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**Seasonal variations of stable carbon isotopic composition of bulk aerosol
carbon from Gosan site, Jeju Island in the East China Sea**

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26 **Abstract**

27
28 This study explores the usefulness of stable isotopic composition ($\delta^{13}\text{C}$) along with
29 other chemical tracers and air mass trajectory to identify the primary and secondary sources
30 of carbonaceous aerosols. Aerosol samples ($n = 84$) were collected continuously from April
31 2003 to April 2004 at Gosan site in Jeju Island, South Korea. The concentrations of total
32 carbon (TC), HCl fumed carbonate-free total carbon (fumed-TC) and their $\delta^{13}\text{C}$ were
33 measured online using elemental analyzer interfaced to isotope ratio mass spectrometer (EA-
34 IRMS). Similar concentrations of TC and fumed-TC and their similar $\delta^{13}\text{C}$ values suggest the
35 insignificant contribution of inorganic carbon to Gosan aerosols. The monthly averaged
36 $\delta^{13}\text{C}_{\text{TC}}$ showed the lowest in April/May (-24.2 to -24.4‰), which is related with the highest
37 concentrations of oxalic acid (a secondary tracer). The result indicates an enhanced
38 contribution of TC from secondary sources. The monthly averaged $\delta^{13}\text{C}_{\text{TC}}$ in July/August (-
39 23.0 to -22.5‰) were similar to those in January/February (-23.1‰ to -22.7‰). However,
40 chemical tracers and air mass transport pattern suggest that the pollution source regions in
41 January/February are completely different from those in July/August. Higher $\delta^{13}\text{C}$ values in
42 July/August are aligned with higher concentration ratios of marine tracers (azelaic acid/TC
43 and methanesulfonate/TC), suggesting an enhanced contribution of marine organic matter to
44 the aerosol loading. Higher $\delta^{13}\text{C}$ values in January/February are associated with higher
45 concentrations of phthalic acid and K^+/TC , indicating more contributions of carbonaceous
46 aerosols from fossil fuel and C_4 -plant biomass combustion. This study demonstrates that
47 $\delta^{13}\text{C}_{\text{TC}}$, along with other chemical tracers and air mass trajectory, can be used as a tracer to
48 understand the importance of primary versus secondary pollution sources of carbonaceous
49 aerosols in the atmosphere.

50

51 Keywords: Marine aerosol; Air pollution; Organic aerosol; $\delta^{13}\text{C}$; Isotopic enrichment; Gosan

52

53 **1. Introduction**

54 Atmospheric particulate matter (PM) affects the earth's radiative balance by absorbing
55 and scattering solar radiation (direct aerosol effect) (McCormick and Ludwig, 1967;
56 Ramanathan et al., 2001) and acting as cloud condensation nuclei (CCN) (indirect aerosol
57 effect) (Roberts et al., 2003; Twomey, 1974). They also indirectly affect the radiative balance
58 by changing land and ocean biogeochemical cycles through physical forcing or by adding
59 nutrients (Mahowald, 2011). The studies on extreme air pollution episode and
60 epidemiological and toxicological studies, have shown the relations between PM mass
61 concentrations and increased human mortality and morbidity (Pope and Dockery, 2006). The
62 climate and health effects largely depend upon the chemical composition of atmospheric
63 aerosols. It is therefore very important to understand the chemical composition and pollution
64 sources of atmospheric aerosols to formulate effective control strategies.

65 The $\delta^{13}\text{C}$ of total carbon ($\delta^{13}\text{C}_{\text{TC}}$) has been successfully used to identify and apportion
66 the pollution sources in different parts of world (Agnihotri et al., 2011; Cachier et al., 1985;
67 Cao et al., 2011; Chesselet et al., 1981; Jung and Kawamura, 2011; Kawamura et al., 2004;
68 Kirillova et al., 2013; Kundu et al., 2010a; Martinelli et al., 2002; Miyazaki et al., 2010;
69 Narukawa et al., 2008; Turekian et al., 2003; Widory et al., 2004). All of these studies used
70 the $\delta^{13}\text{C}_{\text{TC}}$ for understanding the primary pollution sources of carbonaceous aerosols.

