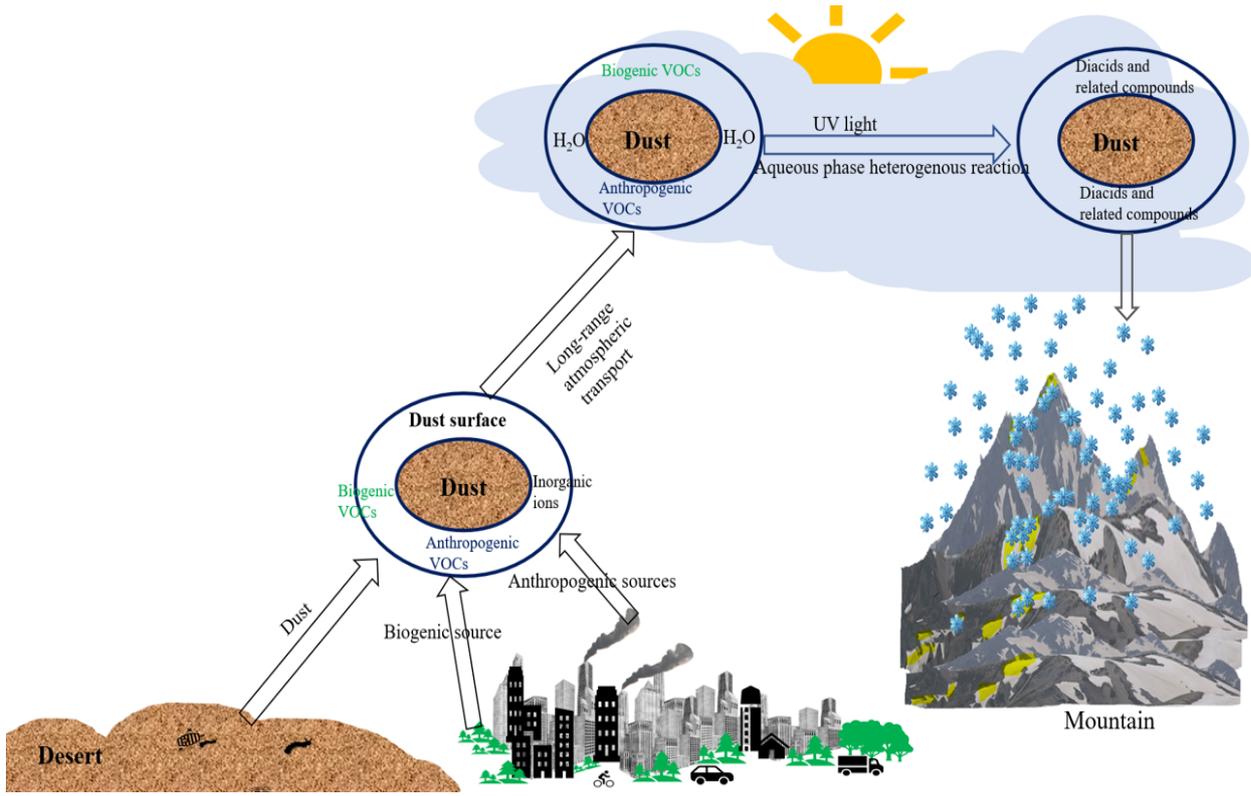
20 3. Atmospheric transport of diacids and oxoacids with Asian dust is important.

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 (C<sub>2</sub>-C<sub>5</sub>) are observed in dusty snow than non-dusty snow  
35 samples. Longer chain diacids (C<sub>7</sub>-C<sub>12</sub>) 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 (C<sub>2</sub>, ave, 20±22 ng/g-snow) followed by  
39 succinic (C<sub>4</sub>, 7.2±5.9 ng/g -snow), and malonic acids (C<sub>3</sub>, 3.3±2.9 ng/g -snow) for all the snow  
40 layers. Lower C<sub>3</sub>/C<sub>4</sub> 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)

