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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Abstract

This study explores the usefulness of stable isotopic composition ($\delta^{13}C$) 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 $\delta^{13}C$ were measured online using elemental analyzer interfaced to isotope ratio mass spectrometer (EA-IRMS). Similar concentrations of TC and fumed-TC and their similar $\delta^{13}C$ values suggest the insignificant contribution of inorganic carbon to Gosan aerosols. The monthly averaged $\delta^{13}C_{TC}$ 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 $\delta^{13}C_{TC}$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 C_4-plant biomass combustion. This study demonstrates that $\delta^{13}C_{TC}$, 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.

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

1. Introduction

Atmospheric particular 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 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‰, which are similar to those of gasoline combustion-derived particles (-24.3 ± 0.6‰) (Widory et al., 2004). The $\delta^{13}C_{TC}$ values of particles derived from the combustion of diesel and fuel oil are -26 ± 0.5‰, 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‰, 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 ± 0.2‰ whereas the $\delta^{13}C_{TC}$ of toluene irradiation-SOA has been reported to be -32.5 ± 0.3‰ (Fisseha et al., 2009; Irei et al., 2006; Irei et al., 2011). The $\delta^{13}C_{TC}$ values of C_4 plants-derived particles are -8 to -18‰ (Das et al., 2010; Turekian et al., 1998) whereas those of marine-derived particles are -20 to -22‰ (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 hours) 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 cm^2) 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 CO_2 was isolated on a gas chromatograph (GC) installed within EA and then measured with a thermal conductivity detector. Aliquots of CO_2 gas were then introduced online into an isotope ratio mass spectrometer (ThermoQuest, Delta Plus) through a ConFlo II interface (ThermoQuest) to monitor $^{13}C/^{12}C$ ratios. The carbon isotopic composition was calculated using the following standard isotopic conversion equation.

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

Another aliquot of filter samples was analyzed for TC and $^{13}C/^{12}C$ ratios after the HCl-fume treatment to remove carbonate carbon (e.g., $CaCO_3$) (Kawamura et al., 2004). The TC concentration in the field blank sample was 0.7-6% of aerosol TC concentrations and the $\delta^{13}C$ 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 46.5-92.4% (average 64.8%) whereas the contributions of EC to TC ranged from 7.6-30.1% (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 6980) 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).

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

The monthly averaged $\delta^{13}C_{TC}$ ranged between -24.4‰ to -22.5‰ with the lowest value in May and the highest value in August (Fig. 3a). The $\delta^{13}C$ 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 $\delta^{13}C$ values of -24.4‰ to -22.4‰ was observed for fumed-TC. No significant difference in the $\delta^{13}C$ values was found before and after the HCl-fume treatment of filter. The result suggests that carbonate such as $CaCO_3$ from dusts was not present and/or it was reacted with H_2SO_4 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 carbon was suggested to remain in the aerosols as the $\delta^{13}C$ values of fumed-TC were lower than the $\delta^{13}C$ values of TC particularly in the spring (Kawamura et al., 2004).

The lower $\delta^{13}C$ 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,

196 2003; Kawamura and Yasui, 2005; Kundu et al., 2010b; Myriokefalitakis et al., 2011). The
197 relation of lowest $\delta^{13}C$ with oxalic acid peak may suggest an increased contribution of
198 secondary organic aerosols to carbonaceous aerosols at Gosan site.

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

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

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

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

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

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

The comparison of $\delta^{13}C_{TC}$ 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). Figs. 5b,c compare the $\delta^{13}C_{TC}$ in aerosols between Gosan site and source regions suggested by air mass trajectory analysis.