71 Secondary organic aerosols, generated in the atmosphere, can account for more than 50% of
72 atmospheric aerosols (Cabada et al., 2004). It is therefore important to understand whether
73 $\delta^{13}\text{C}_{\text{TC}}$ can be used to understand the primary versus secondary pollution sources of
74 carbonaceous aerosols in the atmosphere.

75 Although there are some differences in the $\delta^{13}\text{C}_{\text{TC}}$ in aerosols emitted from various
76 pollution sources, the $\delta^{13}\text{C}_{\text{TC}}$ values of particles significantly overlap among the pollution
77 sources. The $\delta^{13}\text{C}_{\text{TC}}$ values of coal combustion-particles are -24.4 to -23.4‰, which are
78 similar to those of gasoline combustion-derived particles ($-24.3 \pm 0.6\text{‰}$) (Widory et al.,
79 2004). The $\delta^{13}\text{C}_{\text{TC}}$ values of particles derived from the combustion of diesel and fuel oil are -
80 $26 \pm 0.5\text{‰}$, which are different than those of particles from the combustion of coal and
81 gasoline. However, the $\delta^{13}\text{C}_{\text{TC}}$ values of fossil fuel combustion-derived particles fall in the
82 range of -20 to -37‰, which are $\delta^{13}\text{C}_{\text{TC}}$ values of particles emitted from C_3 plants (Das et al.,
83 2010; Jung and Kawamura, 2011; Kohn, 2010; Turekian et al., 1998). The $\delta^{13}\text{C}_{\text{TC}}$ values of
84 biogenic- and anthropogenic- secondary organic aerosols (SOA) also overlap the $\delta^{13}\text{C}_{\text{TC}}$ of
85 particles from C_3 plant. For example, the $\delta^{13}\text{C}_{\text{TC}}$ of β -pinene ozonolysis-SOA has been
86 reported to be $-29.6 \pm 0.2\text{‰}$ whereas the $\delta^{13}\text{C}_{\text{TC}}$ of toluene irradiation-SOA has been reported
87 to be $-32.5 \pm 0.3\text{‰}$ (Fisseha et al., 2009; Irei et al., 2006; Irei et al., 2011). The $\delta^{13}\text{C}_{\text{TC}}$ values
88 of C_4 plants-derived particles are -8 to -18‰ (Das et al., 2010; Turekian et al., 1998) whereas
89 those of marine-derived particles are -20 to -22‰ (Chesselet et al., 1981; Fontugne and
90 Duplessy, 1978; Fry et al., 1998). Due to the overlapping between the major pollution
91 sources, it is not straightforward to delineate among the pollution sources using only the
92 $\delta^{13}\text{C}_{\text{TC}}$. Some previous studies used $\delta^{13}\text{C}_{\text{TC}}$ values along with the air mass transport patterns
93 (e.g., Cachier et al., 1985). The $\delta^{13}\text{C}$ along with air mass transport patterns and chemical
94 tracers are likely to provide better information about the pollution sources.

95 Here we present the seasonal variations of $\delta^{13}\text{C}_{\text{TC}}$ in aerosol samples collected from
96 Gosan site at Jeju Island, South Korea. Then, we interpret the observed isotopic composition
97 and its seasonal variations based on the chemical tracers (oxalic acid, phthalic acid, azelaic
98 acid, methanesulfonate and K^+) and air mass transport pattern to understand the importance

99 of both the secondary and primary sources of carbonaceous aerosols. The chemical tracers
100 used in this study have been adopted from the previous studies (Kundu et al., 2010d).

