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3 Springtime variations of organic and inorganic constituents in submicron

4 aerosols (PM_{1.0}) from Cape Hedo, Okinawa

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15

16 Abstract

17 During the spring season with enhanced Asian outflow, we collected submicron
18 aerosol (PM_{1.0}) samples at Cape Hedo, Okinawa Island in the western North Pacific Rim. We
19 analyzed the filter samples for diacids, oxoacids, pyruvic acid, α -dicarbonyls and fatty acids
20 to better understand the sources and atmospheric processes in the outflow regions of Asian
21 pollutants. Molecular distributions of diacids show a predominance of oxalic acid (C₂)
22 followed by malonic (C₃) and succinic (C₄) acids. Total diacids strongly correlated with
23 secondary source tracers such as SO₄²⁻ (r=0.87), NH₄⁺ (0.90) and methanesulfonate (MSA)
24 (0.84), suggesting that diacids are secondarily formed from their precursor compounds. We
25 also found good correlations among C₂, organic carbon (OC) and elemental carbon (EC) in
26 the Okinawa aerosols, suggesting that diacids are mainly derived from anthropogenic sources.
27 However, a weak correlation of diacids with levoglucosan, a biomass burning tracer, suggests
28 that biomass burning is not the main source of diacids, rather diacids are secondarily formed
29 by photochemical oxidation of organic precursors derived from fossil fuel combustion. We
30 found a strong correlation (r = 0.98) between inorganic nitrogen (NO₃-N + NH₄-N) and total
31 nitrogen (TN), to which organic nitrogen (ON) contributed 23%. Fatty acids were
32 characterized by even carbon number predominance, suggesting that they are derived from
33 biogenic sources. The higher abundances of short chain fatty acids (<C₂₀) than long chain
34 fatty acids (>C₂₀) further suggest that fatty acids are largely derived from marine
35 phytoplankton during spring bloom.

36

37 Keywords: submicron aerosols, diacids and related compounds, organic nitrogen, Okinawa,
38 atmospheric aging

39 **1. Introduction**

40 Atmospheric aerosols are generally enriched with water-soluble organic (dominated
41 by oxalic acid) and inorganic (sulfate) components (e.g., Jimnez et al., 2009; Kawamura et
42 al., 2010). Those atmospheric particles have an impact on the Earth's radiative balance and
43 hydrological cycles (Ramanathan et al., 2001) as well as adverse health effect to the human
44 pulmonary tract (Mitchell et al., 1987). The extent of such impacts largely depends upon the
45 chemical composition of atmospheric aerosols. Aerosols are emitted from the various
46 primarily sources such as soil dust, fossil fuel combustion, vehicular and biomass burning
47 emission, and sea salt via the sea spray. They are also secondarily formed via the atmospheric
48 oxidation of inorganic and organic precursors in the presence of sunlight and oxidants.
49 Primary and secondary aerosols together with their atmospheric circulations have an
50 influence on local to regional air quality, atmospheric loadings and chemical compositions
51 (Pavuluri et al., 2015). Based upon the model study, organic aerosols are known to be largely
52 subjected to chemical transformation (Kanakidou et al., 2005).

53 In East Asia, emissions of pollutants (both organic and inorganic) are increasing due
54 to the growing activities of Chinese industries and biomass burning in Southeast and East
55 Asia (Kunwar and Kawamura, 2014; Zhu et al., 2015). The anthropogenic emissions in East
56 Asia are much more severe than any other regions in the world and this situation will
57 continue to increase for the coming decades (Ohara et al., 2007). For example, the pollutants
58 emitted from China are recognized to have a significant impact on the air quality in the
59 outflow regions, such as Okinawa Island in the western North Pacific Rim, by long range
60 atmospheric transport (Kunwar and Kawamura, 2014a). Similarly, major sources of organic
61 nitrogen in the atmosphere include vehicle exhaust, landfill, marine biological algal blooms
62 and bacteria, dust and biomass burning (Westerholm et al., 1993; Kallinger and Niessner,

63 1999; Wedyan and Preston, 2008; Timperley et al., 1985). Wang et al. (2013) reported the
64 abundant presence of water soluble organic nitrogen (WSON) in Chinese aerosols.

65 In a previous study, we reported the seasonal variations of organic and inorganic
66 aerosols in the TSP samples from Cape Hedo, Okinawa (Kunwar and Kawamura, 2014a, b).
67 However, there are no studies of diacids together with organic nitrogen and related
68 compounds in PM_{1.0} filter samples in marine aerosols in the Asian outflow region, although
69 there are many studies on total suspended particles (Fu et al., 2013 and references therein;
70 Kundu et al., 2010; Wang et al., 2006; Kawamura and Sakaguchi, 1999). Cape Hedo is
71 situated on the northwestern edge of Okinawa Island, Japan, an outflow region of East Asian
72 pollutants. Around the sampling location, there is no major anthropogenic activity
73 (Yamamoto et al., 2011) and thus Cape Hedo has been used as a supersite of Atmospheric
74 Brown Cloud (ABC) project to study the East Asian aerosols (Takami et al., 2007).

75 In this study, we report the day-by-day variations of diacids, oxoacids, α -dicarbonyls
76 and benzoic acid, and fatty acids, together with organic carbon, elemental carbon, major ions
77 and organic nitrogen in PM_{1.0} samples from Cape Hedo. To better understand the sources and
78 atmospheric processing of organic aerosols at Cape Hedo, we compare the data of diacids and
79 related compounds together with inorganic ions and a biomass burning tracer, i.e.,
80 levoglucosan, a specific pyrolysis product of cellulose and hemicellulose (Simoneit, 1999).

81 **2. Samples and analytical procedure**

82 **2.1. Site description and aerosol sampling**

83 Aerosol sample collection was performed at the rooftop of the facility of Cape Hedo
84 Atmosphere and Aerosol Measurement Station (CHAAMS, 26° 9' N, 128° 2' E) during 17
85 March to 13 April, 2008. Figure 1 shows a map of Okinawa along with East Asia and the
86 Pacific Ocean. PM_{1.0} samples (n=28) were collected at CHAAMS station using low volume

87 air sampler and pre-combusted (450°C, 4 hours) quartz fiber filters (Pallflex 2500QAT, 47
88 mm in diameter). The flow rate was 16.7 l/min. Blank filters (n=4) were collected every week.
89 Each sample was collected for 24 hours. Before and after sampling, the filters were stored in
90 a preheated glass vial (50 mL) with a Teflon-lined screw cap. The samples were stored in
91 darkness at -20°C until the analysis. During the sampling period, average temperature and
92 relative humidity were 19.7°C and 71%, respectively. The weather conditions were cloudy
93 and fine during the campaign, but there were rainfall events in March 18 and 30 and April 13.
94 The ambient temperature, rainfall, and relative humidity are shown in Figure S2.

95 **2.3. Chemical analysis**

96 Filter samples were analysed for water-soluble diacids, oxoacids, and α -dicarbonyls
97 by the method reported previously (Kawamura and Ikushima, 1993; Kawamura, 1993).
98 Known area of filter was extracted with organic-free pure water and then carboxylic acids
99 and α -dicarbonyls in the extracts were derivatized with 14% BF_3 /n-butanol to butyl esters
100 and/or dibutoxy acetals. The derivatives were determined using a capillary gas
101 chromatography (GC; HP 6890). The GC peaks were identified by comparing the GC
102 retention times with those of authentic standards and the peak identifications were confirmed
103 by mass spectral examination using a GC/mass spectrometry (GC/MS) system. Both field and
104 laboratory blanks were analyzed. Oxalic acid and other organic species were detected in the
105 blanks. However, their concentrations were less than 5% of the real samples. The
106 concentrations of all species reported here are corrected for blanks. We also performed the
107 recovery test by spiking authentic dicarboxylic acids to the quartz filter. The recoveries of
108 spiked diacids were 94% for oxalic acid (C_2) and more than 97% for C_3 , C_4 , C_5 and C_6
109 diacids. The reproducibility in the measurements of major diacids (C_2 , C_3 , and C_4) was ca.
110 10%.