The $\delta^{13}C_{TC}$ of atmospheric aerosols in spring in China are not available in the literature. It can be assumed that the $\delta^{13}C_{TC}$ in spring will have similar values of summer aerosols as a result of higher contributions of SOA. The average $\delta^{13}C_{TC}$ in summer aerosols collected in 2003 was reported to be -26.4‰ in north China and -25.9‰ in south China (Cao et al., 2011). The average $\delta^{13}C_{TC}$ in spring aerosols at Gosan is -24.1‰, which is about 2‰ higher than the $\delta^{13}C_{TC}$ in summer aerosols in China (Figs. 5b,c). Similarly, the average $\delta^{13}C_{TC}$ in winter aerosols at Gosan site is 1.5‰ higher than those found in north China atmospheric aerosols collected in 2003 winter (Figs. 5b,c). Higher $\delta^{13}C_{TC}$ at Gosan than the source regions may be explained by ^{13}C enrichment during the long-range transport by physical/chemical evolution of organic aerosols and/or mixture of various air masses from China having different $\delta^{13}C$ signatures. The average $\delta^{13}C_{TC}$ in summer aerosols at Gosan is >3‰ higher than those observed in summer aerosols in north and south China (Figs. 5b,c), further confirming the marine contributions to carbonaceous aerosol. The $\delta^{13}C_{TC}$ 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 $\delta^{13}C_{TC}$ 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 $\delta^{13}C$ of both TC and fumed-TC were found in Gosan 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 $\delta^{13}C$ values of TC are overlapping between the pollution sources in the atmosphere, it is risky to solely depend on $\delta^{13}C$ 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 $\delta^{13}C_{TC}$, 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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Table 1. Monthly averaged stable carbon isotope ratios of bulk carbon in atmospheric aerosol samples collected from Gosan site, Jeju Island.

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

[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.

Figure Captions:

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

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.

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

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

Fig. 5. Alignment of $\delta^{13}C_{TC}$ in Gosan atmospheric aerosols (middle panel) with the $\delta^{13}C_{TC}$ in major source aerosols (upper panel) and in source region aerosols (lower panel). Data of source regions are adopted from [a]Cao et al., 2011 and [b]Miyazaki et al., 2010. Data of the sources are adopted from [c]Widory et al., 2004; [d]Turekian et al., 2003; [e]Das et al., 2010; [f]Jung et al., 2011; [g]Fisseha et al., [h]Irei et al., 2006; and [h]Irei et al., 2011.

Figure 1

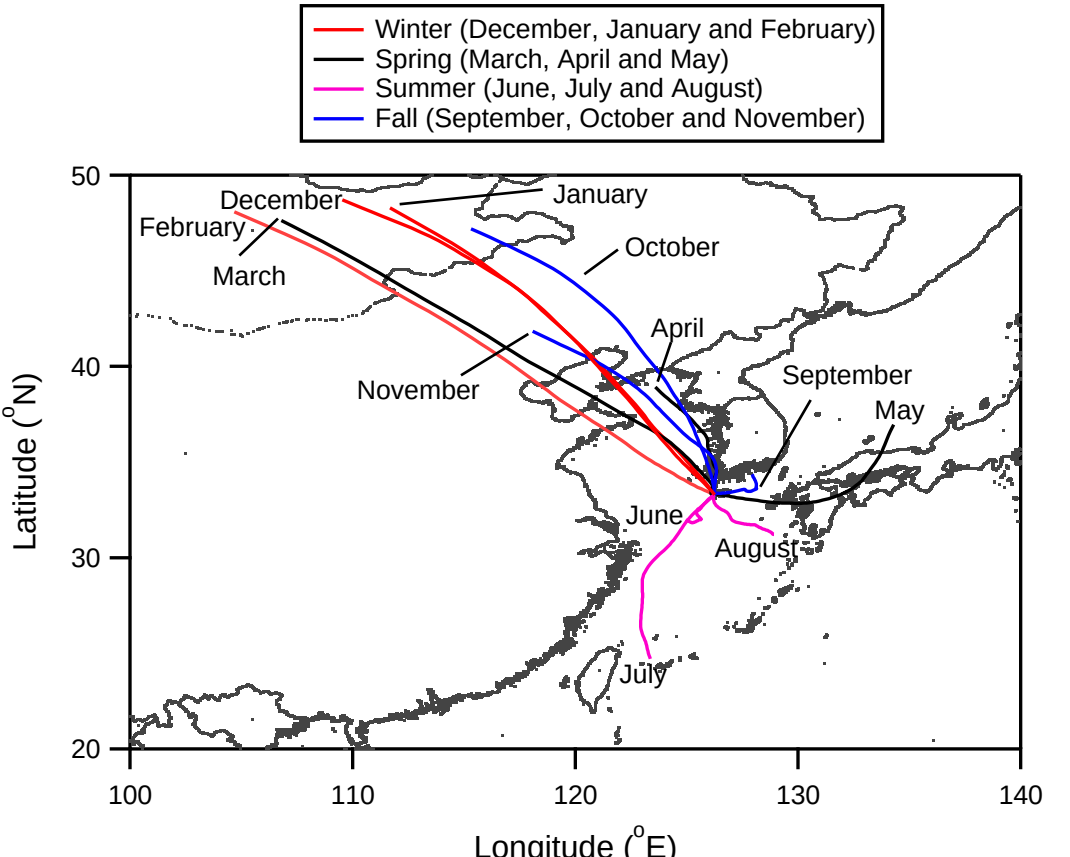
Winter (December, January and February)
Spring (March, April and May)
Summer (June, July and August)
Fall (September, October and November)
December
January
February
March
October
April
November
September
May
June
August
July
50
40
30
20
100
110
120
130
140
Latitude (°N)
Longitude (°E)