50

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 (C<sub>2</sub>-C<sub>5</sub>; S-DCAs)  
55 and long-chain diacids (C<sub>6</sub>-C<sub>12</sub>; L-DCAs), ω-oxoacids (ωC<sub>2</sub>-ωC<sub>9</sub>), 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  $\alpha$ -  
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 (BF<sub>3</sub>)/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  $\mu$ l) containing free oxalic (C<sub>2</sub>), malonic (C<sub>3</sub>), succinic (C<sub>4</sub>), glutaric (C<sub>5</sub>),  
113 and adipic (C<sub>6</sub>) acids with concentrations of 1.03, 1.12, 1.46, 1.04, and 0.83 nmoles/ $\mu$ 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 C<sub>2</sub> and more than 91% for C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub>. Similarly, C<sub>2</sub>  
116 is the most volatile organic compound among these diacids and related compounds, thus C<sub>7</sub> to  
117 C<sub>12</sub> 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  $\mu\text{m}$  and CJ-2, < 100  
126  $\mu\text{m}$ ) and Mongolian Gobi deserts (G-D, < 10  $\mu\text{m}$ ) 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  $\alpha$ -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 C<sub>2</sub> (ave. 8.6±4.5 SD ng/g-snow) followed by C<sub>4</sub>  
 155 (4.2±3 ng/g-snow), C<sub>3</sub> (1.9 ±1.6 ng/g-snow), and phthalic (Ph) acid (1.4±1.1 ng/g-snow).  
 156 Similar distributions (C<sub>2</sub>>C<sub>4</sub>>C<sub>3</sub>) 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 C<sub>2</sub> (12-74 ng/g-snow, ave: 37±28 ng/g-snow), followed by C<sub>4</sub> (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 C<sub>3</sub>/C<sub>4</sub> ratios are  
 165 higher than 2.0 (Kawamura and Bikkina, 2016; Kunwar and Kawamura, 2014a). However, the  
 166 concentration ratios of C<sub>3</sub>/C<sub>4</sub> 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 (C<sub>2</sub>-C<sub>12</sub>), branched-chain (iC<sub>4</sub>-iC<sub>6</sub>), unsaturated (M, F, mM, Ph, iPh,  
 173 and tPh), keto (kC<sub>3</sub> and kC<sub>7</sub>) and hydroxyl (hC<sub>4</sub>) diacids, oxocarboxylic acids (ωC<sub>2</sub>-ωC<sub>9</sub> 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 C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> 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.  $7.2 \pm 4.2$  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<sub>2.5</sub>) 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 ( $\omega C_2$ ), 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 (iC<sub>5</sub>), 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 (iC<sub>4</sub>, iC<sub>5</sub>, and iC<sub>6</sub>). Among the branch chain diacids, methyl succinic acid (iC<sub>5</sub>) is the  
218 dominant ( $1.25 \pm 0.95$  and  $0.28 \pm 0.24$  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 C<sub>4</sub>-C<sub>6</sub> 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 (iC<sub>4</sub>, iC<sub>5</sub> and iC<sub>6</sub>) with C<sub>2</sub> (R<sup>2</sup>=0.96), C<sub>3</sub> (0.94), C<sub>4</sub> (0.98), C<sub>5</sub> (0.98), and suberic (C<sub>8</sub>)  
 224 acid (0.89), suggesting that short-chain (C<sub>2</sub>-C<sub>5</sub>) and long-chain diacids (C<sub>8</sub>) 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 C<sub>2</sub> and C<sub>3</sub>, 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 (C<sub>7</sub>-C<sub>12</sub>),  
 237 oxoacids, pyruvic acid, and  $\alpha$ -dicarbonyls. Among long-chain diacids, C<sub>9</sub> shows the highest  
 238 concentration. Except for C<sub>6</sub>, long-chain diacids (e.g., C<sub>7</sub>-C<sub>9</sub>) showed higher concentrations in  
 239 surface granular (No. 3) and dusty snowpit samples during Asian dust events, whereas C<sub>10</sub> to  
 240 C<sub>12</sub> diacids showed the highest concentration in dusty snow pit layer (Fig. 4c), followed by the  
 241 second (except for C<sub>11</sub>) 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 C<sub>10</sub>), and/or bottom of the snowpit (No. 10). The oxidation  
 244 products of low molecular weight unsaturated fatty acids (e.g., C<sub>14:1</sub>, C<sub>16:1</sub>, C<sub>18:1</sub>, C<sub>18:2</sub>, C<sub>18:3</sub>,  
 245 C<sub>18:1 $\omega$ 7</sub>, and C<sub>18:1 $\omega$ 9</sub>) derived from phytoplankton and bacterial activities and high molecular  
 246 weight unsaturated fatty acids (e.g., C<sub>20:4</sub>, C<sub>20:5</sub>, C<sub>22:1</sub>, C<sub>22:6</sub>, and C<sub>24:1</sub>) are pimelic (C<sub>7</sub>), suberic  
 247 (C<sub>8</sub>), azelaic (C<sub>9</sub>) sebacic (C<sub>10</sub>), undecanedioic (C<sub>11</sub>), and dodecandioic (C<sub>12</sub>) acids (C<sub>7</sub>-C<sub>12</sub>).  
 248 For example, C<sub>9</sub> and C<sub>11</sub> can be produced by the photooxidation of unsaturated fatty acids  
 249 (UFAs) such as oleic acid (C<sub>18:1</sub>) and vaccenic acid (C<sub>18:1 $\omega$ 7</sub>), 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 (C<sub>9</sub>) 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). C<sub>9</sub> is a specific photochemical oxidation

254 product of biogenic UFAs (e.g., C<sub>18:1</sub>) (Kawamura and Gagosian, 1987) and can be further  
 255 oxidized to C<sub>6</sub>, C<sub>7</sub>, and C<sub>8</sub> and short chain diacids (C<sub>2</sub>-C<sub>5</sub>) (Legrand et al., 2007; Pavuluri et al.,  
 256 2015).

## 257 **5.2. Molecular composition and concentration trends of oxoacids, pyruvic acid, and $\alpha$ -** 258 **dicarbonyls**

259 Among oxoacids, glyoxylic ( $\omega$ C<sub>2</sub>) acid is the dominant species (dusty snowpits: ave.  
 260  $9.7 \pm 6.3$  ng/g-snow, and non-dusty snowpits:  $2.7 \pm 2.3$  ng/g-snow), followed by 4-oxobutanoic  
 261 ( $\omega$ C<sub>4</sub>) acid ( $2.6 \pm 1.6$  ng/g-snow and  $0.82 \pm 0.51$  ng/g-snow) and 3-oxopropanoic ( $\omega$ C<sub>3</sub>) acid  
 262 ( $1.3 \pm 0.84$  ng/g-snow, and  $0.32 \pm 0.12$  ng/g-snow) in both dusty and non-dusty snow pit  
 263 samples (Table S2). Oxoacids ( $\omega$ C<sub>2</sub> >  $\omega$ C<sub>4</sub> >  $\omega$ C<sub>3</sub>) showed molecular characteristics similar to  
 264 those of diacids (C<sub>2</sub> > C<sub>4</sub> > C<sub>3</sub>). Predominance of  $\omega$ C<sub>2</sub> and  $\omega$ C<sub>4</sub> were reported from Antarctic  
 265 aerosol samples (Kawamura et al., 1996b) and predominance of  $\omega$ C<sub>2</sub> 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  $\omega$ C<sub>2</sub> 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,  $\omega$ C<sub>3</sub> and  $\omega$ C<sub>4</sub> are oxidation products of unsaturated fatty acids and longer  
 272 chain  $\omega$ -oxoacids (e.g.  $\omega$ C<sub>5</sub>- $\omega$ C<sub>9</sub>) rather than anthropogenic sources (Kawamura et al., 2001a,b;  
 273 Pokhrel, 2015).  $\omega$ C<sub>2</sub>- $\omega$ C<sub>4</sub> 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  $\omega$ -oxoheptanoic ( $\omega$ C<sub>7</sub>),  $\omega$ -oxooctanoic ( $\omega$ C<sub>8</sub>), and  $\omega$ -  
 277 oxononanoic ( $\omega$ C<sub>9</sub>) 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  $\omega$ -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 (hC<sub>4</sub>) 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  $\alpha$ -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., C<sub>2</sub> 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 C<sub>2</sub> (48%) in the dusty snowpit  
303 samples is higher than that of non-dusty samples (40%). In contrast, relative abundances C<sub>4</sub>  
304 and long-chain diacids (C<sub>5</sub>-C<sub>6</sub>) 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 C<sub>2</sub> (>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  $\omega$ C<sub>2</sub> (Legrand et al., 2007; Ervens et  
310 al., 2004). An increased relative abundance of C<sub>2</sub> (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 C<sub>2</sub> 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  $\omega$ C<sub>2</sub> to total oxoacids ( $\omega$ C<sub>2</sub>- $\omega$ C<sub>9</sub>) is higher (62%)  
317 in the dusty snowpit sample than non-dusty samples (56%). Accordingly, those of  $\omega$ C<sub>4</sub> (dusty  
318 snowpit: 18% and non-dusty snowpit: 22%) and  $\omega$ C<sub>5</sub> (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.  $0.50 \pm 0.00$ ) and non-dust snowpit samples (0.23–0.63, ave.  $0.41 \pm 0.14$ ). 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 ( $3.0 \pm 0.8$ ) 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  $C_3/C_4$  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  $\omega C_2$  and finally result in oxalic acid ( $C_2$ ). Hence, it is better to see the correlations between these compounds with Ph and tPh. Ph and benzoic acids show strong correlations with  $C_2$  in the dusty ( $R^2= 1.00$  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,  $C_2$ ,  $\omega C_2$ , 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  $C_2-C_5$  ( $R^2= 0.72$  to  $0.99$ ). Intermediate compounds (e.g.,  $hC_4$ ,  $kC_3$ , and  $kC_7$ ) also showed strong correlations with  $C_2$  (0.70, 0.77, and 0.91, respectively),  $C_3$  (0.92, 0.82, and 0.96),  $C_4$  (0.83, 0.85, and 0.99), and  $C_5$  (0.82, 0.88, and 0.98). The strong correlations of  $C_2-C_5$  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 ( $SO_2$ ). When  $SO_2$  reacts with water, it forms sulfuric acid ( $H_2SO_4$ ) and deposits as sulfate ( $SO_4^{2-}$ ). We found strong correlations of nss- $SO_4^{2-}$  with

