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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HIGHLIGHTS
- Seasonal variations of δ13C in atmospheric aerosols are captured.
- δ13C can be used as a good tracer to study the pollution sources.
- δ13C can distinguish between primary and secondary sources of pollution.
- Isotopic enrichment occurs during a long-range transport of pollution outflow.

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ABSTRACT
This study explores the usefulness of stable isotopic composition (δ13C) along with other chemical tracers and air mass trajectory to identify the primary and secondary sources of carbonaceous aerosols. Aerosol samples (n = 84) were collected continuously from April 2003 to April 2004 at Gosan site in Jeju Island, South Korea. The concentrations of total carbon (TC), HCl fumed carbonate-free total carbon (fumed-TC) and their δ13C were measured online using elemental analyzer interfaced to isotope ratio mass spectrometer (EA-IRMS). Similar concentrations of TC and fumed-TC and their similar δ13C values suggest the insignificant contribution of inorganic carbon to Gosan aerosols. The monthly averaged δ13C showed the lowest in April/May (−24.2 to −24.4‰), which is related with the highest concentrations of oxalic acid (a secondary tracer). The result indicates an enhanced contribution of TC from secondary sources. The monthly averaged δ13C in July/August (−23.0 to −22.5‰) were similar to those in January/February (−23.1‰ to −22.7‰). However, chemical tracers and air mass transport pattern suggest that the pollution source regions in January/February are completely different from those in July/August. Higher δ13C values in July/August are aligned with higher concentration ratios of marine tracers (azelaic acid/TC and methanesulfonate/TC), suggesting an enhanced contribution of marine organic matter to the aerosol loading. Higher δ13C values in January/February are associated with higher concentrations of phthalic acid and K+ /TC, indicating more contributions of carbonaceous aerosols from fossil fuel and C4-plant biomass combustion. This study demonstrates that δ13C, along with other chemical tracers and air mass trajectory, can be used as a tracer to understand the importance of primary versus secondary pollution sources of carbonaceous aerosols in the atmosphere.

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

The $\delta^{13}C$ of total carbon ($\delta^{13}C_{TC}$) has been successfully used to identify and apportion the pollution sources in different parts of the world (Agnihotri et al., 2011; Cachier et al., 1985; Cao et al., 2011; Chesselet et al., 1981; Jung and Kawamura, 2011; Kawamura et al., 2004; Kirillova et al., 2013; Kundu et al., 2010a; Martinelli et al., 2002; Miyazaki et al., 2010; Narukawa et al., 2008; Turekian et al., 2003; Widory et al., 2004). All of these studies used the $\delta^{13}C_{TC}$ for understanding the primary pollution sources of carbonaceous aerosols. Secondary organic aerosols, generated in the atmosphere, can account for more than 50% of atmospheric aerosols (Cabada et al., 2004). It is therefore important to understand whether $\delta^{13}C_{TC}$ can be used to understand the primary versus secondary pollution sources of carbonaceous aerosols in the atmosphere.

Although there are some differences in the $\delta^{13}C_{TC}$ in aerosols emitted from various pollution sources, the $\delta^{13}C_{TC}$ values of particles significantly overlap among the pollution sources. The $\delta^{13}C_{TC}$ values of coal combustion−particles are $-24.4$ to $-23.4\%_{w}$, which are similar to those of gasoline combustion-derived particles ($-24.3 \pm 0.6\%_{w}$) (Widory et al., 2004). The $\delta^{13}C_{TC}$ values of particles derived from the combustion of diesel and fuel oil are $-26 \pm 0.5\%_{w}$, which are different than those of particles from the combustion of coal and gasoline. However, the $\delta^{13}C_{TC}$ values of fossil fuel combustion-derived particles fall in the range of $-20$ to $-37\%_{w}$, which are $\delta^{13}C_{TC}$ values of particles emitted from $C_{3}$ plants (Das et al., 2010; Jung and Kawamura, 2011; Kohn, 2010; Turekian et al., 1998). The $\delta^{13}C_{TC}$ values of biogenic- and anthropogenic−secondary organic aerosols (SOA) also overlap the $\delta^{13}C_{TC}$ of particles from $C_{3}$ plant. For example, the $\delta^{13}C_{TC}$ of β-pinene ozonolysis-SOA has been reported to be $29.6 \pm 0.2\%_{w}$ whereas the $\delta^{13}C_{TC}$ of toluene irradiation-SOA has been reported to be $32.5 \pm 0.3\%_{w}$ (Fisseha et al., 2009; Irie et al., 2009, 2011). The $\delta^{13}C_{TC}$ values of $C_{4}$ plants-derived particles are $8$ to $18\%_{w}$ (Das et al., 2010; Turekian et al., 1998) whereas those of marine-derived particles are $20$ to $22\%_{w}$ (Chesselet et al., 1981; Fontugne and Duplessy, 1978; Fry et al., 1998). Due to the overlapping between the major pollution sources, it is not straightforward to delineate among the pollution sources using only the $\delta^{13}C_{TC}$. Some previous studies used $\delta^{13}C_{TC}$ values along with the air mass transport patterns (e.g., Cachier et al., 1985). The $\delta^{13}C$ along with air mass transport patterns and chemical tracers are likely to provide better information about the pollution sources.