101

102 **2. Experiment**

103

104 **2.1. Site Description**

105 Gosan site is situated on a cliff (~71 m above sea level) at the western edge of Jeju
106 Island (33°29' N, 126°16' E) (Fig. 1). It is ~100 km south of Korean Peninsula, ~500 km east
107 of Jiangsu province or Shanghai in China, ~200 km west of Kyushu Island in Japan, and
108 ~1000 km northeast of Taiwan. The site is covered with grasses but there are no trees. Local
109 anthropogenic emissions are very limited at the Gosan site (Kundu et al., 2010c, d; Lee et al.,
110 2007). Hence, Gosan site has been used as an ideal site to evaluate air pollution as a result of
111 the outflows from East Asia (Arimoto et al., 2004; Kawamura et al., 2004).

112

113 **2.2. Aerosol sampling**

114 Total suspended particles (TSP) in the atmosphere were collected at Gosan site over
115 2–7 days throughout the year from 2003 April to 2004 April. A high volume air sampler
116 (Kimoto AS-810) and prebaked (450 °C for 6 hours) quartz fiber filter (20 × 25 cm, Pallflex
117 2500 QAT-UP) were used to collect TSP samples (n = 84). The sampler was installed on the
118 roof of a trailer house (~3 m above the ground). Filters were placed in clean and prebaked
119 glass jar (150 mL) with a Teflon-lined screw cap before and after the sampling. Samples
120 were shipped to Sapporo, Japan and then preserved in a dark freezer room at -20 °C until
121 analysis. Field blank filters were collected every month.

122

123 2.3. Chemical analysis

124 A small disc (area 2.54 cm²) of each filter sample was wrapped with a cleaned tin cup
125 using tweezers. An autosampler was used to introduce the samples into the elemental
126 analyzer (EA; model: NA 1500 NCS, Carlo Erba Instruments). The samples are oxidized in a
127 combustion column packed with chromium trioxide at 1020 °C in an atmosphere of pure
128 oxygen. The derived CO₂ was isolated on a gas chromatograph (GC) installed within EA and
129 then measured with a thermal conductivity detector. Aliquots of CO₂ gas were then
130 introduced online into an isotope ratio mass spectrometer (ThermoQuest, Delta Plus) through
131 a ConFlo II interface (ThermoQuest) to monitor ¹³C/¹²C ratios. The carbon isotopic
132 composition was calculated using the following standard isotopic conversion equation.

$$\delta^{13}\text{C} (\text{‰}) = \left[\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \right] \times 1000$$

133 Another aliquot of filter samples was analyzed for TC and ¹³C/¹²C ratios after the
134 HCl-fume treatment to remove carbonate carbon (e.g., CaCO₃) (Kawamura et al., 2004). The
135 TC concentration in the field blank sample was 0.7-6% of aerosol TC concentrations and the
136 δ¹³C values are reported after blank correction. The replicate analyses (n=3) of aerosol
137 samples show that the analytical errors are in the range of 0.2-0.3‰. We have compared our
138 TC concentrations with organic carbon (OC) and elemental carbon (EC) concentrations
139 measured by an OC/EC analyzer (Sunset Laboratory Inc., Portland, OR). It shows that
140 monthly average contributions of OC to TC ranged from 46.5-92.4% (average 64.8%)
141 whereas the contributions of EC to TC ranged from 7.6-30.1% (average 18.9%). Overall, the
142 TC concentrations were 19.6% (on average) higher than the sum of OC and EC
143 concentrations.

144 Dicarboxylic acids, including oxalic, phthalic and azelaic acids were determined
145 using GC-FID (GC, Agilent 6980) and GC/MS (Thermoquest, Trace MS) (Kawamura et al.,

146 2010; Kundu et al., 2010d). Methanesulfonate (MSA, a secondary marine tracer), K^+ (a
147 biomass-burning tracer) were measured using a Metrohm 761 ion chromatography (IC)
148 system (Kundu et al., 2010d). The data of dicarboxylic acids, MSA and K^+ are reported
149 elsewhere (Kundu et al., 2010d).

