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3 Stable carbon and nitrogen isotopic compositions of ambient aerosols collected from Okinawa  
4 Island in the western North Pacific Rim, an outflow region of Asian dusts and pollutants

5

6

7 Bhagawati Kunwar<sup>1</sup>, Kimitaka Kawamura<sup>1\*</sup>, and Chunmao Zhu<sup>1</sup>

8

9 <sup>1</sup>Institute of Low Temperature Science, Hokkaido University, N19 W8, Kita-ku, Sapporo,  
10 Japan

11

12 \*Corresponding author (email: kawamura@lowtem.hokudai.ac.jp)

13

**14 Abstract**

15 Stable carbon ( $\delta^{13}\text{C}$ ) and nitrogen ( $\delta^{15}\text{N}$ ) isotope ratios were measured for total carbon  
16 (TC) and nitrogen (TN), respectively, in aerosol (TSP) samples collected at Cape Hedo,  
17 Okinawa, an outflow region of Asian pollutants, during 2009 to 2010. The averaged  $\delta^{13}\text{C}$  and  
18  $\delta^{15}\text{N}$  ratios are -22.2‰ and +12.5‰, respectively. The  $\delta^{13}\text{C}$  values are similar in both spring  
19 (-22.5‰) and winter (-22.5‰), suggesting the similar sources and/or source regions. We  
20 found that  $\delta^{13}\text{C}$  from Okinawa aerosols are ca. 2‰ higher than those reported from Chinese  
21 megacities probably due to photochemical aging of organic aerosols. A strong correlation  
22 ( $r=0.81$ ) was found between nss-Ca and TSP, suggesting that springtime aerosols are  
23 influenced from Asian dusts. However, carbonates in the Asian dusts were titrated with acidic  
24 species such as sulfuric acid and oxalic acid during atmospheric transport although two  
25 samples suggested the presence of remaining carbonate. No correlations were found between  
26  $\delta^{13}\text{C}$  and tracer compounds (levoglucosan, elemental carbon, oxalic acid, and  $\text{Na}^+$ ). During  
27 winter and spring, coal burning is significant source in China. Based on isotopic mass balance,  
28 contribution of coal burning origin particles to total carbon aerosol was estimated as ca. 97%  
29 in winter, which is probably associated with the high emissions in China. Contribution of  
30  $\text{NO}_3^-$  to TN was on average 45% whereas that of  $\text{NH}_4^+$  was 18%. These results suggest that  
31 vehicular exhaust is an important source of TN in Okinawa aerosols. Concentration of water-  
32 soluble organic nitrogen (WSON) is higher in summer, suggesting that WSON is more  
33 emitted from the ocean in warmer season whereas inorganic nitrogen is more emitted in  
34 winter and spring from pollution sources in the Asian continent.

35

36 Keywords: Isotope ratios, total carbon, total nitrogen, nitrate, water-soluble organic nitrogen

## 37 1. Introduction

38 Atmospheric aerosols are solid particles suspended in gaseous and liquid phase. They  
39 are emitted to the atmosphere from natural and anthropogenic sources. In East Asia, fossil  
40 fuel consumption, biomass burning, industrial and vehicular emissions have significantly  
41 increased due to the growing economies (*Ohara et al., 2007*). Primary organic aerosols are  
42 formed by the direct emissions of biogenic and anthropogenic particles to the atmosphere.  
43 Secondary organic aerosols (SOA) are formed by the atmospheric oxidation of biogenic and  
44 anthropogenic volatile organic compounds (VOC) during long-range atmospheric transport  
45 (*Hallquist et al., 2009; Pokhrel et al., 2015a, b*). In East Asia, atmospheric aerosols and their  
46 precursors are significantly emitted from the highly populated and rapidly developing  
47 industrial regions and are transported to the North Pacific. Okinawa Island is located in the  
48 western North Pacific Rim: an outflow region of Asian aerosols and their precursors.

49 Studies on aerosol isotopic composition have been conducted in East Asia. Stable  
50 carbon and nitrogen isotope ratios can be used to identify the sources and transformation  
51 processes of atmospheric particles (*Cachier et al., 1986; Kawamura et al., 2004; Kawashima  
52 and Haneishi, 2012; Kundu et al., 2010, 2014; Cao et al., 2011*). Recently, *Miyazaki et al.  
53 (2012)* discussed the source of water-soluble organic carbon (WSOC) in forest aerosols using  
54  $\delta^{13}\text{C}$  ratios. Kinetic isotope effect (KIE) is defined as the ratio of rate constant for the species  
55 containing  $^{12}\text{C}$  and  $^{13}\text{C}$  atoms ( $k_{12}/k_{13}$ ), which can be obtained from the slope of the regression  
56 line for the relation between the concentrations and stable carbon isotope ratio ( $\delta^{13}\text{C}$ ).  $\delta^{13}\text{C}$   
57 values are largely dependent on the aging of polar compounds such as oxalic acid (*Pavuluri  
58 et al., 2012*). During oxidation processes, the isotopic fractionation occurs leaving the lighter  
59 isotopes in the product and heavier isotopes in the reactants due to the KIE (*Fisseha et al.,  
60 2009*).