388 short chain diacids C<sub>2</sub>-C<sub>5</sub> (0.53-0.79), branched saturated diacids, i.e., iC<sub>5</sub>-iC<sub>6</sub> (0.73-0.74),  
 389 aliphatic unsaturated diacids (0.60-0.77), aromatic diacids (0.80-0.81) and oxoacids such as  
 390 ωC<sub>2</sub> (0.91), ωC<sub>3</sub> (0.53), ωC<sub>8</sub> (0.69), ωC<sub>9</sub> (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-SO<sub>4</sub><sup>2-</sup> is the indicator of marine source, which also showed  
 393 significant correlations with oxoacids ωC<sub>9</sub> (0.63), ωC<sub>8</sub> (0.53), ωC<sub>7</sub> (0.57), and ωC<sub>2</sub> (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 (C<sub>3</sub>) is hardly produced by the oxidation of aromatic structures having  
 399 conjugated double bonds. It is likely produced by the oxidation of succinic acid (C<sub>4</sub>) via an  
 400 intermediate compound (i.e., malic acid). C<sub>4</sub> 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 C<sub>4</sub> with hC<sub>4</sub> (R<sup>2</sup>=0.91), C<sub>3</sub>  
 403 (0.88) and C<sub>2</sub> (0.79) in non-dusty snowpit samples and very strong correlations of C<sub>4</sub> with hC<sub>4</sub>  
 404 (0.99), C<sub>3</sub> (0.99) and C<sub>2</sub> (0.97) observed in dusty snowpit samples suggest that shorter-chain  
 405 diacids are formed by the oxidation of longer-chain diacids.

406 nss-Ca<sup>2+</sup> is a tracer of dust (Kunwar and Kawamura, 2014a). Interestingly, we found  
 407 very strong correlations of nss-Ca<sup>2+</sup> with C<sub>2</sub>, (R<sup>2</sup>= 0.98) C<sub>3</sub> (0.99), C<sub>4</sub> (0.99), and C<sub>5</sub> (1.00), C<sub>7</sub>  
 408 (0.74), C<sub>8</sub> (0.81), C<sub>10</sub> (0.99), C<sub>12</sub> (0.99), iC<sub>4</sub>-iC<sub>5</sub> (range: 0.92–0.99), aliphatic and aromatic  
 409 acids (0.97-1.00), multifunctional diacids such as hC<sub>4</sub> (0.99), kC<sub>3</sub> (0.99), kC<sub>7</sub> (0.97), ω-  
 410 oxoacids from ωC<sub>2</sub> to ωC<sub>9</sub> (0.92-0.99), and α-dicarbonyls such as Gly (0.98), and MeGly  
 411 (0.99). The strong correlations of nss-Ca<sup>2+</sup> with diacids and related compounds suggest that  
 412 dust particles provided the surface for the oxidative reaction. Interestingly, nss-Ca<sup>2+</sup> doesn't  
 413 show any correlation with C<sub>9</sub> (R<sup>2</sup>= 0.28). The strong correlations of nss-Ca<sup>2+</sup> with C<sub>8</sub>, C<sub>10</sub>, and  
 414 C<sub>12</sub> 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 C<sub>8</sub>, C<sub>10</sub>, and C<sub>12</sub> diacids. A strong correlation (0.94) is observed  
 417 between MSA<sup>-</sup> and nss-Ca<sup>2+</sup>, suggesting that dust is the source of MSA<sup>-</sup>. The higher  
 418 concentrations of MSA<sup>-</sup> 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 CO<sub>2</sub> 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<sup>2</sup>) of C<sub>2</sub> with its precursor compounds (except for sample no. 6) such as  
434 ωC<sub>2</sub> (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, C<sub>2</sub> 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 (C<sub>8</sub>) 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 C<sub>2</sub> (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 C<sub>2</sub> (1.00 and 0.84) (Fig. S3).