111 For the determination of levoglucosan, a small punch of each filter was extracted with
112 dichloromethane/methanol (2:1, v/v) under ultrasonication. The extracts were concentrated
113 using a rotary evaporator, and then reacted with N,O-bis-(trimethylsilyl)trifluoroacetamide
114 (BSTFA) to derive TMS ethers of levoglucosan. Levoglucosan was measured by gas
115 chromatography/mass spectrometry (GC/MS). Detailed analytical procedures can be found
116 elsewhere (Fu et al., 2012).

117 To measure total nitrogen (TN), we combusted a small filter disc placed in a tin cup at
118 1400°C using elemental analyzer (EA) (Thermo Scientific, Trace GC Ultra, Delta V
119 Advantage Isotope Ratio MS). All the nitrogen species are converted to NO and further
120 reduced to N₂ in a reduction column. N₂ is separated on a packed column of gas
121 chromatograph installed in EA and measured with a thermal conductivity detector. Organic
122 nitrogen (ON) is calculated using following equation.

$$123 \quad \text{ON} = \text{TN} - \text{IN}$$

124 where IN (inorganic nitrogen) means the summation of nitrate (NO₃⁻) and ammonium (NH₄⁺)
125 nitrogen. NO₃⁻, NH₄⁺ and other major ions were determined using an ion chromatograph (761
126 Compact IC, Metrohm, Switzerland). Details of analytical procedures for ions are reported in
127 Kunwar and Kawamura (2014a).

128 Organic carbon (OC) and elemental carbon (EC) were measured using a Sunset
129 Laboratory carbon (OC/EC) analyzer following Intergency Monitoring Protected Visual
130 Environments (IMPROVE) thermal/optical evolution protocol. Detailed procedure is
131 described in Kunwar and Kawamura (2014a).

132 **2.4. Air Mass backward trajectory analysis and fire counts**

133 Figure 1a shows the 5-day back trajectories above the 500 meter for every day using
134 the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Draxler

135 and Hess, 1998). Except for few days, air masses in the study area were transported from East
136 Asia. During March 17 and 18 and April 6 and 9, air masses were delivered from the Pacific
137 Ocean over the sampling site. Figure 1b shows the fire counts in East Asia obtained by
138 satellite (<https://earthdata.nasa.gov/data/near-real-time-data/firms/active-fire-data>) with 5-day
139 back trajectories.

140

141 3. Results and Discussion

142 3.1. Molecular distributions of dicarboxylic acids, oxoacids and α -dicarbonyls

143 We detected homologous series of α,ω -dicarboxylic acids (C_2 - C_{12}), unsaturated
144 diacids (phthalic, isophthalic, terephthalic, maleic, fumaric and methylmaleic), multi-
145 functional diacids (malic, ketomalonic, and 4-ketopimelic), oxocarboxylic acids (ωC_2 - ωC_9
146 and pyruvic acid), α -dicarbonyls (glyoxal and methylglyoxal) and benzoic acid in the $PM_{1.0}$
147 samples. In addition, we also detected homologous series of fatty acids. Figure 2 shows the
148 average molecular distribution of diacids, oxoacids and α -dicarbonyls.

149 Concentrations of total diacids, oxoacids and α -dicarbonyls ranged from 114-537 ng
150 m^{-3} (av., 273 ± 121 ng m^{-3}), 5.5-53 ng m^{-3} (27 ± 15 ng m^{-3}), and 2.9-19 ng m^{-3} (7.8 ± 4.2 ng m^{-3}),
151 respectively (Table 1). Oxalic acid (C_2) was found as the most abundant species followed by
152 malonic (C_3), succinic (C_4), glyoxylic (ωC_2), ketomalonic (kC_3) and phthalic (Ph) acid. The
153 molecular distributions of diacids in the Cape Hedo aerosols are similar to those reported
154 from Gosan site, Jeju Island, South Korea ($C_2 > C_3 > C_4$) (Kundu et al., 2010). The
155 predominance of ωC_2 and kC_3 after C_2 to C_4 indicates a significant photochemical processing
156 during long range transport. Both ωC_2 and kC_3 are the precursors of C_2 (Kawamura et al.,
157 1996). The highest relative abundance of C_2 in total C_2 - C_{12} (78%) was observed in April 13,
158 whereas the lowest value (55%) was observed in March 20.

159 3.2. Temporal variations of diacids, oxoacids and α -dicarbonyls

160 Figure 3 shows temporal variations of diacids, oxoacids and α -dicarbonyls. Except for
161 azelaic acid (C_9), short chain diacids (C_2 to C_6) present similar temporal variations. The
162 temporal variations suggest that the source and/or formation process of diacids are similar
163 except for C_9 . Oxalic acid shows the highest concentration in April 3, whereas the lowest
164 concentration was observed in March 18 (Figure 3a). Back trajectory analysis revealed that
165 air masses of April 3 originated from Mongolia passing over the northern part of China
166 whereas the air masses of April 18 were delivered from the Pacific Ocean. The temporal
167 variations of C_3 and C_4 are similar with that of C_2 . Interestingly, C_3 and C_4 peaked on April 8
168 (Figure 3b and 3c). On the same date, 9-oxononanoic acid (ωC_9), an oxidation product of
169 unsaturated fatty acids (Kawamura and Gagosian, 1987), maximized (Figure 3i). The
170 different temporal variation between ωC_9 and C_9 is due to the presence of active $-CHO$ group
171 in ωC_9 that makes ωC_9 more reactive and semi-volatile. The air masses of April 8 originated
172 from South Asia. These results suggest that unsaturated fatty acids are oxidized to result in C_3
173 and C_4 diacids as well as ωC_9 during the long range transport from South Asia.

174 Adipid acid (C_6), a tracer of anthropogenic sources (Kawamura and Ikushima, 1993),
175 showed the highest concentration in April 10 followed by April 3 whereas the lowest
176 concentration was found in April 13. Although air masses originated from the Pacific Ocean
177 passing over the Japanese Islands, the air parcels were encountered with rainfall around Cape
178 Hedo in April 13 and thus the concentration was declined. During April 10 and April 5, air
179 masses from East Asia were delivered to Cape Hedo with air pollutants. Phthalic acid (Ph), a
180 tracer of anthropogenic source (Kawamura and Ikushima, 1993), also showed the highest
181 concentration in April 5 (Figure 3f), whereas the lowest concentration was found in April 6,
182 one day before a small rain event was recorded in Okinawa.

183 Terephthalic acid (tPh) has been proposed as an organic tracer of plastic burning
184 (Kawamura and Pavuluri, 2010; Pavuluri et al., 2010; Simoneit et al., 2005). This tracer
185 maximized in April 3 (not shown as a figure). Azelaic acid (C_9), a tracer for the oxidation of
186 biogenic unsaturated fatty acids such as $C_{18:1}$ (Kawamura and Gagosian, 1987), peaked in
187 April 3 (Figure 3e), whereas lower concentration was found in April 7 although the air mass
188 source region is East Asia. C_9 is the first oxidation product of unsaturated fatty acids emitted
189 from biogenic sources, biomass burning of plants, meat cooking operation and plant leaf
190 abrasion (e.g., Ho et al., 2010). Glyoxylic acid (ωC_2), which is a precursor of C_2 and is
191 formed by the oxidation of aromatic hydrocarbons such as benzene and toluene, showed the
192 highest concentration in April 3. The peaks of C_2 and ωC_2 in April 3 suggest a significant
193 oxidation of precursor compounds. Both glyoxal (Gly) and methylglyoxal (MeGly) show
194 higher concentrations in April 1. The temporal variation of ωC_2 is similar to C_2 whereas that
195 of ωC_4 is similar to C_4 . These results suggest that C_2 and C_4 are formed by the oxidation of
196 corresponding oxoacids (ωC_2 and ωC_4). The temporal variations of Gly and MeGly are
197 similar to that of C_2 , suggesting that C_2 may be the oxidation product of α -dicarbonyls.

