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

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Abstract

Stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotope ratios were measured for total carbon (TC) and nitrogen (TN), respectively, in aerosol (TSP) samples collected at Cape Hedo, Okinawa, an outflow region of Asian pollutants, during 2009 to 2010. The averaged $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios are -22.2‰ and +12.5‰, respectively. The $\delta^{13}\text{C}$ values are similar in both spring (-22.5‰) and winter (-22.5‰), suggesting the similar sources and/or source regions. We found that $\delta^{13}\text{C}$ from Okinawa aerosols are ca. 2‰ higher than those reported from Chinese megacities probably due to photochemical aging of organic aerosols. A strong correlation ($r=0.81$) was found between nss-Ca and TSP, suggesting that springtime aerosols are influenced from Asian dusts. However, carbonates in the Asian dusts were titrated with acidic species such as sulfuric acid and oxalic acid during atmospheric transport although two samples suggested the presence of remaining carbonate. No correlations were found between $\delta^{13}\text{C}$ and tracer compounds (levoglucosan, elemental carbon, oxalic acid, and Na^+). During winter and spring, coal burning is significant source in China. Based on isotopic mass balance, contribution of coal burning origin particles to total carbon aerosol was estimated as ca. 97% in winter, which is probably associated with the high emissions in China. Contribution of NO_3^- to TN was on average 45% whereas that of NH_4^+ was 18%. These results suggest that vehicular exhaust is an important source of TN in Okinawa aerosols. Concentration of water-soluble organic nitrogen (WSON) is higher in summer, suggesting that WSON is more emitted from the ocean in warmer season whereas inorganic nitrogen is more emitted in winter and spring from pollution sources in the Asian continent.

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

1. Introduction

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

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

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

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

Oxidation products of VOC have lower vapour pressure than the precursor VOC and can partition into the particle phase, forming SOA (*Hallquist et al., 2009*). Organic compounds that are present in particulate matter can be scavenged from the atmosphere by dry and wet deposition. During deposition process of particles, isotope fractionation does not occur. However, reactions within the particles can change the isotope ratios. Although these reactions are not fully understood, it is known that if photochemical degradation of oxalic acid catalysed by iron species is significant, the isotope ratios of remaining oxalic acid become higher due to KIE effects (*Pavuluri et al., 2012*). If oxalic acid were the major component of organic aerosol, $\delta^{13}\text{C}$ of aerosol TC should become higher during long range atmospheric transport. Organic compounds produced by the oxidation processes show smaller isotope ratios (*Fisseha et al., 2009*) while the remaining precursors are enriched with heavier isotopes (*Anderson et al., 2004*). $\delta^{13}\text{C}$ of aerosols can also be used to distinguish the contribution of C_3 versus C_4 vegetation type (*Martinelli et al., 2002*).

Nitrogen (N_2) in the atmosphere can be converted into NO_3^- and NH_4^+ via nitrification or denitrification process (*Hem, 1985; Raven et al., 1992*). Volatile organic nitrogen is

released to the atmosphere during the plant and animal decay. Fossil fuel combustion and industrial emission contribute gaseous NO_x and nitrate, which can travel long distances. The use of $\delta^{15}\text{N}$ can decipher the origin, cycling of organic and inorganic nitrogen as well as atmospheric processing of nitrogen species (Cornell *et al.*, 1995; Yeatman *et al.*, 2001, Kelly *et al.*, 2005). The importance of $\delta^{15}\text{N}$ in the atmosphere is well documented in many literatures (e.g., Kundu *et al.*, 2010). In the atmosphere there are naturally occurring two stable isotopes of ^{14}N and ^{15}N . ^{14}N is most common and its abundance in N_2 gas is 99.63% (Mariotti, 1983). With regard to reaction kinetics, two nitrogen isotopes show different behaviors. Thus, depending upon the nature of formation processes and their precursors, isotopic composition of particular nitrogen species will be different (Pavuluri *et al.*, 2011).