150

151 **3. Results and discussion**

152 **3.1. Seasonality of total carbon (TC) and carbonate-free total carbon (fumed-TC)**

153 Fig. 2 and Table 1 show the seasonal variations in monthly averaged concentrations
154 of TC and fumed-TC in Gosan aerosols. The seasons in this study are defined as December to
155 February as winter, March to May as spring, June to August as summer and September to
156 November as fall. The average concentrations of TC and fumed-TC were found to be the
157 highest in April/May (6.7 and $7.6 \mu\text{g m}^{-3}$) and the lowest in July/August (2.0 and $2.2 \mu\text{g m}^{-3}$).
158 The intermediate levels of concentrations were observed in the colder months
159 (October/November: 3.5 and $3.4 \mu\text{g m}^{-3}$ and January/February: 5.0 and $4.8 \mu\text{g m}^{-3}$). Similar
160 levels of TC and fumed-TC suggest that most of carbonaceous aerosols are composed of
161 organic carbon and elemental carbon and the contribution of inorganic carbon is insignificant
162 in Gosan aerosols. The concentration levels of this study are comparable with those (0.6 – 16
163 $\mu\text{g m}^{-3}$) reported for aerosol samples collected from April 2001 to March 2002 at Gosan site
164 (Kawamura et al., 2004). The contributions of TC to aerosol mass ranged from 0.1% to
165 16.2% with an annual average of 6.6% . Higher contributions of TC to aerosol mass (7.3 –
166 10.0%) were observed in the spring (7.3 – 10.0%) and fall (7.8 – 9.9% , except November)
167 months. The lowest TC contributions were recorded in summer (4.2 – 6.5%) and winter (5.3 –
168 6.0%) months.

169 Highest concentrations and contributions of TC in spring months are consistent with
170 the facts that almost all of the air masses in spring are transported from the heavily polluted

171 regions in east China, Korea and Japan (Fig. 1) and higher photochemical activity in the East
172 Asian atmosphere (Mauzerall et al., 2000). The lowest concentrations and contributions in
173 July are due to the transport of clean air masses from the East China Sea and Yellow Sea
174 (Fig. 1). Higher concentrations of TC in the colder months (autumn and winter) are
175 associated with air mass transport from northeastern provinces of China (Fig. 1) where the
176 emissions from coal and other fossil fuel-combustion, as well as biofuel combustion, increase
177 significantly in cold seasons (Cao et al., 2011; Kundu et al., 2010c). Higher contribution of
178 TC to aerosol mass in the autumn months may be associated with an enhanced emissions
179 from agricultural straw burning (Yang et al., 2008; Wang et al., 2009).

180

181 **3.2. Seasonality of $\delta^{13}\text{C}$ for TC and fumed-TC**

182 The monthly averaged $\delta^{13}\text{C}_{\text{TC}}$ ranged between -24.4‰ to -22.5‰ with the lowest
183 value in May and the highest value in August (Fig. 3a). The $\delta^{13}\text{C}$ values in July/August (-23.0
184 to -22.5‰) were similar to those in the colder months (October: -23.2‰, December: -23.4‰,
185 January: -22.7‰ and February: -23.1‰). A similar trend with $\delta^{13}\text{C}$ values of -24.4‰ to -
186 22.4‰ was observed for fumed-TC. No significant difference in the $\delta^{13}\text{C}$ values was found
187 before and after the HCl-fume treatment of filter. The result suggests that carbonate such as
188 CaCO_3 from dusts was not present and/or it was reacted with H_2SO_4 in the atmosphere during
189 a long-range transport from the source regions. This is in contrast to the situation of 2001 and
190 2002 spring, when carbonate carbon was suggested to remain in the aerosols as the $\delta^{13}\text{C}$
191 values of fumed-TC were lower than the $\delta^{13}\text{C}$ values of TC particularly in the spring
192 (Kawamura et al., 2004).