198 Benzoic acid has been proposed as a primary pollutant emitted from vehicular exhaust
199 (Kawamura et al., 1985; Ho et al., 2006) and secondary photochemical oxidation of aromatic
200 hydrocarbons such as toluene from automobiles (Suh et al., 2003). Very high ambient levels
201 of toluene ($11.4 \mu\text{g m}^{-3}$) were detected in Beijing (Duan et al., 2008). Guo et al. (2004)
202 reported daily concentration of toluene up to $50 \mu\text{g m}^{-3}$ in Hong Kong. Higher concentrations
203 of benzoic acid were recorded in March 20, 28 and 29, and April 3 and 8 in Cape Hedo. The
204 high abundance of benzoic acid in this study suggests a significant contribution of toluene
205 and subsequent oxidation during the long range atmospheric transport from the Asian
206 Continent.

207 During the campaign, there were many but minor rainfall events in the study site
208 (March 17, 18, 23 and 30, and April 3, 10 and 13), suggesting that these organic species were
209 washed out from the atmosphere near the sampling site. In fact, during these rainy days, we
210 found lower concentrations of diacids, oxoacids and α -dicarbonyls, except for April 3.

211 Malonic (C_3) to succinic (C_4) acid ratio has been used as an indicator of
212 photochemical aging of organic aerosol (OA) (e.g., Kawamura and Ikushima, 1993). The
213 C_3/C_4 ratios are higher in March 30 and April 6, whereas it was lowest in April 5. Except for
214 the samples of March 30 and April 5 and 6, C_3/C_4 ratios do not show a significant variation,
215 suggesting that Cape Hedo aerosols are photochemically more aged probably during long-
216 range atmospheric transport. In fact, the air mass source regions associated with the high
217 C_3/C_4 ratios are located in Northwest and Northeast China, from which polluted aerosols
218 were transported long distances to the sampling site in Okinawa. The average C_3/C_4 ratio in
219 this study is 1.3. Similar but higher ratio (1.7) was observed for TSP samples from the same
220 site (Kunwar and Kawamura 2014b), the Southern Ocean (1.7) (Fu et al., 2013) and Western
221 North Pacific (0.91 to 1.5) (Fu et al., 2013). Average C_3/C_4 ratio in this study is lower than
222 those from the Indian Ocean (2.1) (Fu et al., 2013), South China Sea (2.7) (Fu et al., 2013)
223 and Pacific Ocean (4) (Kawamura and Sakaguchi, 1999), suggesting that photochemical
224 aging of Okinawa aerosols are less significant than the open ocean aerosols.

225 C_6 and Ph acids are produced by the oxidation of anthropogenic cyclohexane and
226 aromatic hydrocarbons, respectively (Kawamura and Ikushima, 1993), whereas C_9 is
227 produced by the oxidation of biogenic unsaturated fatty acids having double bond at C_9
228 position as stated above. Hence, C_6 to C_9 and Ph to C_9 ratios can be useful tracers to evaluate
229 the relative contributions of anthropogenic and biogenic sources (Ho et al., 2006; Wang et al.,
230 2009). Both C_6/C_9 and Ph/ C_9 ratios peaked in April 7 (Figure 4). On this date, the air mass
231 source regions are the coasts of China (Guangzhou, Shantou and Xiamen, not shown as a

232 figure). The lowest concentration of C₉ at this day is due to the difference in source region.
233 Lower C₆/C₉ ratios were observed in March 18, 19, 23, 30, and April 5 and 13. Lower Ph/C₉
234 ratios were also observed in March 23 and 30. These results suggest that there are more
235 biogenic contributions on those days. Spring is a growing season with more biogenic
236 emissions. Maleic acid (M) can be isomerized to fumaric acid (F) under strong solar radiation
237 during long range atmospheric transport. A significant photo-isomerization of M to F was
238 observed in April 2 and 3 (Figure 4d) when air masses were delivered from North China and
239 local temperature in Okinawa was not high (Figure S2). This result suggest that photo-
240 isomerization is enhanced during long range atmospheric transport.

241 The average F/M ratio in this study is 0.43. This value is several times lower than that
242 of the springtime TSP aerosols (1.9) from the same sampling site (Kunwar and Kawamura,
243 1014b), the South China Sea (1.9) (Fu et al., 2003), North Atlantic (2) (Fu et al., 2013),
244 Indian Ocean (3.8) (Fu et al., 2013), and Western North Pacific (1.1) (Fu et al., 2013). These
245 comparison suggests that larger particles may be photochemically more aged in the marine
246 atmosphere during the accumulation and coagulation process of fine particules.

247 **3.2. Carbonaceous components and organic nitrogen**

248 Concentrations of organic carbon (OC) and elemental carbon (EC) ranged from 0.41
249 to 2.49 $\mu\text{g m}^{-3}$ (av. 1.2 $\mu\text{g m}^{-3}$) and 0 to 0.85 (av. 0.36 $\mu\text{g m}^{-3}$), respectively. Higher
250 concentrations of OC were observed in March 28 and April 3, whereas the lowest
251 concentrations were observed in March 23 and April 6 (Figure 5a). Similarly, the highest
252 concentration of EC was found in March 28, whereas the lowest value was observed in
253 March 18. A strong correlation ($r=0.82$) between OC and EC (Figure 6a) during the whole
254 campaign suggests that they have similar sources. OC to EC ratio is a useful tool to discuss
255 the sources of aerosols (Kunwar and Kawamura 2014a). The OC/EC ratios > 2.0 indicate a
256 significant contribution of secondary organic aerosol (SOA) (Cao et al., 2003). OC/EC ratios

257 in the study area are > 2 , suggesting a significant fraction of OC in Cape Hedo aerosols is of
258 SOA origin. The highest OC/EC ratio (12.7) was found in March 18 (not shown as a figure),
259 which may be due to more biogenic emission of organic aerosols and precursors from marine
260 sources and/or lower contributions of EC. Back trajectory analysis shows that air masses of
261 March 18 were delivered from oceanic regions (Figure 1). We found similar temporal
262 variations of total diacids with OC and EC. A strong correlation between OC with total
263 diacids ($r=0.84$) suggests that diacids are mostly derived from anthropogenic sources from
264 East Asia via long-range transport.

265 Concentrations of organic nitrogen (ON) ranged from 0.0 to $1.5 \mu\text{g m}^{-3}$ (av. $0.54 \mu\text{g}$
266 m^{-3}) (Figure 5b). The temporal variation of ON is similar to those of OC, NH_4^+ and nss-SO_4^{2-} ,
267 suggesting that source of ON is East Asia. There are various sources of organic nitrogen in
268 the atmosphere; e.g., emission from vehicular exhaust (Westerholm et al., 1993) marine algal
269 blooms and bacteria (Sorooshian et al., 2008), biomass burning, cooking (Simoneit et al.,
270 2002), etc. Higher concentration of ON was observed in April 3, when air mass came from
271 northern part of China. Contribution of ON to total nitrogen is 23%. We found higher
272 percentage of ON for one year observation of TSP samples (37%) (unpublished data),
273 suggesting that organic nitrogen is present in larger size fraction of aerosols. In fact, very
274 high concentration of WSON have been reported in China during the dust storm event (Wang
275 et al., 2013). We found higher contribution of $\text{NH}_4\text{-N}$ to TN in $\text{PM}_{1.0}$ samples than TSP
276 samples (unpublished data). The higher concentration of $\text{NO}_3\text{-N}$ in coarse fraction suggests
277 that NO_3^- is associated with coarse particles during long range atmospheric transport. We
278 found strong correlation between IN and ON ($r=0.98$) (Figure 7), suggesting the similar
279 sources of these nitrogenous compounds. We did not find statistically significant correlation
280 between levoglucosan and ON, suggesting that ON is not emitted from the biomass burning

281 in this region. However, Mace et al. (2003) reported that organic nitrogen is emitted from
282 biomass burning.