458 The occurrence of normal short-chain diacids (C<sub>2</sub>-C<sub>5</sub>), Pyr, Gly, MeGly and long-chain  
459 diacids (C<sub>8</sub>, C<sub>11</sub>, C<sub>12</sub>), 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 C<sub>6</sub>. In contrast, C<sub>9</sub> is a  
471 specific oxidation product of biogenic unsaturated fatty acids having a double bond at C<sub>9</sub>  
472 position. Hence, Ph/C<sub>9</sub> and C<sub>6</sub>/C<sub>9</sub> ratios have been used as tracers to better distinguish  
473 anthropogenic versus biogenic emissions (Pavuluri et al., 2010). The Ph/C<sub>9</sub> (dust: 8.0 and non-  
474 dust: 2.3) and C<sub>6</sub>/C<sub>9</sub> (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 C<sub>2</sub> is formed by the oxidation of long-chain diacids such as C<sub>9</sub>. Hence, C<sub>2</sub>/C<sub>9</sub> ratios can  
483 decipher the formation of low molecular diacids from long-chain diacids. C<sub>2</sub>/C<sub>9</sub> (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 (C<sub>2</sub>) followed by succinic acid (C<sub>4</sub>) and phthalic (Ph) in dusty snowpit samples  
 500 (C<sub>2</sub>>C<sub>4</sub>>Ph), whereas malonic (C<sub>3</sub>) acid is predominant after C<sub>4</sub> in the non-dusty snowpit  
 501 samples (C<sub>2</sub>>C<sub>4</sub>>C<sub>3</sub>). Glyoxylic ( $\omega$ C<sub>2</sub>) acid is the most abundant oxoacid followed by 4-  
 502 oxobutanoic ( $\omega$ C<sub>4</sub>) and 3-oxopropanoic ( $\omega$ C<sub>3</sub>) acid for dusty and non-dusty snowpit samples.  
 503 The molecular characteristics are consistent between oxoacids ( $\omega$ C<sub>2</sub>> $\omega$ C<sub>4</sub>) and diacids (C<sub>2</sub>>C<sub>4</sub>),  
 504 suggesting that organic compounds in snowpit sequences have a similar photochemical process  
 505 and/or similar source. The C<sub>3</sub>/C<sub>4</sub> 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 C<sub>2</sub> (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 (R<sup>2</sup>) of C<sub>2</sub> with its precursors such as  $\omega$ C<sub>2</sub> (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 C<sub>6</sub>/C<sub>9</sub> (dusty snowpit samples: 2.0, non-dusty snowpit samples: 1.27), Ph/C<sub>9</sub> (8.0 and 2.3), and  
 516 C<sub>2</sub>/C<sub>9</sub> (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-Ca<sup>2+</sup> with short-chain diacids, i.e., C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>,  
 519 and C<sub>5</sub> (range: 0.98-1.00), long-chain diacids, e.g., C<sub>7</sub> (0.74), C<sub>8</sub> (0.81), C<sub>10</sub> (0.99), C<sub>12</sub> (0.99),  
 520 iC<sub>4</sub>-iC<sub>5</sub> (0.92-0.99), aliphatic and aromatic acids (0.97-1.00), multifunctional diacids such as  
 521 hC<sub>4</sub> (0.99), kC<sub>3</sub> (0.99) and kC<sub>7</sub> (0.97),  $\omega$ -oxoacids from  $\omega$ C<sub>2</sub> to  $\omega$ C<sub>9</sub> (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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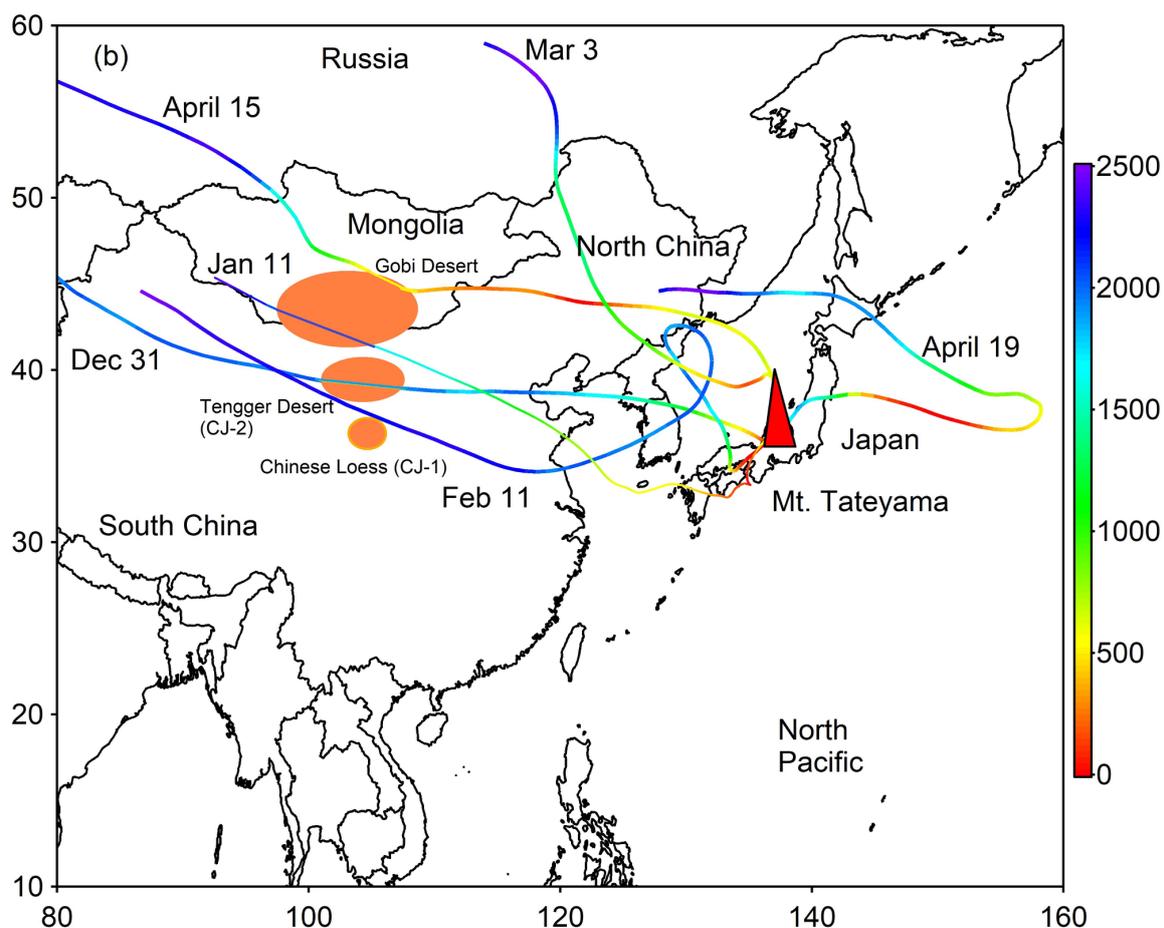
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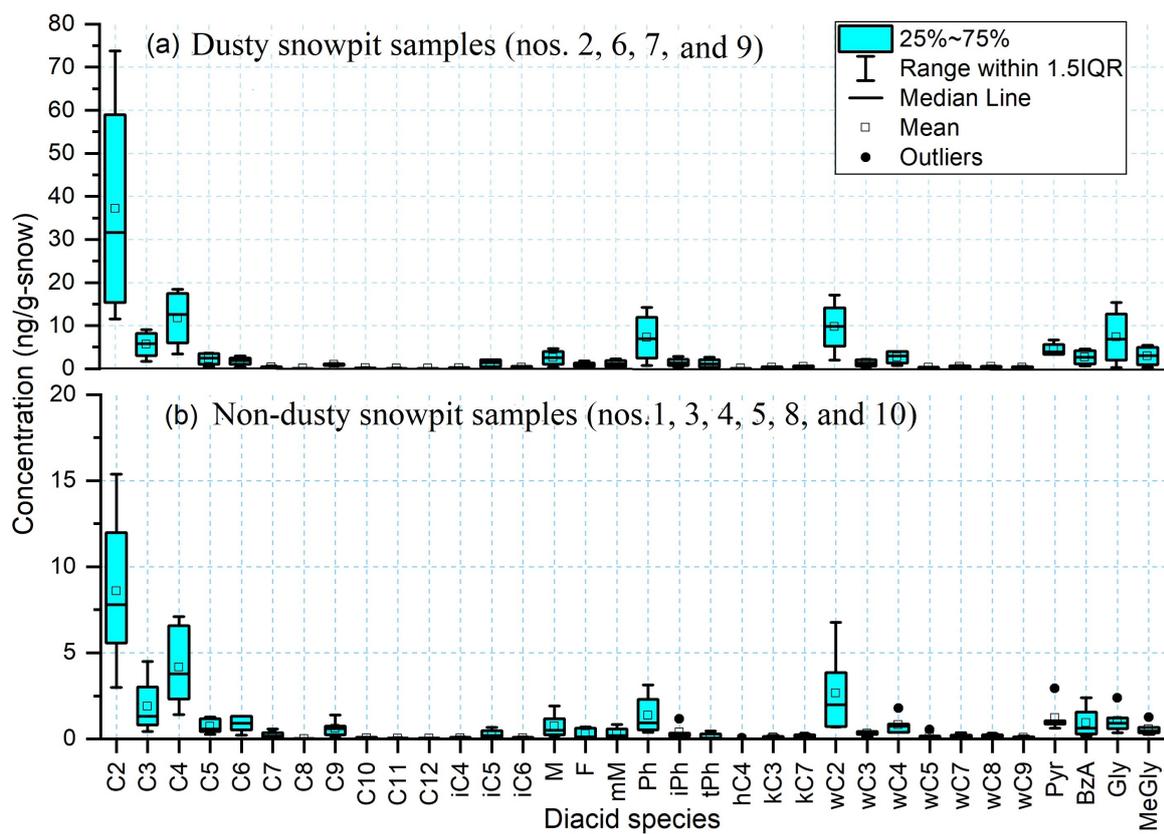
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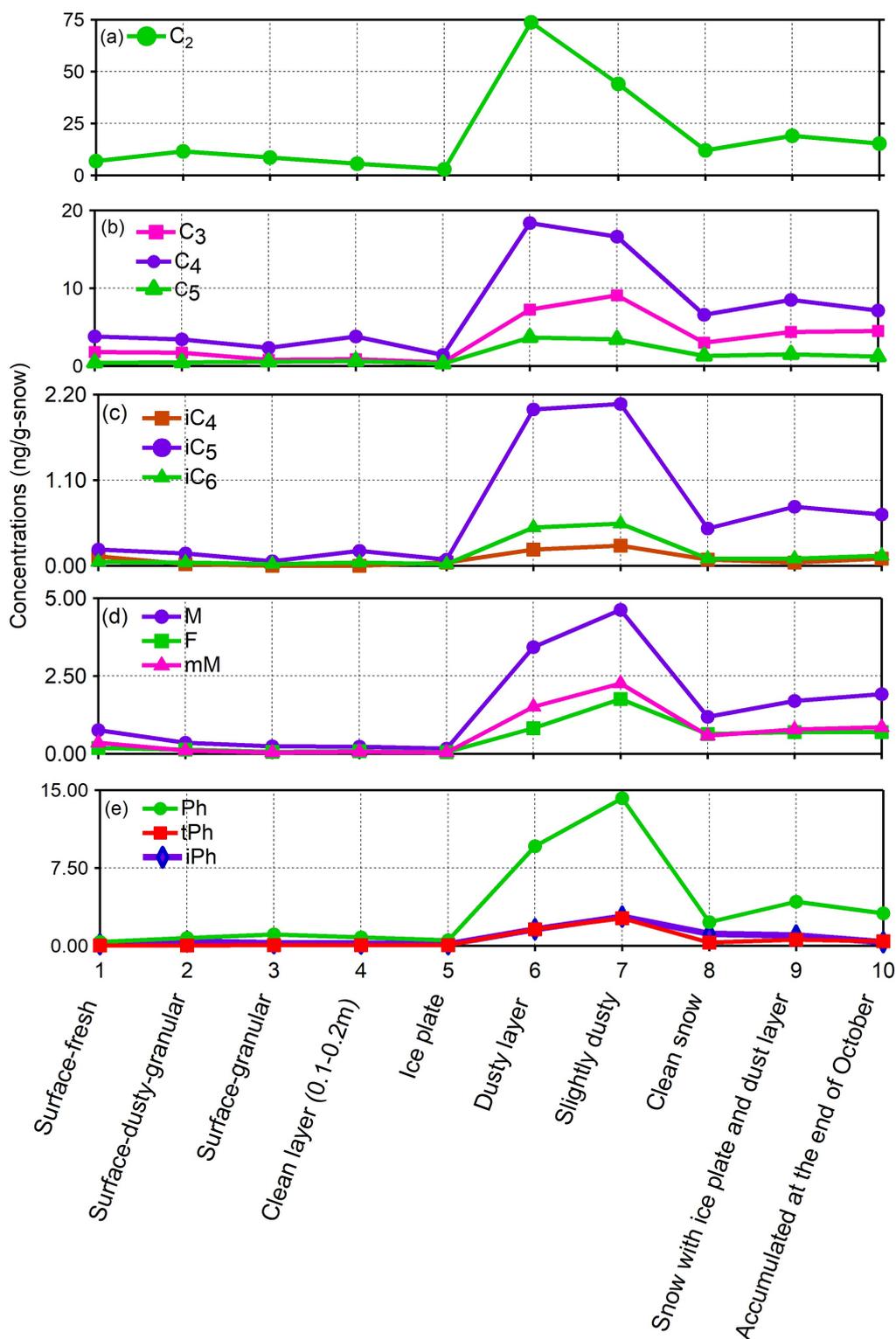
769  
 770 Figure 1. (a) Map showing the geographical region of Murodo-Daira, Mt. Tateyama of Central  
 771 Japan, 6.5 m long snowpit samples were excavated (19 April, 2008) at elevation of 2450 m  
 772 a.s.l. and (b) map showing 5 days (2500 m a.s.l. above sea level in meter) backward trajectory  
 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  $\alpha$ -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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783 Figure 3. Concentration changes of (a, b) short-chain low molecular weight diacids (s-