Figure 2

Figure 2.

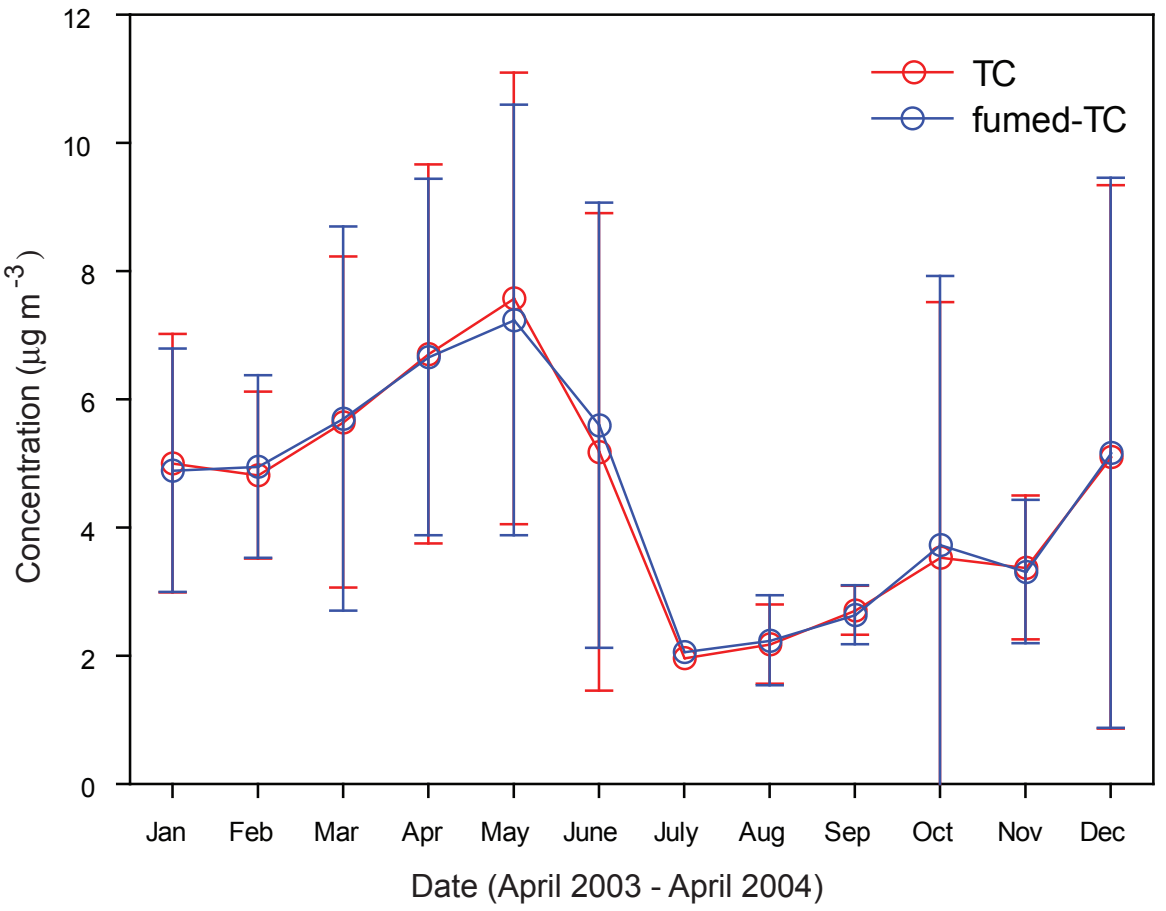

Figure 3.

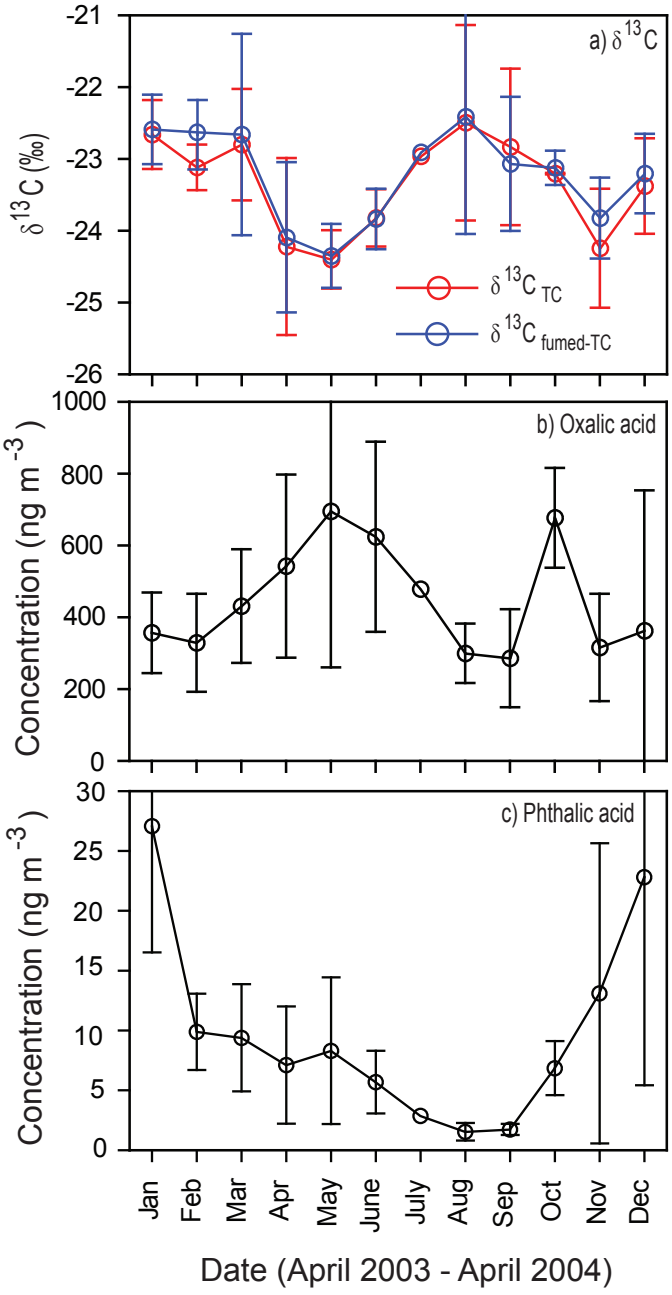
a) δ13C
δ13C (‰)
δ13C TC
δ13C fumed-TC
b) Oxalic acid
Concentration (ng m-3)
c) Phthalic acid
Concentration (ng m-3)
Jan
Feb
Mar
Apr
May
June
July
Aug
Sep
Oct
Nov
Dec
Date (April 2003 - April 2004)

Figure 4.