283 **3.3. Temporal variation of anthropogenic tracers and evidence for secondary** 284 **formation of diacids**

285 nss-SO_4^{2-} can be used as an anthropogenic tracer of industrial origin and NH_4^+ is a
286 tracer of biomass burning, agricultural wastes and animal excreta (Pavuluri et al., 2011). The
287 temporal variations of NH_4^+ and SO_4^{2-} are similar (Figure 5c, 5d). Both nss-SO_4^{2-} and NH_4^+
288 show higher concentrations in March 29. A strong correlation ($r=0.98$) between nss-SO_4^{2-} and
289 NH_4^+ supports a similar oxidation pathway to form NH_4HSO_4 or $(\text{NH}_4)_2\text{SO}_4$ (Figure 6b).
290 nss-SO_4^{2-} and MSA^- are formed by the photochemical oxidation in the atmosphere.

291 Total diacids show strong correlations with NH_4^+ ($r=0.90$), nss-SO_4^{2-} (0.87) and MSA^-
292 (0.84) (Figure 8a, b, c). MSA^- is formed by the oxidation of dimethyl sulfide (DMS) that is
293 emitted from industrial emission (Yuan et al., 2004) although DMS is also emitted from the
294 ocean by microbial activity (Saltzman et al., 1983). A strong correlation between MSA^- and
295 total diacids suggests that diacids are mainly formed from the secondary formation from
296 industrial emission. Yuan et al. (2004) reported significant concentrations of MSA^- in Beijing.
297 Although Na^+ is emitted primarily from the ocean, we found a negative correlation ($r=0.31$)
298 between Na^+ and diacids (Figure 8d), suggesting that diacids are not of marine origin. nss-
299 Ca^{2+} is a major component of dust. In spring, our sampling site is influenced from dust
300 emitted from the arid regions in East Asia (Kunwar and Kawamura, 2014a). Although nss-
301 Ca^{2+} was not detected in the $\text{PM}_{1.0}$ samples, we found abundant nss-Ca^{2+} in TSP samples
302 collected at the same site in spring (Kunwar and Kawamura, 2014a).

303 Levoglucosan is a specific sugar compound formed by the pyrolysis of cellulose at
304 high temperature ($>300^\circ\text{C}$) (Simoneit et al., 1999). Concentrations of levoglucosan ranged

305 from 0.43 to 8.1 ng m⁻³ (3.4±2.5 ng m⁻³). Higher concentrations of levoglucosan were
306 observed in March 20, 22, 28, and April 1, 2, 3, 4 and April 10. nss-K⁺ is another tracer for
307 biomass burning, which showed co-varied peaks with levoglucosan (Figure 5g). However, we
308 observed relatively weak correlation between the two tracers (r=0.44). We checked the back
309 trajectory along with fire counts during March 20, 22 and 28, and April 1, 2, 3, 4, and 10.
310 Except for March 28 and April 2, air masses were influenced from the areas with high fire
311 counts, whereas during March 28 and April 2, air masses did not pass over the areas with
312 high fire counts. This result may suggest that, in addition to open biomass burning, closed or
313 domestic biomass burning is also important in East Asia (Sang et al., 2011 and references
314 therein).

315 To better understand the sources and transformation process, we performed
316 correlation analyses for selected diacids, oxoacids, inorganic ions, and levoglucosan (Table 2).
317 We found that C₂ is strongly correlated with its precursor compounds such as C₃ (r=0.94), C₄
318 (0.90), ωC₂ (0.83), and pyr (0.73). These strong correlations suggest that the predominance of
319 C₂ is involved with chain reactions of its precursors. The fair correlation (0.64) between C₂
320 and benzoic acid suggest that C₂ come in part from vehicular emission or atmospheric
321 oxidation of aromatic hydrocarbons because benzoic acid is a tracer of vehicular emission
322 (Ho et al., 2010; Kawamura and Kaplan, 1987) and is produced by the oxidation of toluene
323 (Suh et al., 2003). It is interesting to note that there is no correlation between C₉ and short
324 chain (C₂-C₄) diacids, suggesting that small diacids are not derived from biological sources.
325 We observed a weak correlation (r=0.46) between oxalic acid and levoglucosan, instead,
326 correlations are strong among oxalic acid, NH₄⁺ and nss-SO₄²⁻, suggesting that the Okinawa
327 aerosols are largely involved with the secondary formation with vigorous photochemical
328 processing.

329 **3.4. Possible sources of diacids and ionic species**

330 To understand the possible sources of diacids and major ions, we performed principal
331 component analysis using varimax rotation with Kaiser Normalization (SPSS software). As
332 shown in Table 3, four components were found. C_2 to C_5 , ωC_2 , NH_4^+ , MSA^- and $nssSO_4^{2-}$
333 show high loadings in Component 1. Component 1 is associated with anthropogenic sources
334 followed by photochemical oxidation because $nss-SO_4^{2-}$, NH_4^+ , MSA^- are emitted from
335 anthropogenic sources including industrial emissions, biofuel burning, and animal excreta.
336 ωC_2 is formed by the oxidation of aromatic hydrocarbons. Component 2 is associated with
337 biogenic sources because C_7 and C_8 diacids are produced by photochemical oxidation of
338 biogenic unsaturated fatty acids emitted from terrestrial higher plants and marine
339 phytoplankton (Pavuluri et al., 2010). Higher loadings of C_9 and levoglucosan in Component
340 3 suggest that C_9 diacid is associated with biomass burning. High loadings of Na^+ and NO_3^-
341 in Component 4 suggest the adsorption of HNO_3 on the surface of sea-salts (Deshmukh et al.,
342 2013). These results suggest that springtime aerosols are largely influenced from industrial
343 emission, terrestrial and marine biological emission, agricultural activity and biomass burning.

344 **3.5. Molecular distributions of fatty acids**

345 Figure 9 shows average molecular distribution of fatty acids. Short chain fatty acids
346 ($\leq C_{19}$) are emitted from vascular plants, microbes, and marine phytoplankton, while long
347 chain fatty acids ($\geq C_{20}$) are limited to terrestrial higher plant waxes (Kawamura et al., 2004;
348 Simoneit, 1978; Kolattukudy, 1976). Average molecular distribution showed the peak of $C_{14:0}$
349 fatty acid followed by $C_{16:0}$ and $C_{18:0}$. The predominance of even carbon number fatty acids
350 suggests an important contribution of biological sources to the Okinawa aerosols. $C_{18:1}$ is
351 highly reactive compared to $C_{18:0}$ in the atmosphere due to the presence of double bond. Thus,
352 the ratios of $C_{18:1}/C_{18:0}$ can be used to evaluate the aging process of organic aerosols (Ho et
353 al., 2011). Very high ratios were observed in April 7 followed by April 10 and 9 whereas
354 lower ratios were observed in March 31, April 1 and 2. The lower ratios are associated with

355 the photochemical oxidation process. The fresh organic aerosols were obtained in April 7
356 whereas the aged aerosols were obtained during March 31 and April 1. In April 7, air masses
357 were delivered from the coastal region of China, whereas air masses of March 31 were
358 delivered from Mongolia via North China and air masses of April 1 were originated from
359 North China.