61 In addition,  $\delta^{13}\text{C}$  can be used to evaluate the source from coal combustion, biogenic

62 and vehicular emission (*Gorka and Jedrysek, 2008; Gorka et al., 2009, 2014*). *Takahashi et al.*  
63 (2008) measured  $\delta^{13}\text{C}_{\text{elemental carbon (EC)}}$  in TSP samples in Beijing, China (annual average -  
64  $24.6 \pm 0.7\%$ ) and in Tokyo ( $-25.1 \pm 0.1\%$ ). They reported higher values ( $-23.4 \pm 1.2\%$ ) in China  
65 during winter due to significant emissions from coal combustion. *Lopez-Veneroni (2009)*  
66 reported  $\delta^{13}\text{C}_{\text{TC}}$  in  $\text{PM}_{2.5}$  and in  $\text{PM}_{10}$  in Mexico, which was influenced from the dust, diesel  
67 and gasoline vehicles. Similarly, *Kawashima et al. (2012)* reported  $\delta^{13}\text{C}_{\text{EC}}$  for the emissions  
68 from gasoline-powered vehicles ( $-24.4$  to  $-20.6\%$ ), diesel-powered vehicles ( $-24.2$  to  $-24.9\%$ ),  
69 coal burning ( $-23.3\%$ ) and soils ( $-18.8\%$ ). Based on the isotopic mass balance equation,  
70 *Gorka et al. (2014)* estimated the contribution of biogenic and anthropogenic sources for  
71  $\text{PM}_{10}$  samples.

72 Oxidation products of VOC have lower vapour pressure than the precursor VOC and  
73 can partition into the particle phase, forming SOA (*Hallquist et al., 2009*). Organic  
74 compounds that are present in particulate matter can be scavenged from the atmosphere by  
75 dry and wet deposition. During deposition process of particles, isotope fractionation does not  
76 occur. However, reactions within the particles can change the isotope ratios. Although these  
77 reactions are not fully understood, it is known that if photochemical degradation of oxalic  
78 acid catalysed by iron species is significant, the isotope ratios of remaining oxalic acid  
79 become higher due to KIE effects (*Pavuluri et al., 2012*). If oxalic acid were the major  
80 component of organic aerosol,  $\delta^{13}\text{C}$  of aerosol TC should become higher during long range  
81 atmospheric transport. Organic compounds produced by the oxidation processes show smaller  
82 isotope ratios (*Fisseha et al., 2009*) while the remaining precursors are enriched with heavier  
83 isotopes (*Anderson et al., 2004*).  $\delta^{13}\text{C}$  of aerosols can also be used to distinguish the  
84 contribution of  $\text{C}_3$  versus  $\text{C}_4$  vegetation type (*Martinelli et al., 2002*).

85 Nitrogen ( $\text{N}_2$ ) in the atmosphere can be converted into  $\text{NO}_3^-$  and  $\text{NH}_4^+$  via nitrification  
86 or denitrification process (*Hem, 1985; Raven et al., 1992*). Volatile organic nitrogen is

87 released to the atmosphere during the plant and animal decay. Fossil fuel combustion and  
88 industrial emission contribute gaseous NO<sub>x</sub> and nitrate, which can travel long distances. The  
89 use of δ<sup>15</sup>N can decipher the origin, cycling of organic and inorganic nitrogen as well as  
90 atmospheric processing of nitrogen species (*Cornell et al., 1995; Yeatman et al., 2001, Kelly*  
91 *et al., 2005*). The importance of δ<sup>15</sup>N in the atmosphere is well documented in many  
92 literatures (e.g., *Kundu et al., 2010*). In the atmosphere there are naturally occurring two  
93 stable isotopes of <sup>14</sup>N and <sup>15</sup>N. <sup>14</sup>N is most common and its abundance in N<sub>2</sub> gas is 99.63%  
94 (*Mariotti, 1983*). With regard to reaction kinetics, two nitrogen isotopes show different  
95 behaviors. Thus, depending upon the nature of formation processes and their precursors,  
96 isotopic composition of particular nitrogen species will be different (*Pavuluri et al., 2011*).

97 Here, we report one year observation of stable carbon and nitrogen isotope ratios of  
98 the ambient aerosols (TSP samples) collected at Cape Hedo, Okinawa Island in the western  
99 North Pacific Rim: an outflow region of Asian dusts and pollutants. The major goal of this  
100 study is to identify the specific sources of carbonaceous aerosols in the Asian outflow regions  
101 during winter, spring, summer and autumn. In winter and spring, anthropogenic activities are  
102 known to influence the study site, whereas in summer marine activities influence the site  
103 (*Kunwar and Kawamura, 2014a*). Here, we also discuss seasonal changes of the isotope ratios  
104 in terms of source and source regions, and the aging of organic aerosols during long-range  
105 atmospheric transport.

## 106 **2. Experimental**

### 107 **2.1 Site Description and Aerosol Sampling**

108 Aerosol samples were collected from November 2009 for two years and half on the  
109 rooftop of the facility of Cape Hedo Atmosphere and Aerosol Measurement Station  
110 (CHAAMS, 26.87°N, 128.26°E). CHAAMS is located at the northwestern edge of Okinawa  
111 Island, Japan (see Figure 1), which is within the outflow region of East Asian dusts and

112 pollutants. Because of its location, CHAAMS has been used as a supersite of the Atmospheric  
113 Brown Clouds (ABC) project by the United Nations Environment Programme (UNEP) for the  
114 study of atmospheric aerosols (*Takami et al., 2007*). The surroundings of Cape Hedo are  
115 covered with subtropical rain forest and thus there are no major industries near the station and  
116 anthropogenic activities are insignificant (*Yamamoto and Kawamura, 2011; Sato et al., 2009;*  
117 *Takami et al., 2007; Duncan et al., 2003; Verma et al., 2011*). It is influenced by the East  
118 Asian monsoon in winter to spring whereas the monsoon from the Pacific Ocean affects the  
119 region in summer to fall (*Sato et al., 2009*). Therefore, continental air masses arrive over the  
120 sampling site in winter to spring. This is supported by air mass trajectory analyses (Figure S1).