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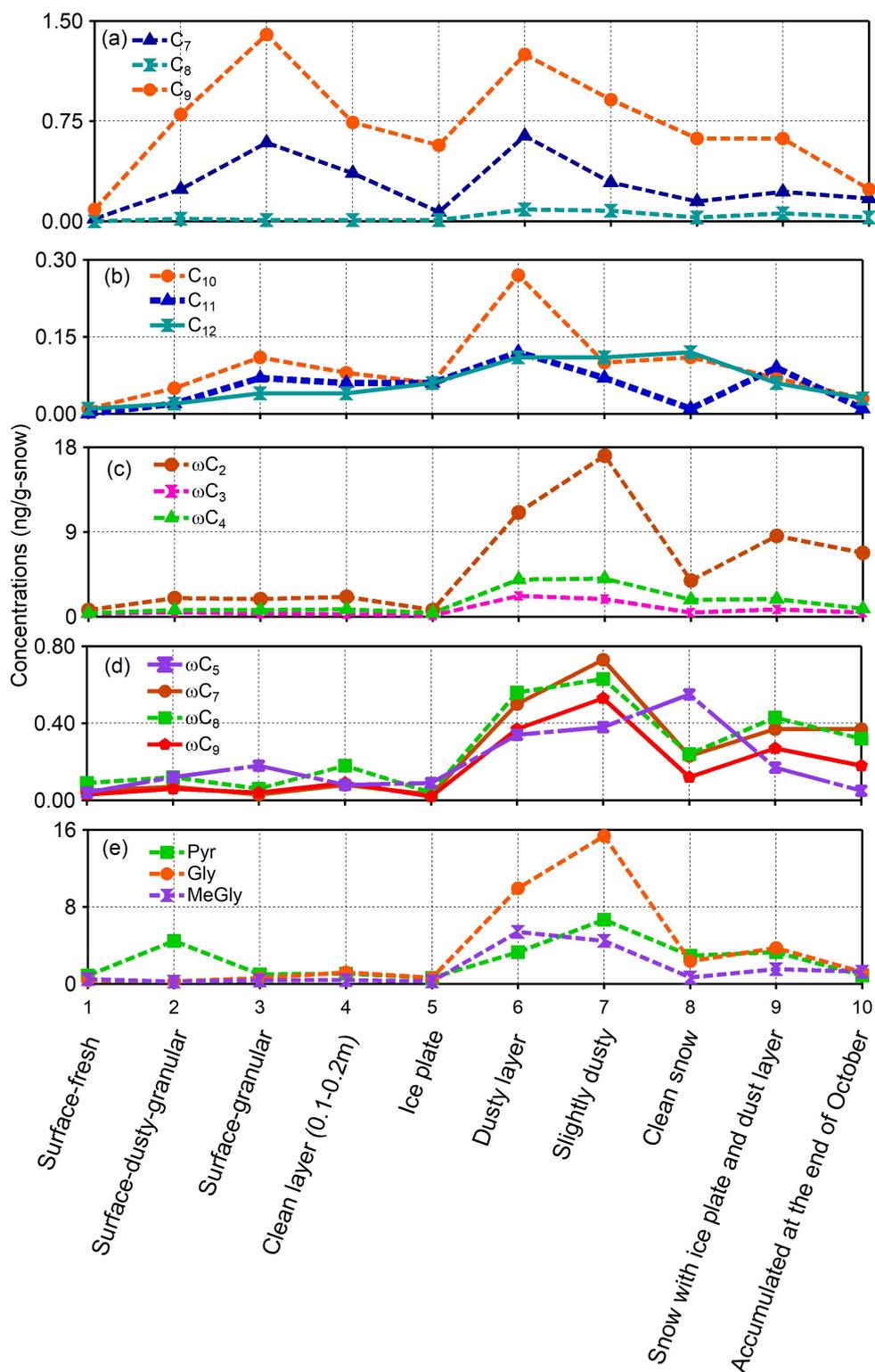
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DCAs) of (a) C<sub>2</sub> (b) C<sub>3</sub>, C<sub>4</sub>, and C<sub>5</sub>, (c) branched-chain saturated diacids (iC<sub>4</sub>, iC<sub>5</sub>, and