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

2. Experimental

2.1 Site Description and Aerosol Sampling

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

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

Aerosol (TSP) samples (n=50) were collected on a weekly basis using a pre-combusted quartz fiber filter and high-volume air sampler (*Kunwar and Kawamura, 2014a, 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 9500 m^3 . Filter samples were placed in a preheated glass jar with a Teflon-lined screw cap, shipped from Cape Hedo to Sapporo and stored in a freezer room at -20°C until analysis. The sampling period for each sample is 7 days. Quartz fiber filter may adsorb organic vapor, causing positive artifacts on the measurements. However, due to relatively long sampling period (one week), we consider that artifacts were minimal.

2.2. Measurements of TC and TN, and their Stable Isotopes

To measure total carbon (TC) and nitrogen (TN), we combusted a small filter disc (3.14 cm^2) placed in a tin cup at 1400°C using elemental analyzer (EA) (Carlo Ebra, EA 1500). All the nitrogen species are converted to NO and further reduced to N_2 in a reduction column. Carbonaceous species are oxidized to carbon dioxide (CO_2). N_2 and CO_2 are separated on a packed column of gas chromatograph installed in EA and measured with a thermal conductivity detector (*Pavuluri et al 2010; Kawamura et al., 2004*). Portions of CO_2 and N_2 gases were transferred to EA/isotope ratio mass spectrometer (irMS) via an interface

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

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

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

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

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

NO_3^- and NH_4^+ are the major ions detected in our samples.

2.3. Measurements of WSOC, WSTN, and Major Inorganic Ions

Concentrations of water-soluble organic carbon (WSOC) and water-soluble total nitrogen (WSTN) were measured using a total carbon and nitrogen analyzer (Shimadzu TOC-V_{CSH}). Cation (NH_4^+) and anion (NO_3^-) was measured using ion chromatograph (IC) (761 Compact IC, Metrohm, Switzerland), as reported in *Kunwar and Kawamura (2014a)*. The analytical errors in duplicate analysis of the authentic standards were within 5%. We also measured organic carbon (OC)/elemental carbon (EC) using a Sunset Laboratory carbon analyzer (*Kunwar and Kawamura, 2014a*).

2.4. Backward Air Mass Trajectory Analysis

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

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

3. Results and Discussion

3.1. Seasonal variations of TC, TN

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

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

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

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

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

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

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

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

$\delta^{13}\text{C}$ of TC range from -24.2 to -21.6‰ (av. $-22.5 \pm 0.62\text{‰}$) in winter, -23.5 to -21.6‰ ($-22.5 \pm 0.7\text{‰}$) in spring, -23.9 to -21.6‰ ($-22.9 \pm 0.69\text{‰}$) in summer and -22.9 to -19.5‰ ($-21.37 \pm 0.98\text{‰}$) in autumn. Although $\delta^{13}\text{C}$ values are similar in winter, spring and summer, back trajectories demonstrated the continental outflow in winter and spring (Figure 2). We got two higher $\delta^{13}\text{C}$ values (Figure 3a) of -14.6‰ (November 3, 2009) and -18.2‰ (March 16, 2010). We suspect that the high values may be due to the influence of carbonate carbon in dust. Hence, we exposed these two samples to HCl fumes overnight to remove potential carbonate carbon. We found that TC and $\delta^{13}\text{C}$ after HCl treatment changed from 1.50 to $1.39 \mu\text{g m}^{-3}$ and from -14.6‰ to -16.1‰ for the sample of November 3 and from $7.3 \mu\text{g m}^{-3}$ to $5.7 \mu\text{g m}^{-3}$ and from -18.2‰ to -22.1‰ for the sample of March 16. These results demonstrate that moderate to significant amount of carbonate carbon was present in those samples, suggesting that atmospheric titration of carbonate was not completed in some dust samples (Kawamura et al., 2004). Carbonate in Asian dust could contribute to the higher $\delta^{13}\text{C}$ values

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

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

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

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

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

To confirm the Asian dust contribution to the Okinawa aerosols, we performed correlation analyses between nss-Ca and TC in spring. We found a strong correlation ($r^2 = 0.67$) between nss-Ca and TC, suggesting a significant influence from Asian dust in which nss-Ca is enriched (*Kawamura et al., 2004*). However, we did not obtain any good correlation ($r=0.06$) between nss-Ca/TC and $\delta^{13}\text{C}$, suggesting that most carbonate is titrated by acidic species (such as H_2SO_4) in the aerosols during the long-range transport from China to Okinawa. This result is in contrast to that of Gosan site (*Kawamura et al., 2004*), where atmospheric titration of carbonate is less significant due to the short distance from the source regions in China. This may suggest that, during long-range atmospheric transport, organic aerosols are internally mixed with mineral dust when they pass over the continent, coast and ocean.