121 Aerosol (TSP) samples (n=50) were collected on a weekly basis using a pre-  
122 combusted quartz fiber filter and high-volume air sampler (*Kunwar and Kawamura, 2014a,*  
123 *b*) at a flow rate of  $60 \text{ m}^3 \text{ h}^{-1}$  on a weekly basis. The average volume of the air collected is  
124  $9500 \text{ m}^3$ . Filter samples were placed in a preheated glass jar with a Teflon-lined screw cap,  
125 shipped from Cape Hedo to Sapporo and stored in a freezer room at  $-20^\circ\text{C}$  until analysis. The  
126 sampling period for each sample is 7 days. Quartz fiber filter may adsorb organic vapor,  
127 causing positive artifacts on the measurements. However, due to relatively long sampling  
128 period (one week), we consider that artifacts were minimal.

## 129 **2.2. Measurements of TC and TN, and their Stable Isotopes**

130 To measure total carbon (TC) and nitrogen (TN), we combusted a small filter disc  
131 ( $3.14 \text{ cm}^2$ ) placed in a tin cup at  $1400^\circ\text{C}$  using elemental analyzer (EA) (Carlo Ebra, EA  
132 1500). All the nitrogen species are converted to NO and further reduced to  $\text{N}_2$  in a reduction  
133 column. Carbonaceous species are oxidized to carbon dioxide ( $\text{CO}_2$ ).  $\text{N}_2$  and  $\text{CO}_2$  are  
134 separated on a packed column of gas chromatograph installed in EA and measured with a  
135 thermal conductivity detector (*Pavuluri et al 2010; Kawamura et al., 2004*). Portions of  $\text{CO}_2$   
136 and  $\text{N}_2$  gases were transferred to EA/isotope ratio mass spectrometer (irMS) via an interface

137 (ConFlo II) for isotope ratio measurement. The  $\delta^{13}\text{C}$  values of TC and  $\delta^{15}\text{N}$  of TN are  
 138 calculated using the following equation:

$$139 \quad \delta^{13}\text{C} (\text{‰}) = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}}/({}^{13}\text{C}/{}^{12}\text{C})_{\text{standard}} - 1] \times 1000 \quad (1)$$

$$140 \quad \delta^{15}\text{N} (\text{‰}) = [({}^{15}\text{N}/{}^{14}\text{N})_{\text{sample}}/({}^{15}\text{N}/{}^{14}\text{N})_{\text{standard}} - 1] \times 1000 \quad (2)$$

141 Organic nitrogen (ON) is calculated using following equation (*Wang et al., 2010*):

$$142 \quad \text{ON} = \text{TN} - 14 \times ([\text{NO}_3^-]/62 + [\text{NH}_4^+]/18) \quad (3)$$

143  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are the major ions detected in our samples.

### 144 **2.3. Measurements of WSOC, WSTN, and Major Inorganic Ions**

145 Concentrations of water-soluble organic carbon (WSOC) and water-soluble total  
 146 nitrogen (WSTN) were measured using a total carbon and nitrogen analyzer (Shimadzu TOC-  
 147 V<sub>C</sub>SH). Cation ( $\text{NH}_4^+$ ) and anion ( $\text{NO}_3^-$ ) was measured using ion chromatograph (IC) (761  
 148 Compact IC, Metrohm, Switzerland), as reported in *Kunwar and Kawamura (2014a)*. The  
 149 analytical errors in duplicate analysis of the authentic standards were within 5%. We also  
 150 measured organic carbon (OC)/elemental carbon (EC) using a Sunset Laboratory carbon  
 151 analyzer (*Kunwar and Kawamura, 2014a*).

### 152 **2.4. Backward Air Mass Trajectory Analysis**

153 Five-day back trajectory analyses were performed to identify the source regions of air  
 154 masses arriving over Cape Hedo, at 500 meters above ground level for selected samples using  
 155 the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model  
 156 (<http://www.arl.noaa.gov/ready/hysplit4.html>), NOAA Air Resources Laboratory, Silver  
 157 Spring, Maryland, United States (*Draxler and Hess, 1997*). Figure 2 shows the air mass  
 158 trajectories calculated for selected weeks during winter (December, January and February),  
 159 spring (March, April and May), summer (June, July and August) and autumn (September,  
 160 October and November). In spring and winter, our sampling site was strongly influenced by

161 the outflows from East Asia whereas in summer the site was largely affected by oceanic air  
162 masses (Figure S1).

163

### 164 **3. Results and Discussion**

#### 165 **3.1. Seasonal variations of TC, TN**

166 Table 1 summarizes the data for TC, TN and their stable isotopes with averages and  
167 ranges. Concentrations of TC ranged from 1.0 to 5.2  $\mu\text{g m}^{-3}$  (av.  $2.3\pm 1.0 \mu\text{g m}^{-3}$ ). Very high  
168 concentration was observed on March 16 ( $7.3 \mu\text{g m}^{-3}$ ) during dust event whereas very high  
169 concentration of TN was observed on June 8. Concentration data of TC on March 16 and of  
170 TN on June 8 are treated as outliers, which are not included in the calculation but explained  
171 separately. Weekly concentrations of TC are given in Figure 3a. The seasonal TC  
172 concentrations were  $2.0\pm 0.60 \mu\text{g m}^{-3}$  (range:  $1.1\text{-}3.2 \mu\text{g m}^{-3}$ ) in winter,  $2.3\pm 1.0 \mu\text{g m}^{-3}$  ( $1.2\text{-}$   
173  $5.2 \mu\text{g m}^{-3}$ ) in spring,  $2.1\pm 0.63 \mu\text{g m}^{-3}$  ( $1.1\text{-}3.7 \mu\text{g m}^{-3}$ ) in summer, and  $1.7\pm 0.63 \mu\text{g m}^{-3}$  ( $1.0\text{-}$   
174  $2.6 \mu\text{g m}^{-3}$ ) in autumn. However, seasonal differences are not statistically significant between  
175 winter and spring season ( $t=-0.7$ ,  $p=0.45$ ), and spring and summer ( $t=1.6$ ,  $p=0.13$ ). Higher TC  
176 concentrations in spring and winter suggest that Cape Hedo is seriously influenced by  
177 polluted air masses from the Asian continent (Figure 2). Trajectory analyses show that air  
178 masses occasionally passed over the ocean. In addition, there is an influence of dust and soils,  
179 and biogenic emission during spring. Spring is a growing season in both continent and ocean  
180 (*Tambunan et al., 2007; Kunwar and Kawamura, 2014a*). Biogenic emission from local  
181 vegetation is also important in spring.