iC<sub>6</sub>), and (d, e) unsaturated diacids (M, F, mM, Ph, tPh, and iPh) in the snowpit

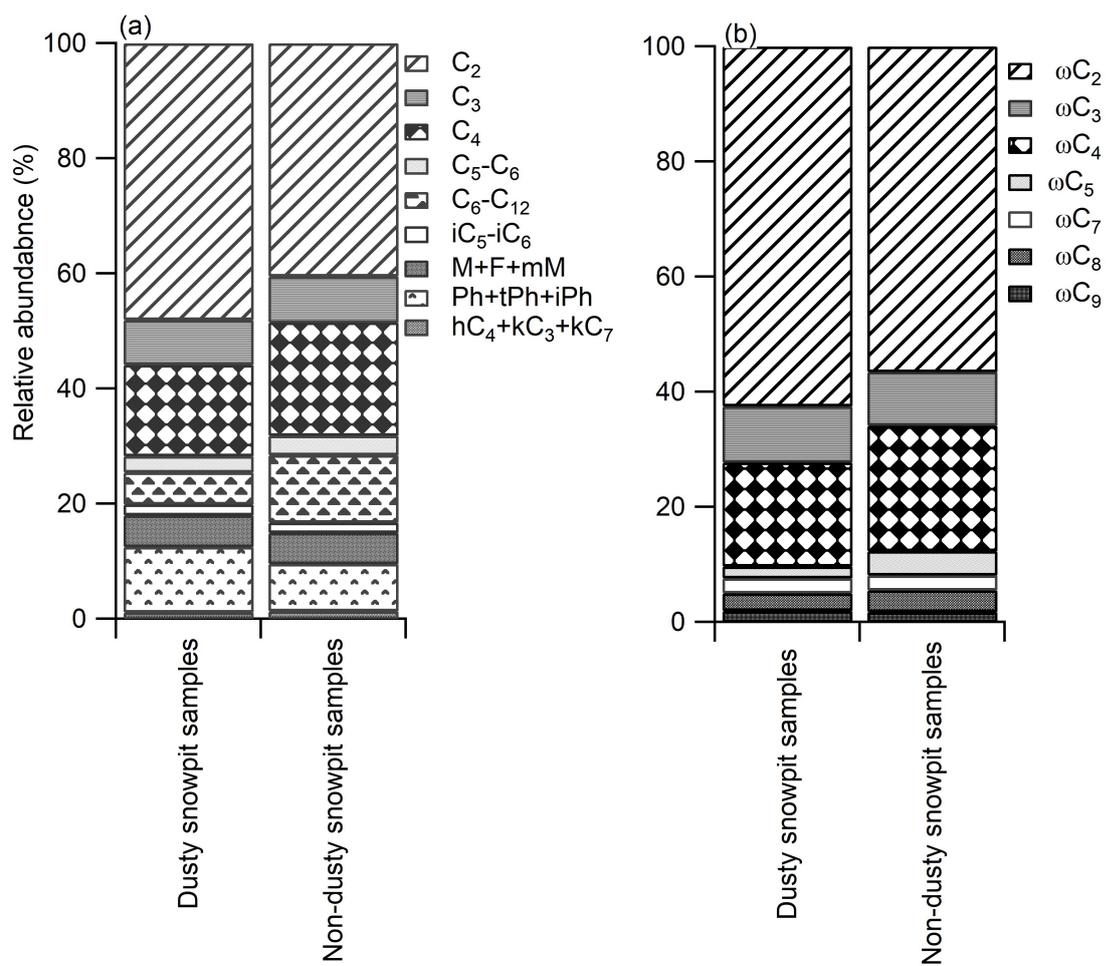
sequences (6.5 m) collected from the Murodo-Daira site, Mt. Tateyama in Central Japan.