Here we present the seasonal variations of $\delta^{13}C_{TC}$ in aerosol samples collected from Gosan site at Jeju Island, South Korea. Then, we interpret the observed isotopic composition and its seasonal variations based on the chemical tracers (oxalic acid, phthalic acid, azelaic acid, methanesulfonate and K') and air mass transport pattern to understand the importance of both the secondary and primary sources of carbonaceous aerosols. The chemical tracers used in this study have been adopted from the previous studies (Kundu et al., 2010d).

2. Experiment

2.1. Site description

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

2.2. Aerosol sampling

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

2.3. Chemical analysis

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

$$\delta^{13}C_{(s)} = \left( \frac{^{13}C/^{12}C}_{\text{sample}} - 1 \right) \times 1000$$

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

Dicarboxylic acids, including oxalic, phthalic and azelaic acids were determined using GC-FID (GC, Agilent 6890) and GC/MS (Thermoquest, Trace MS) (Kawamura et al., 2010; Kundu et al., 2010d). Methanesulfonate (MSA, a secondary marine tracer), K+ (a biomass-burning tracer) were measured using a Metrohm 761 ion chromatography (IC) system (Kundu et al., 2010d). The data of dicarboxylic acids, MSA and K+ are reported elsewhere (Kundu et al., 2010d).

3. Results and discussion

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

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

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

Table 1

<table>
<thead>
<tr>
<th>Date</th>
<th>Number of samples</th>
<th>δ13C (%)</th>
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<tbody>
<tr>
<td>TC</td>
<td>Fumed-TC</td>
<td></td>
</tr>
<tr>
<td>Januaryd</td>
<td>8</td>
<td>-22.7</td>
</tr>
<tr>
<td>February</td>
<td>8</td>
<td>-23.1</td>
</tr>
<tr>
<td>March</td>
<td>10</td>
<td>-22.8</td>
</tr>
<tr>
<td>April</td>
<td>17</td>
<td>-24.2</td>
</tr>
<tr>
<td>May</td>
<td>11</td>
<td>-24.4</td>
</tr>
<tr>
<td>June</td>
<td>7</td>
<td>-23.8</td>
</tr>
<tr>
<td>Julyc</td>
<td>1</td>
<td>-23.0</td>
</tr>
<tr>
<td>August</td>
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<td>-22.5</td>
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<td>2</td>
<td>-23.2</td>
</tr>
<tr>
<td>November</td>
<td>6</td>
<td>-24.2</td>
</tr>
<tr>
<td>December</td>
<td>8</td>
<td>-23.4</td>
</tr>
</tbody>
</table>

a TC stands for total carbon.

b Fumed-TC is the remaining carbon on the filter after removal of inorganic carbon by HCl.

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

d Date Number of samples

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

3.2. Seasonality of δ13C for TC and fumed-TC

The monthly averaged δ13C values ranged between -24.4‰ and -22.5‰ with the lowest value in May and the highest value in August (Fig. 3a). The δ13C values in July/August (-23.0 to -22.5‰) were similar to those in the colder months (October: -23.2‰, December: -23.4‰, January: -22.7‰ and February: -23.1‰). A similar trend with δ13C values of -24.4‰ to -22.4‰ was observed for fumed-TC. No significant difference in the δ13C values was found before and after the HCl-fume treatment of filter. The result suggests that carbonate such as CaCO3 from dusts was not present and/or it was reacted with H2SO4 in the atmosphere during a long-range transport from the source regions. This is in contrast to the situation of 2001 and 2002 spring, when carbonate was suggested to remain in the aerosols as the δ13C values of fumed-TC were lower than the δ13C values of TC particularly in the spring (Kawamura et al., 2004).

The lower δ13C values in April/May are involved with the higher concentrations of oxalic acid (Fig. 3b). It is well established that oxalic acid is predominantly generated in the 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 $\delta^{13}C$ with oxalic acid peak may suggest an increased contribution of secondary organic aerosols to carbonaceous aerosols at Gosan site. The $\delta^{13}C$ values in April/May at Gosan site are 5.5–8.4‰ higher than those observed in SOA from the ozonolysis of $\beta$-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 $\delta^{13}C$ values, and (b) enrichment of $^{13}C$ by the isotopic fractionation due to the chemical aging 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 $\delta^{13}C$. Higher $\delta^{13}C$ 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 $\delta^{13}C$ 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 associated with the burning crop residue by the end of harvest period and air mass transport from polluted East China Sea and Yellow Sea.
The $\delta^{13}$C values in colder months are similar to those in July/August (Fig. 3). However, the trajectory analysis shows that pollution sources in the colder months are different than the pollution sources in July/August at Gosan site (Fig. 1). The higher $\delta^{13}$C values in the colder months are linked with the higher concentrations of phthalic acid (Fig. 3c). Phthalic acid is either generated in the atmosphere by the oxidation of aromatic hydrocarbons emitted from fossil fuel combustion or emitted primarily from fossil fuel combustion (Fraser et al., 2003; Kawamura and Kaplan, 1987). Thus the higher $\delta^{13}$C values in cold seasons can be interpreted by an enhanced contribution from coal and gasoline burning. Particles produced by the combustion of coal and gasoline are generally more enriched in $^{13}$C than other sources such as diesel and fuel oil, SOA and C$_3$-plant derived particles (Fig. 5a). Large quantities of coal are burned for residential heating in north China during November to March (Cao et al., 2011). Air mass transport patterns also suggest that most of the air masses in cold seasons are transported to Gosan site from northeast China (Fig. 1).