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

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

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

$\delta^{15}\text{N}$ derived from the combustion of natural gas and fuel oil ranged from 2.9 to 15.4‰, -19 to 2.9‰, respectively (*Widory, 2007*). Those of diesel oil varied from 3.9 to 5.4‰ whereas that of unleaded gasoline was 4.6‰ (*Widory, 2007*). *Heaton (1990)* reported that $\delta^{15}\text{N}$ of NO_x derived from diesel engines range from -13 to -2‰ whereas those from coal-fired power stations range from 6 to 13‰. In spite of an increase in the concentration of TN, $\delta^{15}\text{N}$ value is stable around at ~12.4‰, which is most likely a dominant nitrogen source during winter and spring (Figure 4b). This value from Okinawa is similar to that reported from coal-fired power station and combustion of natural gases (*Heaton et al., 1990*). In addition, $\delta^{15}\text{N}$ value of our study is similar to those (5.0 to 13.7‰, av. 9.9 ± 2.0 ‰) reported by *Gorka et al. (2012)* and those (5.3 to 16.1‰, 10.7 ± 3.1 ‰) by *Widory (2007)* for PM_{10} aerosol samples. *Yeatman et al. (2001)* reported lesser $\delta^{15}\text{N}$ value in coastal region (-20 to 22‰) for NH_4^+ . In the Okinawa aerosols, there is no correlation between $\delta^{15}\text{N}$ and TN.

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

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



In equation (1), the conversion of gaseous NH_3 to particle NH_4^+ occurs under the lower pH conditions of aerosols. It is meaningful to describe that the measured pH of the water extracts from Okinawa aerosol samples is on average 5.3, which is lower than that of spring samples (5.6). Sulfuric acid probably contributed to lower the pH of the atmospheric aerosols. However, the N budget and possible isotopic reactions/exchanges in the atmosphere are very complicated (*Widory, 2007; Ciezka et al., 2015*).

3.3. Sources of WSOC and ON

We found a strong correlation ($r=0.88$) between TC and TN in spring (Figure 6). We also found a fairly good correlation ($r=0.74$) between TC and TN in winter. The high OC/EC ratios throughout four seasons in Okinawa suggest that organic aerosols are secondarily formed by the oxidation of organic precursors (*Kunwar and Kawamura, 2014a*). To better understand the variation of $\delta^{13}\text{C}$ (primary or secondary), we conducted correlation analysis for WSOC vs $\delta^{13}\text{C}$ because WSOC is mainly formed by the atmospheric oxidation of precursor organics. However, we did not find any significant correlation ($r=0.14$) in four seasons. Levoglucosan, which is an excellent tracer of biomass burning (*Simoneit, 2002; Fu et al., 2011*), did not present any significant correlation with $\delta^{13}\text{C}$ in all seasons (Table 2). EC that is a tracer of primary source of incomplete combustion, showed no correlation ($r=0.01$) with $\delta^{13}\text{C}$ in all seasons. Oxalic acid (C_2), a tracer of SOA, showed no correlation with $\delta^{13}\text{C}$, suggesting the different sources and formation processes. Further, Na^+ , a tracer of primary marine source, showed no correlation with $\delta^{13}\text{C}$ in all seasons (Table 2); even in summer when most of the air masses come from the Pacific Ocean.

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

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

To better understand the sources of ON and WSON in summer, we performed correlation analysis between ON and Na^+ ; the latter is a tracer of primary oceanic emission. However, we did not find any correlation, suggesting that ON and also WSON are not primarily derived from the ocean, but derived secondarily by the oxidation of organic precursors emitted from marine biogenic sources. Wang *et al.* (2010) reported that the 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 Chinese aerosols. However, in our sampling site winter and springtime WSON levels are almost same, suggesting that there are additional biogenic sources of WSON in spring.