193 The lower $\delta^{13}\text{C}$ values in April/May are involved with the higher concentrations of
194 oxalic acid (Fig. 3b). It is well established that oxalic acid is predominantly generated in the
195 atmosphere due to the oxidation of various organics in the gas and aqueous phase (Warneck,

2003; Kawamura and Yasui, 2005; Kundu et al., 2010b; Myriokefalitakis et al., 2011). The relation of lowest $\delta^{13}\text{C}$ with oxalic acid peak may suggest an increased contribution of secondary organic aerosols to carbonaceous aerosols at Gosan site.

The $\delta^{13}\text{C}$ values in April/May at Gosan site are 5.5-8.4‰ higher than those observed in SOA from the ozonolysis of β -pinene and from the OH oxidation of toluene (Fig. 5a). This could be interpreted by (a) dilution of secondary sources by the other primary sources having higher $\delta^{13}\text{C}$ values, and (b) enrichment of ^{13}C by the isotopic fractionation due to the chemical ageing of organic aerosols during long-range atmospheric transport. Dilution of the secondary sources can be evidenced by the transport of various air masses during April/May at Gosan site (Fig. 1). Recently, a significant enrichment of ^{13}C in remaining oxalic acid has been demonstrated during the photolysis of oxalic acid under aqueous phase in the presence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ (Pavuluri and Kawamura, 2012).

The concentrations of azelaic acid, methanesulfonate and K^+ were normalized to better understand the role of oceanic and biomass burning emissions in driving the seasonal variations of $\delta^{13}\text{C}$. Higher $\delta^{13}\text{C}$ values in summer are related with the higher concentration ratios of methanesulfonate/TC and azelaic acid/TC (Fig. 4a,b). Azelaic acid and methanesulfonate are oxidation products of oleic acid and dimethylsulfide, respectively, which are emitted from the oceans (Karl et al., 2007; Kawamura and Gagosian, 1987). The association of higher $\delta^{13}\text{C}$ with higher ratios of methanesulfonate/TC and azelaic acid/TC suggests an increased contribution of sea spray to carbonaceous aerosols. Marine-derived carbonaceous particles are enriched with ^{13}C in comparison to particles resulting from vehicular emissions, C_3 plants and secondary sources (Fig. 5a). K^+/TC ratios in summer were also observed to be higher than those in May and September. The result indicates higher contribution from biomass burning of C_4 plants such as wheat, rice and corn straws which is

220 associated with the burning crop residue by the end of harvest period and air mass transport
221 from polluted East China Sea and Yellow Sea.

222 The $\delta^{13}\text{C}$ values in colder months are similar to those in July/August (Fig. 3).
223 However, the trajectory analysis shows that pollution sources in the colder months are
224 different than the pollution sources in July/August at Gosan site (Fig. 1). The higher $\delta^{13}\text{C}$
225 values in the colder months are linked with the higher concentrations of phthalic acid (Fig.
226 3c). Phthalic acid is either generated in the atmosphere by the oxidation of aromatic
227 hydrocarbons emitted from fossil fuel combustion or emitted primarily from fossil fuel
228 combustion (Fraser et al., 2003; Kawamura and Kaplan, 1987). Thus the higher $\delta^{13}\text{C}$ values
229 in cold seasons can be interpreted by an enhanced contribution from coal and gasoline
230 burning. Particles produced by the combustion of coal and gasoline are generally more
231 enriched in ^{13}C than other sources such as diesel and fuel oil, SOA and C_3 -plant derived
232 particles (Fig. 5a). Large quantities of coal are burned for residential heating in north China
233 during November to March (Cao et al., 2011). Air mass transport patterns also suggest that
234 most of the air masses in cold seasons are transported to Gosan site from northeast China
235 (Fig. 1).