Higher $\delta^{13}$C values in the cold seasons are also associated with higher concentration ratio of K$^+$/TC (Fig. 4c), suggesting an enhanced contribution from biomass burning of C$_4$ plants such as wheat, rice and corn straws. Biomass combustion has been legally prohibited in urban areas of China since 1998 (Cao et al., 2011). China has large rural population living in the village and straws are not a high-demand fuel. Hence during and after the harvest season, farmers often burn crop straws in the field as a convenient and inexpensive way to dispose agricultural waste to advance crop rotation (Yang et al., 2008; Wang et al., 2009; Fu et al., 2012). In addition, straws are also used for domestic heating during cold seasons and for cooking fuels in the rural areas throughout the year.

Fig. 5. Alignment of $\delta^{13}$C in Gosan atmospheric aerosols (middle panel) with the $\delta^{13}$C in major source aerosols (upper panel) and in source region aerosols (lower panel). Data of source regions are adopted from aCao et al. (2011) and bMiyazaki et al. (2010). Data of the sources are adopted from cWidory et al. (2004); dTurekian et al. (2003); eDas et al. (2010); fJung et al. (2011); gFisseha et al. (2009); hIrei et al. (2006); and hIrei et al. (2011).
3.3. Identification of the source regions using δ13C of total carbon (TC)

The comparison of δ13C in aerosols between source regions and receptor site will provide important information about the sources and source regions. This approach may also present information on potential isotopic fractionation due to the evolution of organic aerosols as a result of chemical and physical processes. The major pollution sources at Gosan site are east China, Korea and Japan in spring, the East China Sea/ Yellow Sea in summer, and northeastern China in fall and winter (Fig. 1). Fig. 5bc compare the δ13C in aerosols between Gosan site and source regions suggested by air mass trajectory analysis.

The δ13C of atmospheric aerosols in spring in China are not available in the literature. It can be assumed that the δ13C in spring will have similar values of summer aerosols as a result of higher contributions of SOA. The average δ13C in summer aerosols collected in 2003 was reported to be −26.4±0.9‰ in north China and −29.9±1.0‰ in south China (Cao et al., 2011). The average δ13C in spring aerosols at Gosan is −24.1±0.9‰ which is about 2‰ higher than the δ13C in summer aerosols in China (Fig. 5bc). Similarly, the average δ13C in winter aerosols at Gosan site is 1.5‰ higher than those found in north China atmospheric aerosols collected in 2003 winter (Fig. 5bc). Higher δ13C at Gosan than the source regions may be explained by 13C enrichment during the long-range transport by physical/chemical evolution of organic aerosols and/or mixture of various air masses from China having different δ13C signatures. The average δ13C in summer aerosols at Gosan is −3‰ higher than those observed in summer aerosols in north and south China (Fig. 5bc), further confirming the marine contributions to carbonaceous aerosol. The δ13C of marine aerosols collected during the season of higher biological activity (HBA) has been reported to be higher than those of marine aerosols collected during lower biological activity (LBA) in the western Pacific Ocean (Miyazaki et al., 2010). The δ13C has also been observed to increase in the continental aerosols when air masses were transported from the oceans (Cachier et al., 1996; Narukawa et al., 2008; Cao et al., 2013).

4. Conclusions

We found that total carbon (TC) in atmospheric aerosols collected from Golan site, Jeju Island is mainly composed of organic carbon and elemental carbon with negligible amount of inorganic carbon. Inorganic carbon was insignificant even in spring when Asian dusts emitted from arid regions in China and Mongolia are often transported over the sampling site, indicating that Asian dusts may have been titrated by acids such as sulfuric acid in aerosols during a long-range atmospheric transport. Significant seasonal variations of the δ13C of both TC and fumed-TC were found in Golan aerosols with larger values in July/August and January/February and smaller values in April/May. Seasonal variations were interpreted by the differences in pollution sources, source regions and secondary formation of organic aerosols in the atmosphere. Since the δ13C values of TC are overlapping between the pollution sources in the atmosphere, it is risky to solely depend on δ13C to identify the pollution sources. The overlapping issue was dealt in this study with the considerations of the air mass transport patterns and secondary chemical tracers including oxalic, azelaic, and phthalic acids, methanesulfonate and K⁺. This study demonstrates that δ13C along with chemical tracers and air mass trajectory, can be used as a tracer to understand the importance of primary versus secondary sources of carbonaceous pollution. This study also shows the possible isotopic enrichment of TC in aerosols by 1.5–3‰ during a long-range transport of atmospheric aerosols from the source regions to Gosan site.

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