182 We detected the highest concentration of TC ( $7.3 \mu\text{g m}^{-3}$ ) during dust event (March  
183 16). In this filter sample, we observed lots of dust particles, suggesting that high TC content is  
184 associated with dust loading. Fine dust particles can enrich organic carbon than coarse  
185 particles (*Kawamura et al., 2004*). Dust particles also contain carbonate carbon. In fact, soil

186 dust particles collected from Gansu Province, China (CJ-1 and CJ-2 yellow sand standards)  
187 showed the presence of inorganic (carbonate) carbon, whose contents are equivalent to  
188 organic carbon (*Kawamura et al., 2004*). *Wang et al. (2013)* also found higher concentration  
189 of TC during dust event in China.

190 OC/EC ratios are higher in summer (12.5) than winter (4.4), suggesting that major  
191 fraction of OC come from biogenic sources probably due to the enhanced activities of oceanic  
192 phytoplankton and other biota. However, no statistically significant correlation ( $r = 0.0$ ) was  
193 found between OC and  $\text{Na}^+$  even in summer, although most of the air masses came from the  
194 ocean (Figure S1).  $\text{Na}^+$  is primarily emitted from the marine source. No correlation between  
195 OC and  $\text{Na}^+$  suggests the secondary source of OC. Concentrations of TC in Cape Hedo are  
196 several times lower than those reported from many Chinese cities including Beijing (*Ho et al.,*  
197 *2006; Wang et al., 2010*), Gosan, Korea (*Kawamura et al., 2004; Kundu et al., 2010*),  
198 Chennai, India (*Pavuluri et al., 2010*) and Tokyo (*Kawamura and Ikushima, 1993*). But, they  
199 are ca. 5 times higher than those from the western North to Equatorial Pacific (*Kawamura*  
200 *and Sakaguchi, 1999*) during winter and are significantly higher than those from the High  
201 Arctic aerosols (*Narukawa et al., 2008*) and marine aerosols from the Arctic Ocean  
202 (*Kawamura et al., 2012*).

203 Average concentration of TN in the Cape Hedo aerosols was  $0.72 \pm 0.54 \mu\text{g m}^{-3}$  (range:  
204  $0.15\text{-}2.4 \mu\text{g m}^{-3}$ ), which is 3 times lower than that ( $2.5 \mu\text{g m}^{-3}$ ) from Gosan (*Kundu et al.,*  
205 *2010*) and 4 times lower than that ( $3.1 \mu\text{g m}^{-3}$ ) from the same Gosan site during spring  
206 (*Kawamura et al., 2004*). In contrast, average TN concentration of Cape Hedo is 6 times  
207 higher than those from the North to Equatorial Pacific (*Kawamura and Sakaguchi, 1999*). The  
208 seasonally averaged TN concentration was highest in winter ( $1.19 \pm 0.58 \mu\text{g m}^{-3}$ ), followed by  
209 spring ( $0.93 \pm 0.50 \mu\text{g m}^{-3}$ ), summer ( $0.50 \pm 0.64 \mu\text{g m}^{-3}$ ) and autumn ( $0.43 \pm 0.19 \mu\text{g m}^{-3}$ ).  
210 However, differences in the seasonal concentrations are not statistically significant between

211 winter and spring season ( $t = 1.1$ ,  $p = 0.2$ ), and spring and summer ( $t = 1.4$ ,  $p = 0.1$ ), except  
212 for winter and summer samples ( $t = 2.1$ ,  $p = 0.04$ ). The higher concentration of TN in winter  
213 and spring (Figure 3b) suggest that the source of TN is associated with polluted continental  
214 outflow from East Asia (see Figure 2).

215 We found sporadic peaks of TN on June 8 and April 27. On June 8, air masses arrived  
216 from coastal South China and northern Japan (Figure 2) whereas on April 27 all air masses  
217 arrived from Russia, Mongolia and north China (Figure 2), suggesting that the nitrogenous  
218 species were originated from continental sources in East Asia. The averaged C/N  
219 concentration ratio during whole campaign was  $5.3 \pm 3.4$ . Because the highest C/N ratio was  
220 observed in summer (7.1), particulate carbon may be more emitted to the atmosphere due to  
221 the enhanced marine biological activity in warm season.

### 222 **3.2. Carbon and nitrogen isotopic signatures in aerosols collected from the Okinawa**

223  $\delta^{13}\text{C}$  of TC range from -24.2 to -21.6‰ (av.  $-22.5 \pm 0.62\%$ ) in winter, -23.5 to -21.6‰  
224 ( $-22.5 \pm 0.7\%$ ) in spring, -23.9 to -21.6‰ ( $-22.9 \pm 0.69\%$ ) in summer and -22.9 to -19.5‰ ( $-$   
225  $21.3.7 \pm 0.98\%$ ) in autumn. Although  $\delta^{13}\text{C}$  values are similar in winter, spring and summer,  
226 back trajectories demonstrated the continental outflow in winter and spring (Figure 2). We got  
227 two higher  $\delta^{13}\text{C}$  values (Figure 3a) of -14.6‰ (November 3, 2009) and -18.2‰ (March 16,  
228 2010). We suspect that the high values may be due to the influence of carbonate carbon in  
229 dust. Hence, we exposed these two samples to HCl fumes overnight to remove potential  
230 carbonate carbon. We found that TC and  $\delta^{13}\text{C}$  after HCl treatment changed from 1.50 to 1.39  
231  $\mu\text{g m}^{-3}$  and from -14.6‰ to -16.1‰ for the sample of November 3 and from 7.3  $\mu\text{g m}^{-3}$  to 5.7  
232  $\mu\text{g m}^{-3}$  and from -18.2‰ to -22.1‰ for the sample of March 16. These results demonstrate  
233 that moderate to significant amount of carbonate carbon was present in those samples,  
234 suggesting that atmospheric titration of carbonate was not completed in some dust samples  
235 (Kawamura et al., 2004). Carbonate in Asian dust could contribute to the higher  $\delta^{13}\text{C}$  values