360

361 **4. Summary and Conclusions**

362 We measured dicarboxylic acids, oxoacids, α -dicarbonyls and benzoic acid as well as
363 fatty acids in the springtime PM_{1.0} aerosols from Cape Hedo, Okinawa to better understand
364 the source and formation processes. Among diacids and related compounds, C₂ is most
365 abundant species (172±73 ng m⁻³) followed by C₃ (26±13 ng m⁻³) and C₄ (21±11 ng m⁻³).
366 Molecular distribution of diacids suggests that they are formed by the photochemical
367 oxidation of anthropogenic and biogenic precursors during long range atmospheric transport.
368 Higher concentrations of C₂, C₆ and benzoic acid in the aerosols (April 3) suggest significant
369 influences from anthropogenic activities including vehicular emission. Strong correlations
370 between total diacids and EC suggest that diacids are mostly transported from the polluted
371 regions of East Asia. We found a strong correlation between MSA⁻ and total diacids,
372 suggesting that some fractions of diacids were derived with industrial emissions from
373 Chinese megacities. Temporal variations of OC, EC, nss-SO₄²⁻, NH₄⁺ and ON are similar,
374 suggesting that organic nitrogen is emitted from the anthropogenic sources in East Asia. No
375 correlation between ON and levoglucosan suggests that ON is not emitted from biomass
376 burning. The even carbon number predominance of short chain fatty acids (<C₂₀) further
377 suggests that marine emission is also important source during the campaign.

378

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541 Figure Captions

542 Figure 1. (a) 5-day backward trajectories during study period. Back trajectory analysis was
543 performed at 500 m above ground level with the NOAA HYSPLIT model. (b) 5-day backward
544 trajectories with fire counts for specific days.

545 Figure 2. Averaged molecular distributions of straight chain diacids (C_2 - C_{12}), branched chain
546 diacids (iC_4 - iC_6), unsaturated diacids (M, F, mM, Ph, iPh, and tPh), multifunctional diacids
547 (hC_4 , kC_3 and kC_7), oxoacids (ωC_2 - ωC_9 , and pyruvic), and α -dicarbonyls (Gly and MeGly) in
548 $PM_{1.0}$ aerosols collected at Cape Hedo. The error bars represent the standard deviation.

549 Figure 3. Temporal variations of (a) oxalic acid (C_2), (b) malonic acid (C_3), (c) succinic acid (C_4),
550 (d) adipic acid (C_6), (e) azelaic acid (C_9), and (f) phthalic acid (Ph), (g) glyoxylic acid (ωC_2),
551 (h) 4-oxobutanoic acid (ωC_4), (i) 9-oxononanoic acid (ωC_9), (j) glyoxal (Gly), (k)
552 methylglyoxal (MeGly), and (l) benzoic acid in $PM_{1.0}$ aerosols collected at Cape Hedo,
553 Okinawa.

554 Figure 4. Temporal variations in the concentration ratios of (a) malonic/succinic (C_3/C_4), (b)
555 adipic/azelaic (C_6/C_9), (c) phthalic/azelaic (Ph/ C_9), and (d) fumaric/maleic (F/M) acids in
556 $PM_{1.0}$ aerosols collected at Cape Hedo, Okinawa.

557 Figure 5. Temporal variations of (a) organic carbon (OC) and elemental carbon (EC), (b) organic
558 nitrogen (ON), (c) NH_4^+ , (d) $nss-SO_4^{2-}$, (e) MSA^- , (f) $nss-K^+$, and (g) levoglucosan in $PM_{1.0}$
559 aerosols collected at Cape Hedo, Okinawa.

560 Figure 6. Scatterplot between (a) OC and EC, and (b) SO_4^{2-} and NH_4^+ in aerosols collected from
561 Cape Hedo, Okinawa.

562 Figure 7. Scatterplot between total nitrogen (TN) and NH_4-N+NO_3-N in aerosols collected from
563 Cape Hedo, Okinawa.

564 Figure 8. Scatterplots between (a) NH_4^+ and total diacids, (b) SO_4^{2-} and total diacids, (c) MSA^- and
565 total diacids, and (d) Na^+ and total diacids in aerosols collected from Cape Hedo, Okinawa.

566 Figure 9. Averaged molecular distributions of fatty acids in $PM_{1.0}$ aerosols collected from Cape
567 Hedo, Okinawa. The first number of fatty acid indicates the carbon numbers whereas the
568 second number indicates the number of double bond.

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Table 1. Concentrations of diacids and related compounds in atmospheric aerosols from Cape Hedo, Okinawa (2007 spring).

Species	Concentrations (ng m ⁻³)	
	AV±SD	Range
Diacids		
Oxalic, C ₂	172±73	78-329
Malonic, C ₃	26±13	7.5-58
Succinic, C ₄	20±11	5.2-53
Glutaric, C ₅	4.5±2.5	1.0-9.9
Adipic, C ₆	2.9±2.0	0.31-9.3
Pimelic, C ₇	0.60±0.71	BDL-3.1
Suberic, C ₈	0.93±2.2	BDL-11
Azelaic, C ₉	3.3±0.75	0.37-4.5
Sebacic, C ₁₀	0.39±0.37	BDL-1.2
Dodecanedioic, C ₁₂	0.91±0.43	0.32-1.9
Methylmalonic, iC ₄	4.3±2.5	1.3-9.8
Methylsuccinic, iC ₅	1.2±0.91	0.17-3.1
Methylglutaric, iC ₆	0.36±0.26	BDL-0.95
Maleic, M	1.6±1.0	0.33-4.9
Fumaric, F	0.68±0.47	0.20-2.2
Methylmaleic, mM	2.0±3.9	BDL-11
Phthalic, Ph	12±8.4	2.39-35
Isophthalic, iPh	0.74±0.63	0.04-2.2
Terephthalic, tPh	0.22±2.2	BDL-7.2
Hydroxysuccinic, hC ₄	0.21±0.15	0.07-0.87
Ketomalonic, kC ₃	15±14	0.45-69
Ketopimelic, kC ₇	3.4±2.0	0.61-7.8
Total diacids	273±121	114-537
Oxoacids		
Glyoxylic, ωC ₂	22±12	4.7-44
3-Oxopropanoic, ωC ₃	0.02±0.04	BDL-0.14
4-Oxobutanoic, ωC ₄	2.9±2.0	0.15-7.32
9-Oxononoic, ωC ₉	2.2±1.3	0.46-6.2
Total oxoacids	27±15	5.5-53
Pyruvic acid	4.9±2.5	1.7-10
Benzoic acid	17±9.2	4.3-36
α-Dicarbonyls		
Glyoxal, Gly	2.9±2.3	0.44-9.0
Methylglyoxal, MeGly	4.9±2.0	2.0-9.6
Total α-dicarbonyls	7.8±4.2	2.9-18

574 Note: BDL means below detection limit (<0.001 ng m⁻³)

575

576 Table 2: Correlation (r) analyses among diacids species and selected major ions in aerosols from Cape Hedo, Okinawa, Japan.

	C ₂	C ₃	C ₄	C ₆	C ₇	C ₉	Ph	ωC ₂	ωC ₉	Pyr	Na ⁺	nssK ⁺	NO ₃ ⁻	nssSO ₄ ²⁻	MSA ⁻	Levo
C ₂	1.00															
C ₃	0.94	1.00														
C ₄	0.90	0.95	1.00													
C ₆	0.58	0.63	0.62	1.00												
C ₇	0.44	0.49	0.50	0.86	1.00											
C ₉	0.19	0.11	0.14	0.32	0.32	1.00										
Ph	0.42	0.46	0.65	0.61	0.57	0.31	1.00									
ωC ₂	0.83	0.89	0.87	0.70	0.55	0.35	0.62	1.00								
ωC ₉	0.81	0.90	0.86	0.47	0.33	0.10	0.36	0.78	1.00							
Pyr	0.73	0.86	0.81	0.69	0.61	0.27	0.62	0.93	0.78	1.00						
Na ⁺	-0.02	0.10	0.17	-0.07	-0.02	-0.17	0.00	-0.02	0.20	0.08	1.00					
nssK ⁺	0.57	0.61	0.54	0.33	0.36	0.26	0.28	0.58	0.45	0.43	-0.17	1.00				
NO ₃ ⁻	-0.10	-0.25	-0.26	-0.19	-0.13	-0.04	-0.16	-0.27	-0.27	-0.27	-0.09	-0.22	1.00			
nssSO ₄ ²⁻	0.81	0.85	0.84	0.55	0.45	0.42	0.45	0.85	0.81	0.75	0.10	0.69	-0.29	1.00		
MSA ⁻	0.82	0.80	0.86	0.56	0.43	0.21	0.52	0.74	0.72	0.64	0.16	0.47	-0.14	0.84	1.00	
Levo	0.46	0.52	0.46	0.64	0.60	0.33	0.50	0.76	0.32	0.71	-0.27	0.44	-0.20	0.49	0.38	1.00

577

578

579 Table 3. Principal component analysis of selected diacids, oxoacid and major ions in the
 580 aerosols from Cape Hedo, Okinawa.