236 Higher $\delta^{13}\text{C}$ values in the cold seasons are also associated with higher concentration
237 ratio of K^+/TC (Fig. 4c), suggesting an enhanced contribution from biomass burning of C_4
238 plants such as wheat, rice and corn straws. Biomass combustion has been legally prohibited
239 in urban areas of China since 1998 (Cao et al., 2011). China has large rural population living
240 in the village and straws are not a high-demand fuel. Hence during and after the harvest
241 season, farmers often burn crop straws in the field as a convenient and inexpensive way to
242 dispose agricultural waste to advance crop rotation (Yang et al., 2008; Wang et al., 2009; Fu
243 et al., 2012). In addition, straws are also used for domestic heating during cold seasons and
244 for cooking fuels in the rural areas throughout the year.

245

246 **3.3. Identification of the source regions using $\delta^{13}\text{C}$ of total carbon (TC)**

247 The comparison of $\delta^{13}\text{C}_{\text{TC}}$ in aerosols between source regions and receptor site will
248 provide important information about the sources and source regions. This approach may also
249 present information on potential isotopic fractionation due to the evolution of organic
250 aerosols as a result of chemical and physical processes. The major pollution sources at Gosan
251 site are east China, Korea and Japan in spring, the East China Sea/Yellow Sea in summer,
252 and northeastern China in fall and winter (Fig. 1). Figs. 5b,c compare the $\delta^{13}\text{C}_{\text{TC}}$ in aerosols
253 between Gosan site and source regions suggested by air mass trajectory analysis.

254 The $\delta^{13}\text{C}_{\text{TC}}$ of atmospheric aerosols in spring in China are not available in the
255 literature. It can be assumed that the $\delta^{13}\text{C}_{\text{TC}}$ in spring will have similar values of summer
256 aerosols as a result of higher contributions of SOA. The average $\delta^{13}\text{C}_{\text{TC}}$ in summer aerosols
257 collected in 2003 was reported to be -26.4‰ in north China and -25.9‰ in south China (Cao
258 et al., 2011). The average $\delta^{13}\text{C}_{\text{TC}}$ in spring aerosols at Gosan is -24.1‰, which is about 2‰
259 higher than the $\delta^{13}\text{C}_{\text{TC}}$ in summer aerosols in China (Figs. 5b,c). Similarly, the average
260 $\delta^{13}\text{C}_{\text{TC}}$ in winter aerosols at Gosan site is 1.5‰ higher than those found in north China
261 atmospheric aerosols collected in 2003 winter (Figs. 5b,c). Higher $\delta^{13}\text{C}_{\text{TC}}$ at Gosan than the
262 source regions may be explained by ^{13}C enrichment during the long-range transport by
263 physical/chemical evolution of organic aerosols and/or mixture of various air masses from
264 China having different $\delta^{13}\text{C}$ signatures. The average $\delta^{13}\text{C}_{\text{TC}}$ in summer aerosols at Gosan is
265 >3‰ higher than those observed in summer aerosols in north and south China (Figs. 5b,c),
266 further confirming the marine contributions to carbonaceous aerosol. The $\delta^{13}\text{C}_{\text{TC}}$ of marine
267 aerosols collected during the season of higher biological activity (HBA) has been reported to
268 be higher than those of marine aerosols collected during lower biological activity (LBA) in

269 the western Pacific Ocean (Miyazaki et al., 2010). The $\delta^{13}\text{C}_{\text{TC}}$ has also been observed to
270 increase in the continental aerosols when air masses were transported from the oceans
271 (Cachier et al., 1996; Narukawa et al., 2008; Cao et al., 2013).