236 (*Kawamura et al., 2004*). *Lopez-Veneroni et al. (2009)* also reported similar value of  $\delta^{13}\text{C}$  in  
237 TC, which is associated with dusts and soil.

238 We found no correlation between TC and  $\delta^{13}\text{C}$  but with increasing TC concentration,  
239 the  $\delta^{13}\text{C}$  value is more stable at  $\approx -22.7\text{‰}$  during winter and spring which is most likely to be  
240 influenced from the coal combustions and biomass burning (Figure 4a). *Mori et al. (1999)*  
241 reported the  $\delta^{13}\text{C}$  of Chinese coal is  $-23.4 \pm 1.2\text{‰}$ . Similarly, *Kawashima and Haneishi (2012)*  
242 reported the  $\delta^{13}\text{C}_{\text{EC}}$  ( $-23.3\text{‰}$ ) for  $\text{PM}_{2.5}$  in Akita Prefecture of Japan, suggesting an influence  
243 from coal burning in China during winter. *Widory et al. (2004)* reported that  $\delta^{13}\text{C}$  value of  
244 coal in Paris ranged from  $-24.4$  to  $-23.4\text{‰}$ . However, the petroleum fuel ( $-26.8$  to  $-23.0\text{‰}$ ,  
245 *Okuda et al., 2002*) is lighter than those of coal and crude oil (*Kawashima and Haneishi, 2012*  
246 and reference therein). In addition, *Mkoma et al. (2014)* reported  $\delta^{13}\text{C}$  value of biomass  
247 burning aerosols dominated by C4 plants during dry ( $-23.9$  to  $-22.4\text{‰}$ ) and wet season ( $-24.4$   
248 to  $-23\text{‰}$ ) for  $\text{PM}_{10}$  from South Africa. The  $\delta^{13}\text{C}$  value during winter and spring is higher than  
249 the biomass burning aerosols ( $-26.9$  to  $-24.9\text{‰}$ ) dominated by C3 plants (*Martinelli et al.,*  
250 *2002*). Due to overlapping between the major pollution sources, it is not easy to specify the  
251 exact sources, for instance, biomass burning from C4 plants, coal combustion and  
252 gasoline/diesel soot. In Japan, coal is not used for heating purpose in winter (*Kawashima et*  
253 *al., 2012*). Therefore, the higher  $\delta^{13}\text{C}$  during winter and spring can be explained by the long  
254 range atmospheric transport of organic aerosols from China, where coal burning is common in  
255 winter for space heating.

256 Plotting of reciprocal of TC concentration versus  $\delta^{13}\text{C}$  data (binary mixing model –e.g.,  
257 *Gorka et al., 2014; Sohn, 2005*) can decipher the identification of carbon sources. The  
258 potential  $\delta^{13}\text{C}$  end member of TC during winter is  $-23.4\text{‰}$  (Figure in S2). The relative  
259 contribution of particles originated from coal burning ( $C_{\text{coal}}$ ) during winter can be estimated  
260 by equation 1 in supporting information (SI). Based on the isotopic mass balance equation,

261 the calculated contribution  $C_{\text{coal}}$  in Okinawa aerosols is 97% during winter. This calculation  
262 suggests a significant contribution of coal combustion over Okinawa via long-range  
263 atmospheric transport. China has the highest rate of coal consumption in the world, generating  
264 more than 75% of its energy from coal (*Chen et al., 2005*). Moreover, black carbon emissions  
265 in China are 1499 Gg, of which 36% are consumed in industry and 55% are consumed for  
266 residential heating.

267 As mentioned above, most of the air parcels come from China during winter and  
268 spring (see Figure S1). Thus, it is also important to compare our data with those from Chinese  
269 cities (*Cao et al., 2011*) and Gosan site (*Jung et al., 2011; Kawamura et al., 2004; Kundu et*  
270 *al., 2010*); especially Gosan is located on the pathway from China to Okinawa (see Figure 1).  
271 The average  $\delta^{13}\text{C}$  value in the northern part of China during winter is -24.4‰ (*Cao et al.,*  
272 *2011*), which is slightly lower (by 1.0‰) than that (-23.4‰) of Gosan aerosols (*Kawamura et*  
273 *al., 2004*). The  $\delta^{13}\text{C}$  value of Gosan aerosols is also lower than wintertime Okinawa aerosols  
274 (-22.5‰), suggesting an enrichment of  $^{13}\text{C}$  by 1.9‰ than that of Chinese aerosols.

275 To confirm the Asian dust contribution to the Okinawa aerosols, we performed  
276 correlation analyses between nss-Ca and TC in spring. We found a strong correlation ( $r^2 =$   
277 0.67) between nss-Ca and TC, suggesting a significant influence from Asian dust in which  
278 nss-Ca is enriched (*Kawamura et al., 2004*). However, we did not obtain any good correlation  
279 ( $r=0.06$ ) between nss-Ca/TC and  $\delta^{13}\text{C}$ , suggesting that most carbonate is titrated by acidic  
280 species (such as  $\text{H}_2\text{SO}_4$ ) in the aerosols during the long-range transport from China to  
281 Okinawa. This result is in contrast to that of Gosan site (*Kawamura et al., 2004*), where  
282 atmospheric titration of carbonate is less significant due to the short distance from the source  
283 regions in China. This may suggest that, during long-range atmospheric transport, organic  
284 aerosols are internally mixed with mineral dust when they pass over the continent, coast and  
285 ocean.