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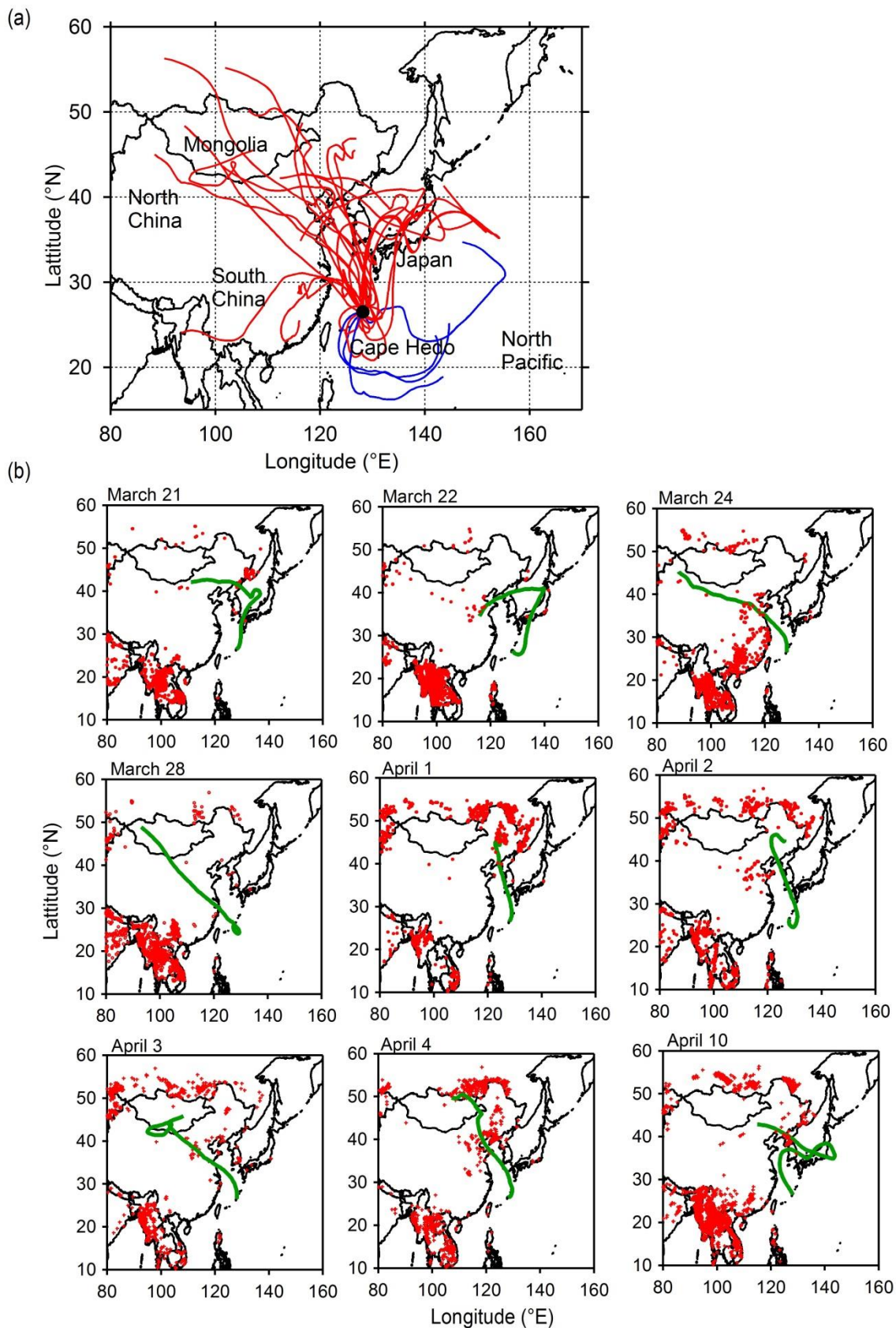
582

		Component			
	Species	1	2	3	4
583	C ₂	0.94	0.14	0.09	-0.03
	C ₃	0.94	0.22	0.08	-0.12
	C ₄	0.91	0.30	0.05	-0.12
584	C ₅	0.83	0.30	0.28	-0.04
	C ₆	0.44	0.79	0.31	-0.01
	C ₇	0.30	0.79	0.35	-0.03
585	C ₈	0.03	0.92	-0.12	-0.07
	C ₉	0.04	0.10	0.79	-0.04
	Ph	0.38	0.58	0.31	0.02
586	ω C ₂	0.82	0.24	0.43	-0.09
	Na ⁺	-0.27	0.09	-0.01	0.88
587	NH ₄ ⁺	0.90	0.12	0.18	-0.24
	nssK ⁺	0.61	-0.02	0.34	-0.27
	NO ₃ ⁻	-0.08	-0.15	-0.06	0.91
588	nssSO ₄ ²⁻	0.90	0.15	0.17	-0.22
	MSA ⁻	0.85	0.28	0.00	-0.04
	levo	0.41	0.28	0.69	-0.00
589	Variance	54%	13%	9%	7%