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789 Figure 4. Concentration changes of long-chain low molecular weight diacids, (a, b)  $C_7$ - $C_{12}$ ,  
 790 (c, d) oxoacids ( $\omega C_2$  -  $\omega C_9$ ), (e) pyruvic acid (Pyr) and  $\alpha$ -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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 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

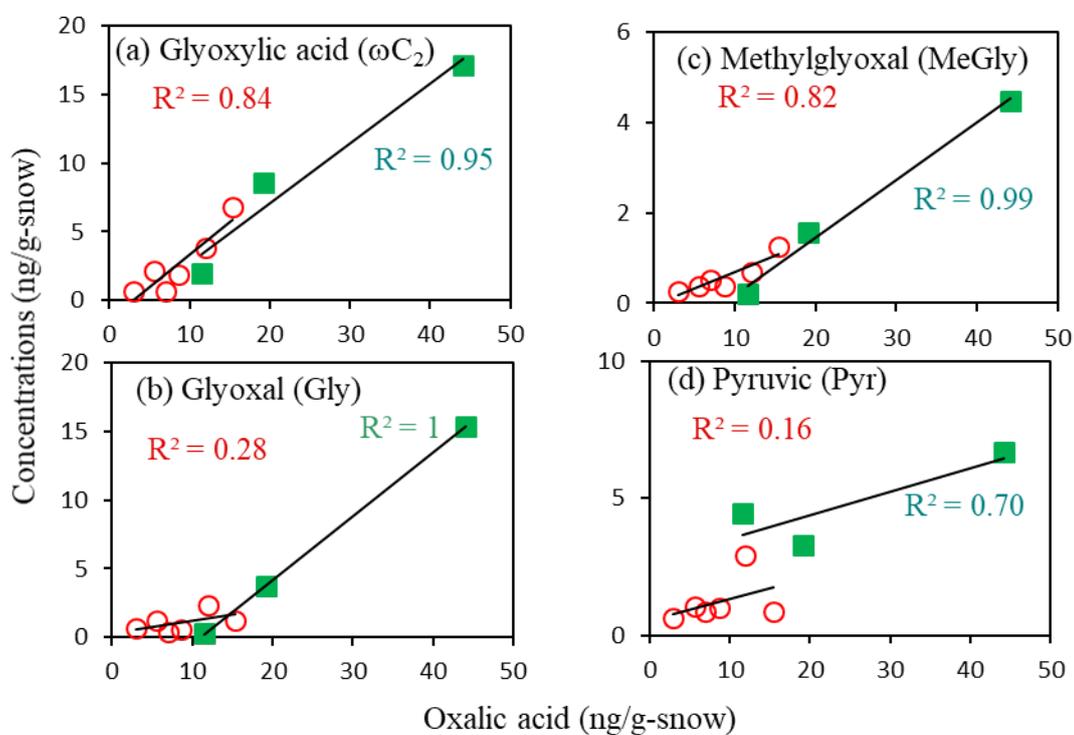
Sampling was conducted from 10:15 to 15:15 on April 19, 2008.

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

801 **Table S2.** Concentrations of dicarboxylic acids,  $\omega$ -oxocarboxylic acids, pyruvic acid, and  $\alpha$ -  
 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 <sub>n</sub> , Abbr.	Min-Max	Ave±Std	Min-Max	Ave±Std	(CJ-1)	(CJ-2)	(G-D)
Oxalic	C <sub>2</sub>	12-74	37±28	3-15	8.6±4.5	5090	36672	38589
Malonic	C <sub>3</sub>	1.7-9.1	5.6±3.2	0.44-4.5	1.9±1.6	202	1855	1957
Succinic	C <sub>4</sub>	3.4-18	12±7	1.4-7.1	4.2±2.3	657	4040	3039
Glutaric	C <sub>5</sub>	0.46-3.6	2.3±1.5	0.28-1.3	0.72±0.42	111	660	776
Adipic	C <sub>6</sub>	0.34-2.9	1.8±1.1	0.21-1.3	0.78±0.46	70	567	3327
Pimeric	C <sub>7</sub>	0.22-0.64	0.35±0.2	0.02-0.59	0.23±0.21	66	714	1160
Suberic	C <sub>8</sub>	0.02-0.09	0.06±0.03	0-0.03	0.02±0.01	0	0	1185
Azelaic	C <sub>9</sub>	0.62-1.2	0.89±0.26	0.09-1.4	0.61±0.46	182	4557	3888
Sebacic	C <sub>10</sub>	0.05-0.27	0.12±0.1	0.01-0.11	0.06±0.04	36	2396	2592
Monodecanoic	C <sub>11</sub>	0.02-0.12	0.08±0.04	0-0.07	0.04±0.03	0	226	6990
Dodecanoic	C <sub>12</sub>	0.02-0.11	0.08±0.04	0.01-0.06	0.03±0.02	0	0	0
Branched saturated diacids								
Methylmalonic	iC <sub>4</sub>	0.02-0.26	0.13±0.12	0-0.12	0.06±0.05	0	0	0
Methylsuccinic	iC <sub>5</sub>	0.16-2.08	1.25±0.95	0.06-0.66	0.28±0.24	91	248	144
Methylglutaric	iC <sub>6</sub>	0.04-0.54	0.29±0.26	0.02-0.13	0.06±0.04	0	36	0
Unsaturated diacids								
Maleic	C <sub>4</sub> , M	0.35-4.6	2.5±1.9	0.17-1.92	0.75±0.7	122	280	597
Fumric	C <sub>4</sub> , F	0.14-1.8	0.86±0.67	0.05-0.7	0.29±0.3	352	169	386
Methylmaleic	C <sub>5</sub> , mM	0.1-2.26	1.16±0.93	0.04-0.85	0.32±0.34	32	384	267
Phthalic	C <sub>8</sub> , Ph	0.75-14	7.2±5.9	0.39-3.1	1.4±1.1	875	4133	1424
Isophthalic	C <sub>8</sub> , iPh	0.41-2.8	1.5±1	0.15-1.2	0.38±0.39	0	0	1918
Terephthalic	C <sub>8</sub> , tPh	0.03-2.7	1.2±1.2	0.02-0.45	0.16±0.18	0	125	170
Hydroxylated diacids								
Hydroxysuccinic	hC <sub>4</sub>	0-0.1	0.05±0.04	0-0.07	0.01±0.03	20	52	45
Ketodiacids								
Ketomalonic	kC <sub>3</sub>	0.14-0.46	0.3±0.14	0.01-0.23	0.11±0.09	0	65	174
Ketopimelic	kC <sub>7</sub>	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
$\omega$ -oxocarboxylic acids								
Glyoxylic	$\omega$ C <sub>2</sub>	1.97-17	9.7±6.3	0.7-6.8	2.7±2.32	347	2061	4412
3-Oxopropanoic	$\omega$ C <sub>3</sub>	0.48-2.2	1.3±0.84	0.12-0.44	0.32±0.12	36	245	569
4-Oxobutanoic	$\omega$ C <sub>4</sub>	0.73-4	2.6±1.6	0.39-1.8	0.82±0.51	27	424	543
5-Oxopentanoic	$\omega$ C <sub>5</sub>	0.12-0.38	0.25±0.13	0.04-0.55	0.17±0.2	35	60	243
7-oxoheptanoic	$\omega$ C <sub>7</sub>	0.07-0.73	0.42±0.27	0.03-0.37	0.13±0.14	21	345	337
8-Oxooctanoic	$\omega$ C <sub>8</sub>	0.12-0.63	0.43±0.23	0.04-0.32	0.16±0.11	0	58	110
9-Oxononoic	$\omega$ C <sub>9</sub>	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 <sub>3</sub> , Pyr	0.63-6.7	2.51±2	0.63-2.9	1.2±0.85	178	975	1549
$\alpha$ -dicarbonyls								
Glyoxal	C <sub>2</sub> , Gly	0.27-15	3.6±5.1	0.37-2.4	1.1±0.73	81	546	667
Methylglyoxal	C <sub>3</sub> , MeGly	0.22-5.4	1.5±1.9	0.27-1.3	0.58±0.36	45	300	541
Total $\alpha$ -dicarbonyls	0	0.49-20.4	10.2±9.1	0.64-3.7	1.68±1.09	126	846	1208