286 To identify the source regions of summer aerosols, we performed air mass back  
287 trajectory analyses for each sample and found that all the samples, except for 4 samples, have  
288 marine influence with some continental influence as seen in Figure 2. We found very narrow  
289 range of  $\delta^{13}\text{C}$  (-21.6 to -23.9‰) in summer. These values are comparable to those (-23.3 to -  
290 20‰) reported for the marine aerosols by *Ceburnis et al. (2011)*. Interestingly, we obtained  
291 lower  $\delta^{13}\text{C}$  value in summer samples, which may be due to potential influence from  
292 Philippines (Figure 2). *Loh et al. (2004)* showed that protein like materials, carbohydrates and  
293 dissolved organic carbon in ocean water ranged from -21.1 to -20.7‰. *Fry and Parker (1987)*  
294 showed larger  $\delta^{13}\text{C}$  values for the marine phytoplankton (-18 to -24‰) and marine macro  
295 algae (-8 to -27‰), suggesting that summertime aerosols are more influenced from  
296 phytoplankton and macro algae in the ocean.

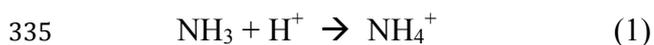
297 In addition, *Xiao et al. (2010)* reported C/N ratios in river phytoplankton with a range  
298 of 4 to 10. Interestingly, summer samples show the similar range (range: 4 to 11.6), which  
299 further supports that marine emission from phytoplankton is an important source of organic  
300 aerosols in summer.

301 The  $\delta^{15}\text{N}$  in Okinawa aerosols ranged from 8.0 to 18.9 ‰ ( $12.2 \pm 2.2\%$ , excluding  
302 outlier), which are slightly smaller than those (6.8 to 26.2‰, av.  $15.1 \pm 3.4\%$ ) from Gosan  
303 aerosols (*Kundu et al., 2010*). The  $\delta^{15}\text{N}$  value ranged from 10.4 to 15.4‰ ( $13.6 \pm 1.7\%$ ) in  
304 winter, 8.3 to 18.9‰ ( $13.3 \pm 0.5\%$ ) in spring, 9.7 to 13.2‰ ( $11.1 \pm 1.2\%$ ) in summer, and 8.0  
305 to 16.1‰ ( $11.9 \pm 2.2\%$ ) in autumn. The average values are similar in winter and spring,  
306 suggesting a similar type of source is likely in winter and spring. Further, the  $\delta^{15}\text{N}$  are similar  
307 during autumn and summer. The average value  $\delta^{15}\text{N}$  of TN for biomass burning aerosols is  
308 23.5‰ (23.5 to 25.7‰) (*Kundu et al., 2010*) whereas it is 15 ‰ in the marine aerosols from  
309 Jeju Island in the East China Sea (*Kundu et al., 2010*).  $\delta^{15}\text{N}$  from Cape Hedo is similar to that  
310 (10.6‰) of aerosol samples from Piracicaba, Brazil (*Martinelli et al., 2002*).

311  $\delta^{15}\text{N}$  derived from the combustion of natural gas and fuel oil ranged from 2.9 to  
312 15.4‰, -19 to 2.9‰, respectively (*Widory, 2007*). Those of diesel oil varied from 3.9 to 5.4‰  
313 whereas that of unleaded gasoline was 4.6‰ (*Widory, 2007*). *Heaton (1990)* reported that  
314  $\delta^{15}\text{N}$  of  $\text{NO}_x$  derived from diesel engines range from -13 to -2‰ whereas those from coal-  
315 fired power stations range from 6 to 13‰. In spite of an increase in the concentration of TN,  
316  $\delta^{15}\text{N}$  value is stable around at ~12.4‰, which is most likely a dominant nitrogen source  
317 during winter and spring (Figure 4b). This value from Okinawa is similar to that reported  
318 from coal-fired power station and combustion of natural gases (*Heaton et al., 1990*). In  
319 addition,  $\delta^{15}\text{N}$  value of our study is similar to those (5.0 to 13.7‰, av.  $9.9 \pm 2.0$ ‰) reported by  
320 *Gorka et al. (2012)* and those (5.3 to 16.1‰,  $10.7 \pm 3.1$ ‰) by *Widory (2007)* for  $\text{PM}_{10}$  aerosol  
321 samples. *Yeatman et al. (2001)* reported lesser  $\delta^{15}\text{N}$  value in coastal region (-20 to 22‰) for  
322  $\text{NH}_4^+$ . In the Okinawa aerosols, there is no correlation between  $\delta^{15}\text{N}$  and TN.

323 Figure 5 shows the relation between  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  with signed level of sources  
324 reported in previous studies. No significant correlation was found between  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ,  
325 suggesting that different sources of aerosol C and N in Okinawa. During winter when  $\delta^{13}\text{C}$   
326 ranged from -24.2 to -21.6‰,  $\delta^{15}\text{N}$  ranged from 10.4 to 15.4‰. During growing season  
327 (spring) when  $\delta^{13}\text{C}$  values ranged from -23.5 to -21.7‰,  $\delta^{15}\text{N}$  ranged from 8.3 to 18.3‰. The  
328  $\delta^{15}\text{N}$  values are higher in spring. The overlapping of data during winter and spring may  
329 suggest emissions from the coal burning for space heating in China, industrial coal-power  
330 plant and biomass burning, which are major sources of nitrogenous species during winter and  
331 spring.