590

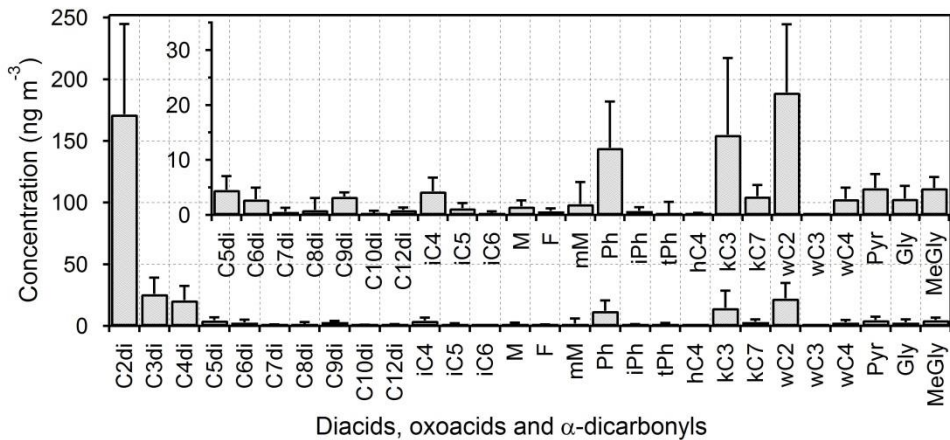
591 Figure

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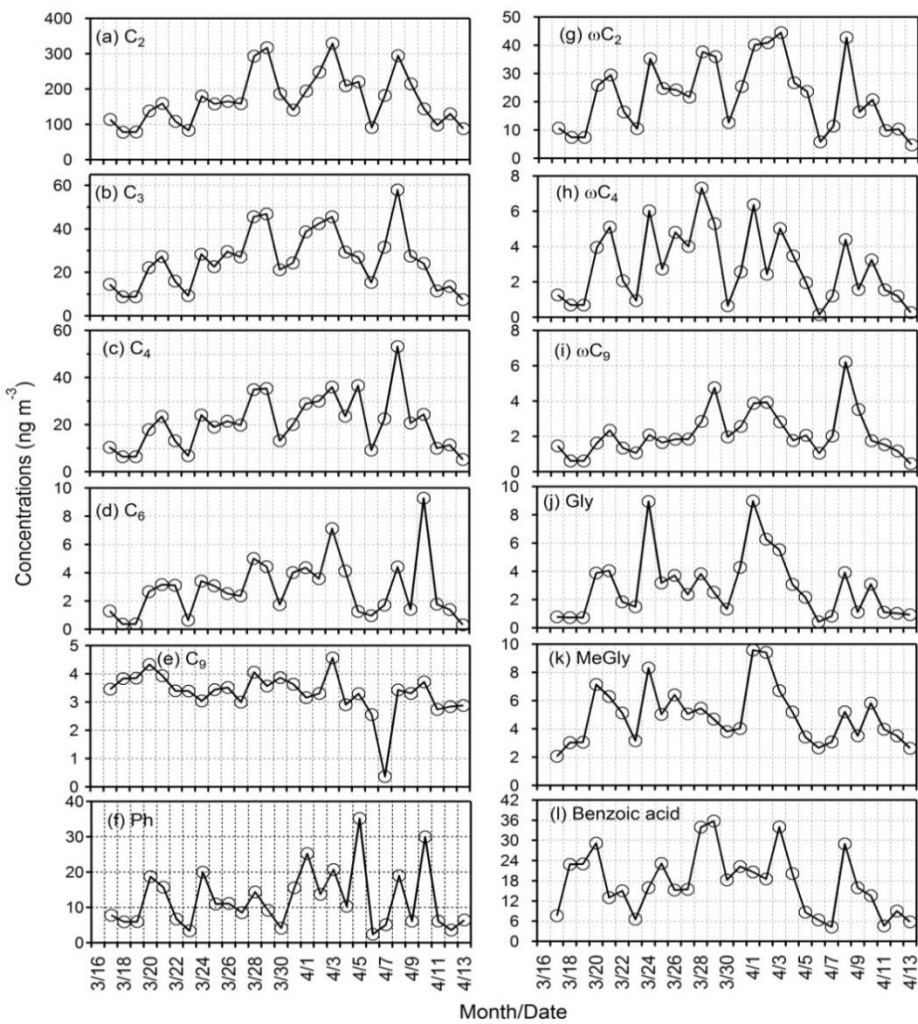
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594 Figure 2



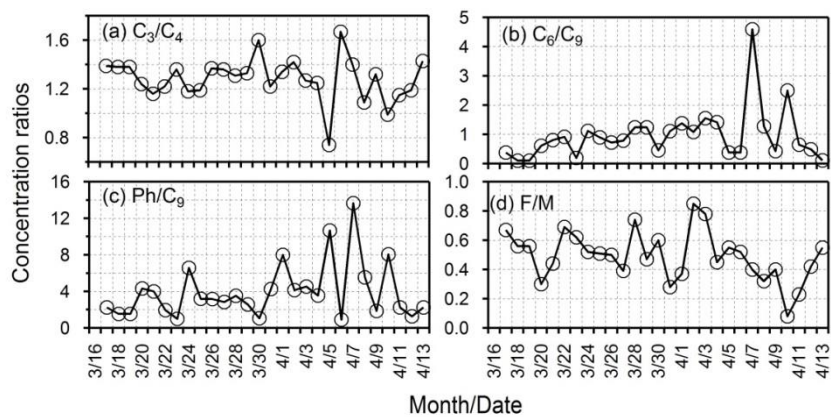
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596 Figure 3



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598 Figure 4



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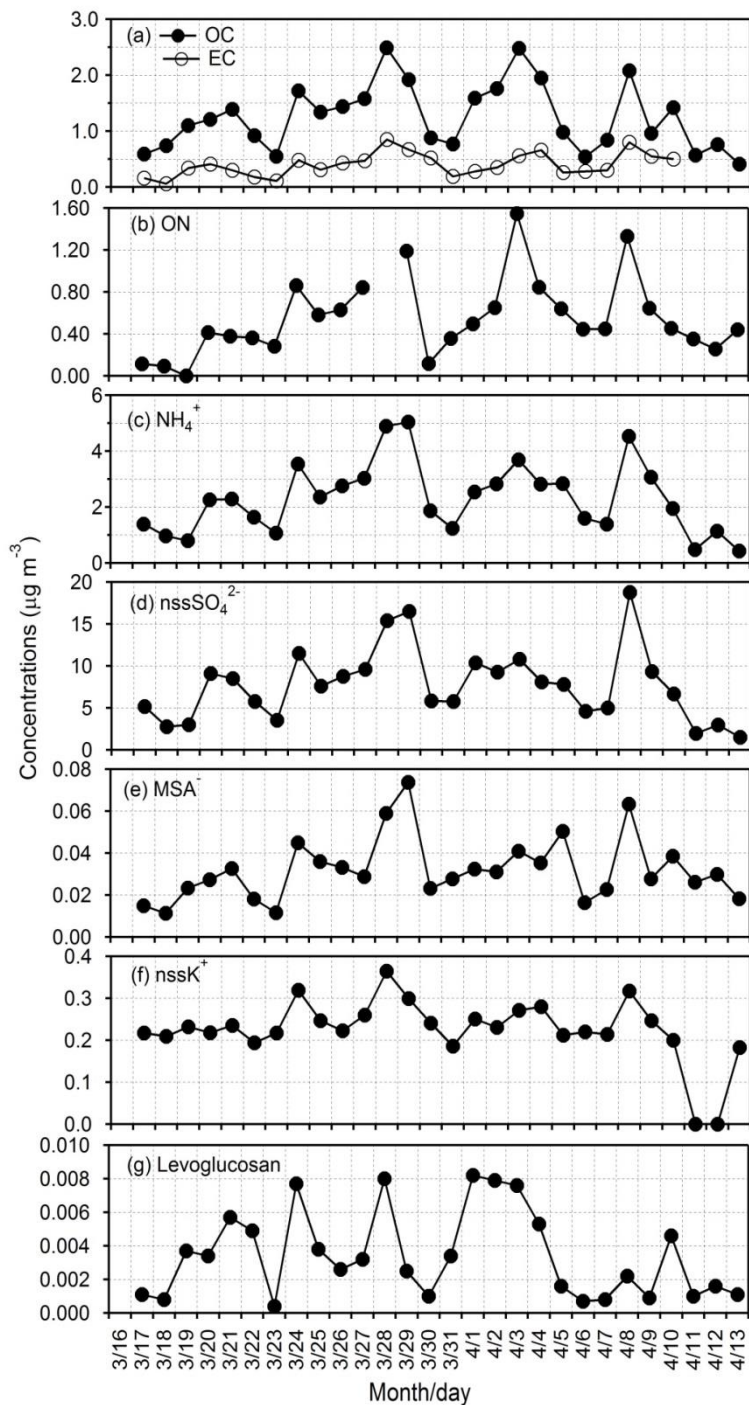
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613 Figure 5



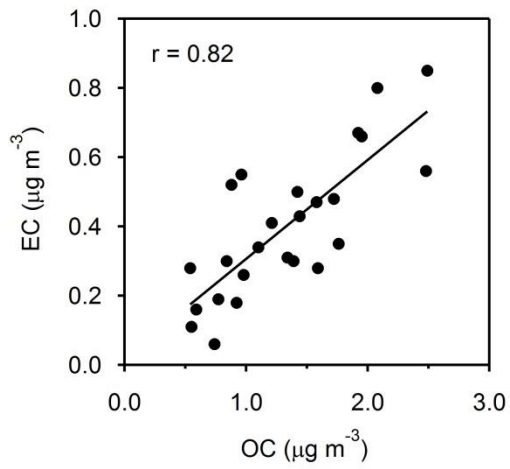
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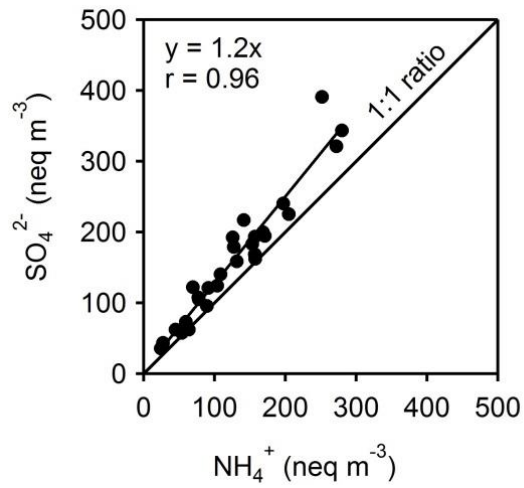
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618 Figure 6a