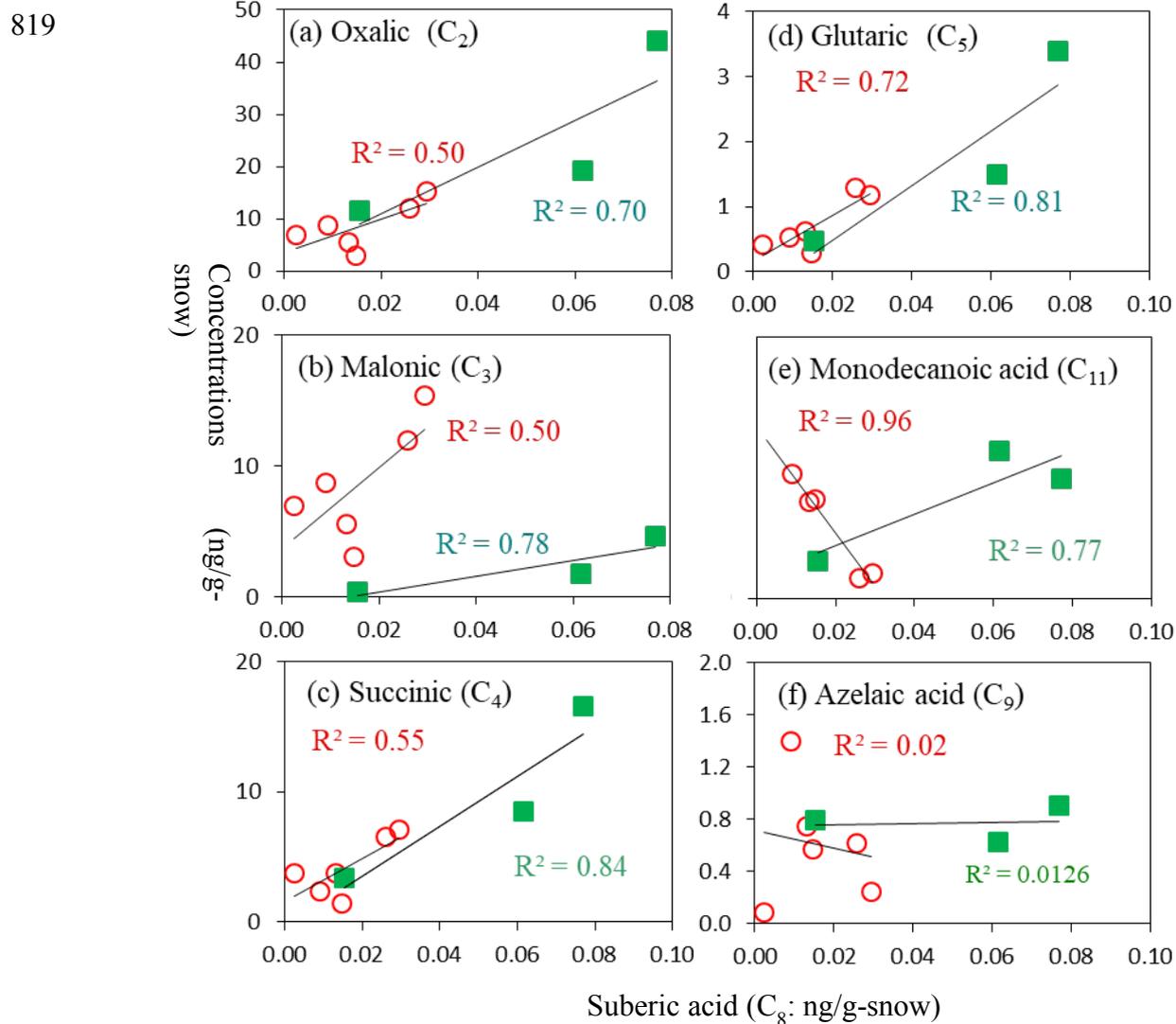
806 **Figure S1:** Correlation plots of oxalic acid with (a) glyoxylic acid ( $\omega\text{C}_2$ ), (b) glyoxal (Gly), (c)  
807 methylglyoxal (MeGly), and (d) pyruvic acid (Pyr) in snowpit samples collected from the  
808 Murodo-Daira site, Mt. Tateyama in Central Japan. Red open circle and green closed 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.