332 As suggested by *Pavuluri et al. (2010)*, the enrichment of  $^{15}\text{N}$  in aerosol is due to the  
333 following two reaction mechanisms between gas and aerosols, leaving larger  $\delta^{15}\text{N}$  values in  
334 the particles:



337 In equation (1), the conversion of gaseous  $\text{NH}_3$  to particle  $\text{NH}_4^+$  occurs under the lower pH  
338 conditions of aerosols. It is meaningful to describe that the measured pH of the water extracts  
339 from Okinawa aerosol samples is on average 5.3, which is lower than that of spring samples  
340 (5.6). Sulfuric acid probably contributed to lower the pH of the atmospheric aerosols.  
341 However, the N budget and possible isotopic reactions/exchanges in the atmosphere are very  
342 complicated (*Widory, 2007; Ciezka et al., 2015*).

### 343 **3.3. Sources of WSOC and ON**

344 We found a strong correlation ( $r=0.88$ ) between TC and TN in spring (Figure 6). We  
345 also found a fairly good correlation ( $r=0.74$ ) between TC and TN in winter. The high OC/EC  
346 ratios throughout four seasons in Okinawa suggest that organic aerosols are secondarily  
347 formed by the oxidation of organic precursors (*Kunwar and Kawamura, 2014a*). To better  
348 understand the variation of  $\delta^{13}\text{C}$  (primary or secondary), we conducted correlation analysis  
349 for WSOC vs  $\delta^{13}\text{C}$  because WSOC is mainly formed by the atmospheric oxidation of  
350 precursor organics. However, we did not find any significant correlation ( $r=0.14$ ) in four  
351 seasons. Levoglucosan, which is an excellent tracer of biomass burning (*Simoneit, 2002; Fu*  
352 *et al., 2011*), did not present any significant correlation with  $\delta^{13}\text{C}$  in all seasons (Table 2). EC  
353 that is a tracer of primary source of incomplete combustion, showed no correlation ( $r=0.01$ )  
354 with  $\delta^{13}\text{C}$  in all seasons. Oxalic acid ( $\text{C}_2$ ), a tracer of SOA, showed no correlation with  $\delta^{13}\text{C}$ ,  
355 suggesting the different sources and formation processes. Further,  $\text{Na}^+$ , a tracer of primary  
356 marine source, showed no correlation with  $\delta^{13}\text{C}$  in all seasons (Table 2); even in summer  
357 when most of the air masses come from the Pacific Ocean.

358 Organic nitrogen (ON) is an important component, but its source and formation  
359 mechanisms are poorly understood although the sources of organic nitrogen are possibly

360 derived from algal blooms and marine bacteria (*Facchini et al., 2008; Muller et al., 2009*),  
361 degraded protein (*Kuznetsova et al., 2005*), livestock/animal husbandry, and biomass burning  
362 (*Mace et al., 2003b*). *Iinuma et al. (2007) and Nojima et al. (1983)* reported that nitrophenols  
363 are originated from biomass burning and vehicular exhaust. Organic nitrogen (ON) showed  
364 higher concentration in winter ( $0.38 \pm 0.24 \mu\text{g m}^{-3}$ ) followed by summer ( $0.35 \pm 0.72 \mu\text{g m}^{-3}$ )  
365 and spring ( $0.28 \pm 0.24 \mu\text{g m}^{-3}$ ) whereas the lowest concentration was obtained in autumn  
366 ( $0.12 \pm 0.05 \mu\text{g m}^{-3}$ ), although the seasonal averages are not statistically significant for winter  
367 and spring ( $t = 1.09$ ,  $p = 0.29$ ), spring and summer ( $t = -0.32$ ,  $p = 0.75$ ), and summer and  
368 autumn ( $t = -1.0$ ,  $p = 0.31$ ). The winter maximum of ON may be associated with influences  
369 from polluted air masses from the Asian continent. We found that concentration of WSON is  
370 lower in winter and higher in summer (*Kunwar and Kawamura, 2014a*).

371 To better understand the sources of ON and WSON in summer, we performed  
372 correlation analysis between ON and  $\text{Na}^+$ ; the latter is a tracer of primary oceanic emission.  
373 However, we did not find any correlation, suggesting that ON and also WSON are not  
374 primarily derived from the ocean, but derived secondarily by the oxidation of organic  
375 precursors emitted from marine biogenic sources. Wang et al. (2010) reported that the  
376 concentration of WSON is 4 times higher in winter ( $22 \mu\text{g m}^{-3}$ ) than in spring ( $5.2 \mu\text{g m}^{-3}$ ) in  
377 Chinese aerosols. However, in our sampling site winter and springtime WSON levels are  
378 almost same, suggesting that there are additional biogenic sources of WSON in spring.

### 379 **3.4. Contribution of $\text{NO}_3^-$ and $\text{NH}_4^+$ to TN**

380 Table 1 shows the seasonal average and concentration range for Okinawa aerosols.  
381 Higher concentrations of  $\text{NO}_3^-$ -N were observed during spring and winter and lower  
382 concentration was observed during summer. Similarly, highest  $\text{NH}_4^+$ -N was observed during  
383 winter. Higher concentrations of  $\text{NO}_3^-$ -N during winter and spring suggest an influence from

384 the vehicular emission. Similarly, higher concentration of  $\text{NH}_4^+$ -N during winter suggests that  
385 biomass burning in East Asia has an impact on the study area.