3.4. Contribution of NO_3^- and NH_4^+ to TN

Table 1 shows the seasonal average and concentration range for Okinawa aerosols. Higher concentrations of NO_3^- -N were observed during spring and winter and lower concentration was observed during summer. Similarly, highest NH_4^+ -N was observed during winter. Higher concentrations of NO_3^- -N during winter and spring suggest an influence from

the vehicular emission. Similarly, higher concentration of NH_4^+ -N during winter suggests that biomass burning in East Asia has an impact on the study area.

Relations of NO_3^- -N and NH_4^+ -N against to TN are shown in Figure 7. The strong correlations of TN with NO_3^- -N ($r=0.84$) and NH_4^+ -N (0.80) suggest that nitrate and ammonium are formed from the similar sources and/or source regions. The main nitrogen species is NO_3^- , which contributes about 45% of TN. In contrast, NH_4^+ contributes only 18% of TN. Meanwhile, ON accounts for 37% of TN (Figure 8). The higher contribution of NO_3^- to TN than NH_4^+ supports that our sampling site is significantly influenced by vehicular emissions and biomass burnings in East Asia through a long-range atmospheric transport (Zhu *et al.*, 2015). The highest contribution of NO_3^- to TN was found to be 51.3% in spring followed by winter (37%) and the lowest value was observed in summer (34%). In contrast, the highest contribution of NH_4^+ to TN was found in winter (29%) followed by spring (23%) whereas the lowest value was found in summer (3%). Both NO_3^- -N and NH_4^+ -N show good correlations with TN ($r=0.91$ and 0.89 , respectively), suggesting that they are originated from similar sources. However, the lowest contribution of NO_3^- and NH_4^+ to TN in summer may suggest that organic nitrogen contributes more to TN in summer probably from marine sources.

4. Summary and Conclusions

Stable carbon and nitrogen isotope ratios were determined for aerosol (TSP) samples from Okinawa, an outflow region of East Asian aerosols. We found similar $\delta^{13}\text{C}$ values in winter ($-22.5\pm0.62\text{‰}$) and spring ($-22.5\text{‰}\pm0.71\text{‰}$), suggesting that winter- and springtime aerosols are influenced by continental sources such as coal combustions. During winter, contribution of coal combustion to aerosol TC is 97%. Very high $\delta^{13}\text{C}$ (-14.6 to -18.2‰) was obtained on March 16 and November 3. We found that significant amount of mineral dust

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

$\delta^{15}\text{N}$ in winter ($13.6 \pm 1.7\text{‰}$) and spring ($13.3 \pm 2.7\text{‰}$) showed almost similar values, suggesting the presence of similar source of nitrogen. The possible dominant source of $\delta^{15}\text{N}$ (~ 12.4) in winter and spring suggest the mixed biomass and coal burning in home heating and coal burning in industries (eg. coal fired-power plants) origin. In contrast, $\delta^{15}\text{N}$ during summer ($11.1 \pm 1.1\text{‰}$) is lower than winter and spring, suggesting that the air quality over Cape Hedo is influenced by clean oceanic air masses during summer. Contribution of NO_3^- to TN is higher (45%) than that of NH_4^+ (18%), suggesting that vehicular emission in East Asia is the most important source of TN in Cape Hedo, Okinawa. Higher concentration of ON in wintertime is due to the enhanced emission of water insoluble organic nitrogen in cold season from East Asia.

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Figure Captions

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

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

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

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

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

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

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

Figure 7. Scatter plots between NO_3^- -N or NH_4^+ -N versus TN in aerosols collected in Cape Hedo, Okinawa. The points in the bracket represent the outliers. The original data of nitrate and ammonium are from Kunwar and Kawamura (2014a).

Figure 8. Scatter plot between NO_3^- -N and NH_4^+ -N versus TN in ambient aerosols collected in Cape Hedo, Okinawa. The point in the bracket represents the outliers. The original data of nitrate and ammonium are from Kunwar and Kawamura (2014a).