272

273 **4. Conclusions**

274 We found that total carbon (TC) in atmospheric aerosols collected from Golan site,
275 Jeju Island is mainly composed of organic carbon and elemental carbon with negligible
276 amount of inorganic carbon. Inorganic carbon was insignificant even in spring when Asian
277 dusts emitted from arid regions in China and Mongolia are often transported over the
278 sampling site, indicating that Asian dusts may have been titrated by acids such as sulfuric
279 acid in aerosols during a long-range atmospheric transport. Significant seasonal variations of
280 the $\delta^{13}\text{C}$ of both TC and fumed-TC were found in Gosan aerosols with larger values in
281 July/August and January/February and smaller values in April/May. Seasonal variations were
282 interpreted by the differences in pollution sources, source regions and secondary formation of
283 organic aerosols in the atmosphere. Since the $\delta^{13}\text{C}$ values of TC are overlapping between the
284 pollution sources in the atmosphere, it is risky to solely depend on $\delta^{13}\text{C}$ to identify the
285 pollution sources. The overlapping issue was dealt in this study with the considerations of the
286 air mass transport patterns and secondary chemical tracers including oxalic, azelaic, and
287 phthalic acids, methanesulfonate and K^+ . This study demonstrates that $\delta^{13}\text{C}_{\text{TC}}$, along with
288 chemical tracers and air mass trajectory, can be used as a tracer to understand the importance
289 of primary versus secondary sources of carbonaceous pollution. This study also shows the
290 possible isotopic enrichment of TC in aerosols by 1.5-3‰ during a long-range transport of
291 atmospheric aerosols from the source regions to Gosan site.

292

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300

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Table 1. Monthly averaged stable carbon isotope ratios of bulk carbon in atmospheric aerosol samples collected from Gosan site, Jeju Island.

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Date	Number of samples	$\delta^{13}\text{C}$ (‰)	
		^a TC	^b fumed-TC
January	8	-22.7	-22.6
February	8	-23.1	-22.6
March	10	-22.8	-22.7
April	17	-24.2	-24.1
May	11	-24.4	-24.4
June	7	-23.8	-23.8
July ^c	1	-23.0	-22.9
August	4	-22.5	-22.4
September ^c	2	-22.8	-23.1
October ^c	2	-23.2	-23.1
November	6	-24.2	-23.8
December	8	-23.4	-23.2

^aTC stands for total carbon.

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^bfumed-TC is the remaining carbon on the filter after removal of inorganic carbon by HCl.

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^cAdditional aerosol samples cannot be collected on July, September and October due to the mechanical failure of the aerosol samplers.

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486 **Figure Captions:**

487 **Fig. 1.** Map showing geographical region around Gosan site along with monthly-averaged
488 patterns of air mass transport. Gosan site is situated in the west coast of Jeju Island, South
489 Korea. Backward trajectories for 3-days at 500 m agl were drawn with NOAA HYSPLIT
490 model.

491

492 **Fig. 2.** Monthly-averaged variations of the concentrations total carbon (TC) and fumed-TC in
493 Gosan aerosols. The fumed-TC was determined after HCl fume treatment. The error bar
494 represents one standard deviation.

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496 **Fig. 3.** Monthly averaged variations of $\delta^{13}\text{C}$ in Gosan aerosols along with chemical tracers. a)
497 $\delta^{13}\text{C}_{\text{TC}}$, and $\delta^{13}\text{C}_{\text{fumed-TC}}$, b) oxalic acid (secondary organic aerosols (SOA) tracer from
498 various precursors), and c) phthalic acid (SOA tracer for the oxidation of aromatic VOC).

499

500 **Fig. 4.** Variations of the monthly averaged concentration ratios of (a) azelaic acid/TC, (b)
501 methanesulfonate/TC and (c). K^+ /TC.

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503 **Fig. 5.** Alignment of $\delta^{13}\text{C}_{\text{TC}}$ in Gosan atmospheric aerosols (middle panel) with the $\delta^{13}\text{C}_{\text{TC}}$ in
504 major source aerosols (upper panel) and in source region aerosols (lower panel). Data of
505 source regions are adopted from ^aCao et al., 2011 and ^bMiyazaki et al., 2010. Data of the
506 sources are adopted from ^cWidory et al., 2004; ^dTurekian et al., 2003; ^eDas et al., 2010;
507 ^fJung et al., 2011; ^gFisseha et al., ^hIrei et al., 2006; and ^hIrei et al., 2011.

Figure 1

Figure 2

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Figure 3

Figure 3.

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Figure 4.

Figure 5

Figure 5.