386 Relations of  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N against to TN are shown in Figure 7. The strong  
387 correlations of TN with  $\text{NO}_3^-$ -N ( $r=0.84$ ) and  $\text{NH}_4^+$ -N ( $0.80$ ) suggest that nitrate and  
388 ammonium are formed from the similar sources and/or source regions. The main nitrogen  
389 species is  $\text{NO}_3^-$ , which contributes about 45% of TN. In contrast,  $\text{NH}_4^+$  contributes only 18%  
390 of TN. Meanwhile, ON accounts for 37% of TN (Figure 8). The higher contribution of  $\text{NO}_3^-$   
391 to TN than  $\text{NH}_4^+$  supports that our sampling site is significantly influenced by vehicular  
392 emissions and biomass burnings in East Asia through a long-range atmospheric transport (*Zhu*  
393 *et al.*, 2015). The highest contribution of  $\text{NO}_3^-$  to TN was found to be 51.3% in spring  
394 followed by winter (37%) and the lowest value was observed in summer (34%). In contrast,  
395 the highest contribution of  $\text{NH}_4^+$  to TN was found in winter (29%) followed by spring (23%)  
396 whereas the lowest value was found in summer (3%). Both  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N show good  
397 correlations with TN ( $r=0.91$  and  $0.89$ , respectively), suggesting that they are originated from  
398 similar sources. However, the lowest contribution of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  to TN in summer may  
399 suggest that organic nitrogen contributes more to TN in summer probably from marine  
400 sources.

401

#### 402 **4. Summary and Conclusions**

403 Stable carbon and nitrogen isotope ratios were determined for aerosol (TSP) samples  
404 from Okinawa, an outflow region of East Asian aerosols. We found similar  $\delta^{13}\text{C}$  values in  
405 winter ( $-22.5\pm 0.62\text{‰}$ ) and spring ( $-22.5\text{‰}\pm 0.71\text{‰}$ ), suggesting that winter- and springtime  
406 aerosols are influenced by continental sources such as coal combustions. During winter,  
407 contribution of coal combustion to aerosol TC is 97%. Very high  $\delta^{13}\text{C}$  ( $-14.6$  to  $-18.2\text{‰}$ ) was  
408 obtained on March 16 and November 3. We found that significant amount of mineral dust

409 (carbonates) is responsible for such a high  $\delta^{13}\text{C}$  for the sample of March 16. In contrast, minor  
410 dust contribution was found for the sample of November 3.  $\delta^{13}\text{C}$  values obtained in the  
411 Okinawa aerosols are higher by ca. 2‰ than those reported from Chinese megacities during  
412 wintertime, suggesting that the photochemical aging of organic aerosols during the long-range  
413 transport. No correlation between nss-Ca/TC and  $\delta^{13}\text{C}$  suggest that carbonates were mostly  
414 disappeared due to the atmospheric titration by acidic species during long-range transport.

415  $\delta^{15}\text{N}$  in winter ( $13.6\pm 1.7\text{‰}$ ) and spring ( $13.3\pm 2.7\text{‰}$ ) showed almost similar values,  
416 suggesting the presence of similar source of nitrogen. The possible dominant source of  $\delta^{15}\text{N}$   
417 ( $\sim 12.4$ ) in winter and spring suggest the mixed biomass and coal burning in home heating and  
418 coal burning in industries (eg. coal fired-power plants) origin. In contrast,  $\delta^{15}\text{N}$  during  
419 summer ( $11.1\pm 1.1\text{‰}$ ) is lower than winter and spring, suggesting that the air quality over  
420 Cape Hedo is influenced by clean oceanic air masses during summer. Contribution of  $\text{NO}_3^-$  to  
421 TN is higher (45%) than that of  $\text{NH}_4^+$  (18%), suggesting that vehicular emission in East Asia  
422 is the most important source of TN in Cape Hedo, Okinawa. Higher concentration of ON in  
423 wintertime is due to the enhanced emission of water insoluble organic nitrogen in cold season  
424 from East Asia.

425

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435

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646 **Figure Captions**

647 Figure 1. Map of Cape Hedo, Okinawa, Japan where one year sampling was performed.

648 Figure 2. Five-day backward trajectories for selected weeks during winter, spring, summer  
649 and autumn. Backward trajectories at 500 m above ground level were drawn with the  
650 NOAA HYSPLIT model.

651 Figure 3. Weekly variations of (a) TC, (b) TN, (c)  $\delta^{13}\text{C}$  and (d)  $\delta^{15}\text{N}$  in ambient aerosols from  
652 Cape Hedo, Okinawa during October 2009 to October 2010. The date in the figure  
653 represents the starting date for each sample.

654 Figure 4a. Relation between TC concentrations and  $\delta^{13}\text{C}$  in TSP samples collected from Cape  
655 Hedo, Okinawa

656 Figure 4b. Relation between TN concentrations and  $\delta^{15}\text{N}$  in TSP samples collected from Cape  
657 Hedo, Okinawa

658 Figure 5. Relation between  $\delta^{13}\text{C}$  versus  $\delta^{15}\text{N}$  with signed level of potential sources in TSP  
659 samples collected from Cape Hedo, Okinawa. Data of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  adopted from (a) Fry  
660 and Parker (1987), (b) Gleason and Kyser (1984), (c) Chesselet et al. (1981), (d) Peng et  
661 al. (2006), (e) Kundu et al. (2010), (f) Heaton (1990), (g) Widory (2007), (h) Mkoma et al.  
662 (2013).

663 Figure 6. Correlation analysis between total nitrogen (TN) and total carbon (TC) in aerosol  
664 samples collected from Cape Hedo, Okinawa.

665 Figure 7. Scatter plots between  $\text{NO}_3^-$ -N or  $\text{NH}_4^+$ -N versus TN in aerosols collected in Cape  
666 Hedo, Okinawa. The points in the bracket represent the outliers. The original data of  
667 nitrate and ammonium are from Kunwar and Kawamura (2014a).

668 Figure 8. Scatter plot between  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N versus TN in ambient aerosols collected  
669 in Cape Hedo, Okinawa. The point in the bracket represents the outliers. The original data  
670 of nitrate and ammonium are from Kunwar and Kawamura (2014a).

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