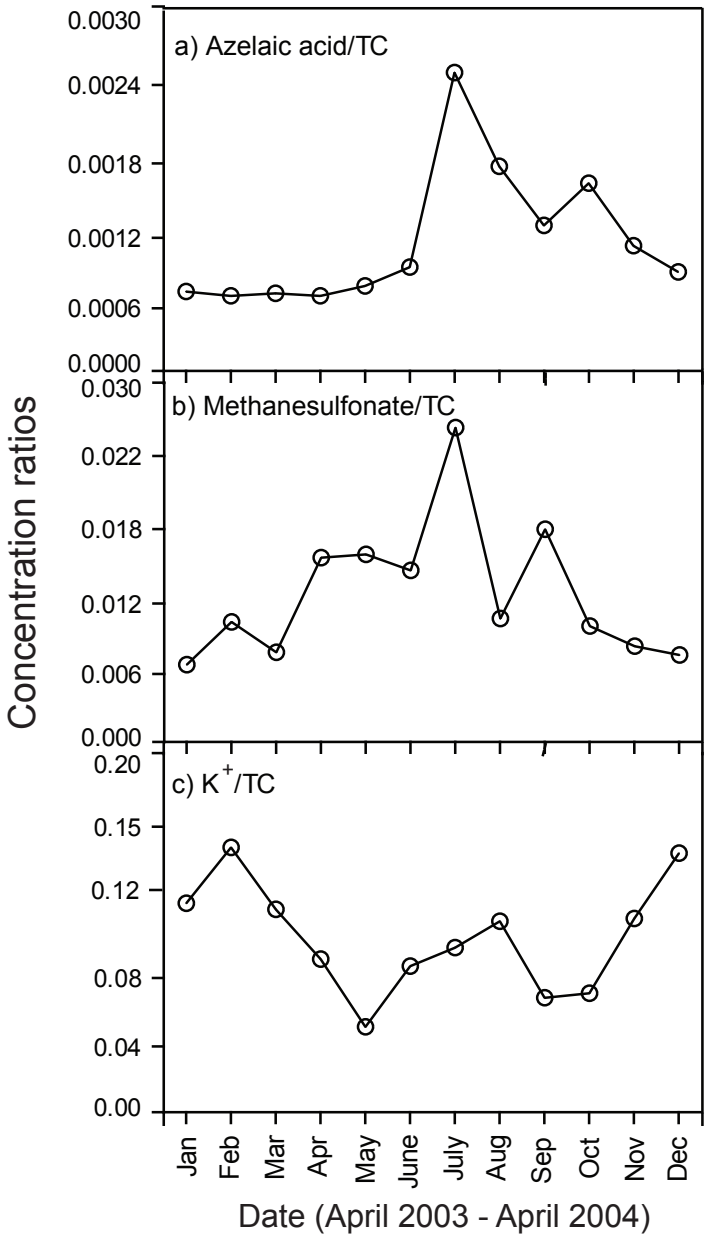
a) Azelaic acid/TC
0.0030
0.0024
0.0018
0.0012
0.0006
0.0000
b) Methanesulfonate/TC
0.030
0.022
0.018
0.012
0.006
0.000
c) K+/TC
0.20
0.15
0.12
0.08
0.04
0.00
Concentration ratios
Jan
Feb
Mar
Apr
May
June
July
Aug
Sep
Oct
Nov
Dec
Date (April 2003 - April 2004)

Figure 5

Figure 5.