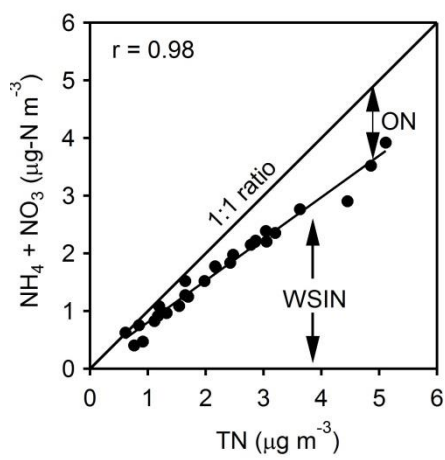
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620 Figure 6b



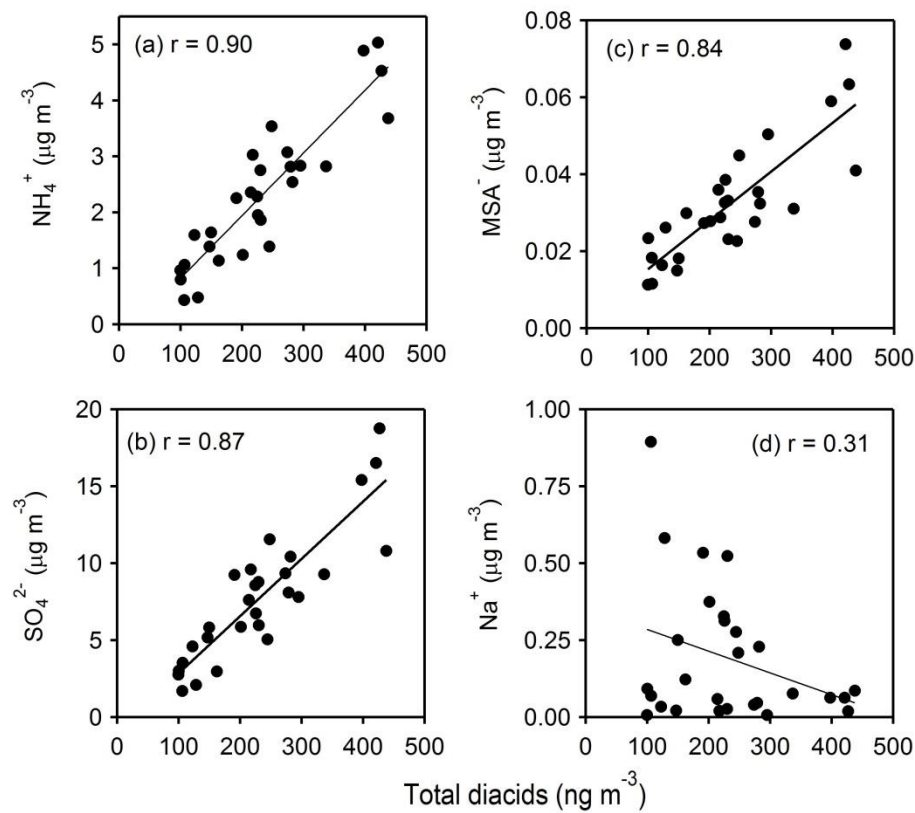
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622 Figure 7



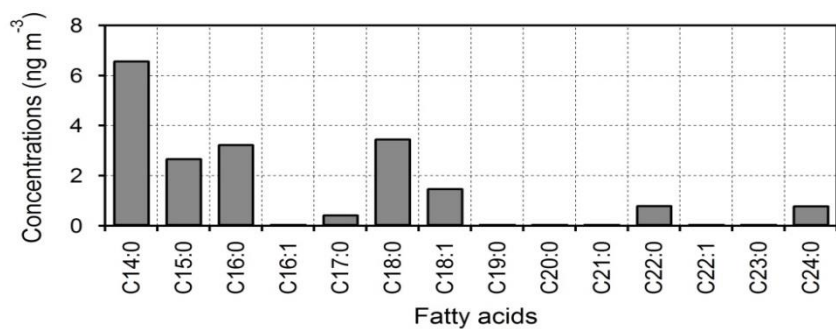
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624 Figure 8



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626 Figure 9



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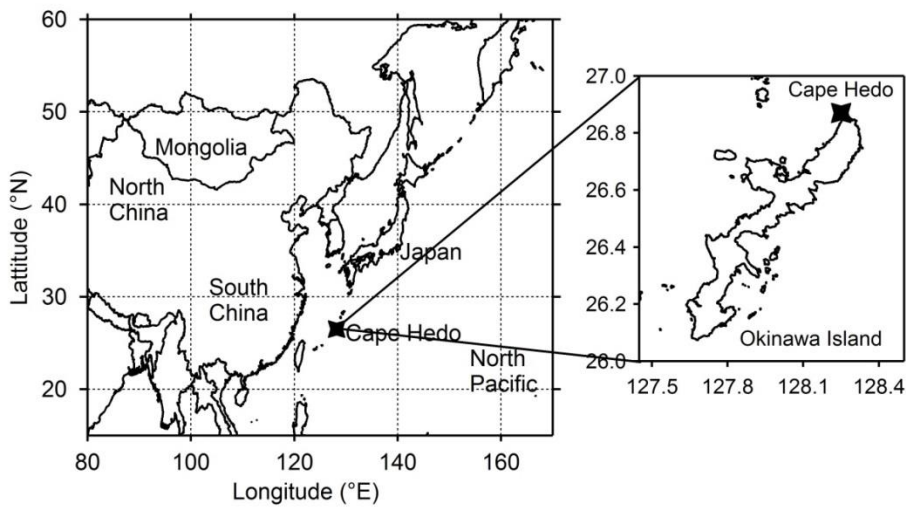
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631 Supporting Information

632 Figure S1. A geographical map of sampling location, Cape Hedo, Okinawa, Japan.

633 Figure S2. Temporal variations of (a) rain fall (b) temperature and (c) relative humidity recorded in
634 Cape Hedo, Okinawa.

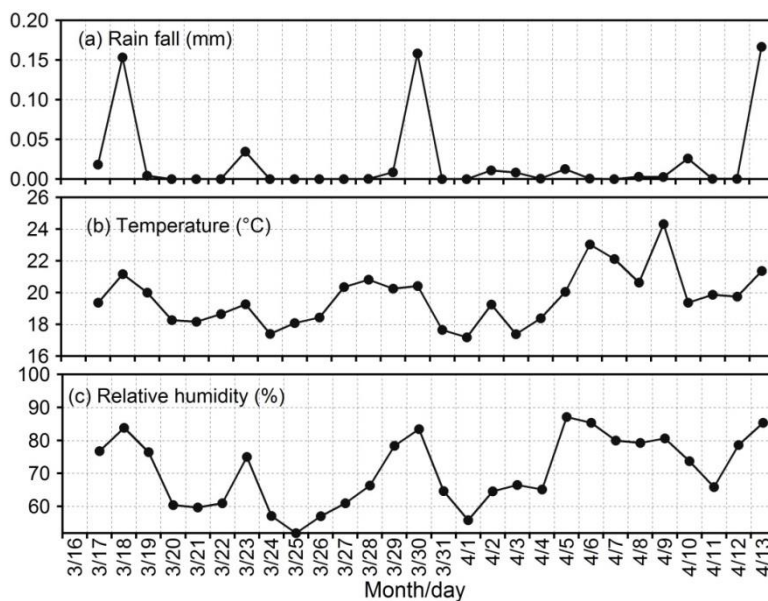
635

636 Figure S1.



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638 Figure S2.



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