Stable carbon isotopic ratios and ionic composition of the high-Arctic aerosols: An increase in δ13C values from winter to spring

M. Narukawa, K. Kawamura, S.-M. Li, and J. W. Bottenheim

Received 5 April 2007; revised 1 September 2007; accepted 24 September 2007; published 31 January 2008.

[1] Atmospheric particles were collected in the high Arctic at Alert during winter (February) and spring (April–May) and were subjected to stable carbon isotopic (δ13C) measurements to better understand the source of carbonaceous aerosols. The mean δ13C values of aerosol total carbon (TC) were observed to increase from winter (−25.7 ± 0.7‰) to spring (−23.7 ± 0.8‰). A strong correlation (r² = 0.92, p < 0.001) was found between the δ13C values and Na+/TC ratios. The increased δ13C values were most likely explained by an enhanced sea-to-air emission of marine organic matter to the high Arctic and also by a decreased atmospheric transport of anthropogenic carbon from the midlatitudes. The backward trajectory analysis together with inorganic ion analysis indicated that spring aerosols were more affected by the Arctic Ocean than winter aerosols that were mainly derived from the primary pollutants emitted in the midlatitudes. On the basis of the δ13C values and Na+/TC ratios, contribution of marine organic matter to aerosol TC was estimated to be 45% in late spring. The enhanced sea-to-air emission of marine organic carbon is probably linked with a melting of sea ice, expansion of leads, and increased biological activity in the Arctic Ocean after the polar sunrise in spring.


1. Introduction

[2] In the lower troposphere of the high Arctic the sources of aerosol particles are mainly characterized by a combination of the marine-derived particles from the Arctic Ocean and continental particles and their precursors that are transported from the midlatitudes [Siros and Barrie, 1999]. In the winter, long-range atmospheric transport of continental aerosols to the high Arctic is maximized when the ambient temperature becomes lowest. The meridional transport of air masses to the north is intensified in winter when the Arctic Ocean is covered by sea ice and the emission from the ocean is suppressed [Barrie, 1997; Klonecki et al., 2003]. After the solar sunrise in spring, ambient temperatures of the high-Arctic increase, and then sea ice starts to melt, expanding leads and open ocean. Hence chemical composition of Arctic aerosols in the marine boundary layer should be more influenced by the sea-to-air emission of marine organic matter from the Arctic Ocean during spring.

[3] To understand the contributions of marine and continental sources to aerosol carbon, stable carbon isotopic composition (δ13C) has successfully been used [Cheselet et al., 1981; Cachier et al., 1986; Narukawa et al., 1999; Martinelli et al., 2002; Turekian et al., 2003; Kawamura et al., 2004; Kelly et al., 2005; Huang et al., 2006; Ho et al., 2006]. On the basis of the δ13C measurement of marine aerosols, for example, Cheselet et al. [1981] reported that terrestrial organic matter is more important (>80%) than marine organic matter in the remote marine atmosphere. Cachier et al. [1986] explained a depletion of 13C in the Northern Hemispheric aerosols relative to the Southern Hemispheric aerosols due to an enhanced contribution of anthropogenic carbon in the Northern Hemisphere. Narukawa et al. [1999] demonstrated a significant contribution from flaming and/or smoldering combustion of C3 plants during large-scale forest fires in Southeast Asia on the basis of the δ13C analyses of aerosols. Thus δ13C measurements of aerosols can provide a useful tool to evaluate the contribution of marine and continental sources to aerosol carbon.

[4] Here stable carbon isotopic composition of aerosol particles was studied in the high-Arctic boundary layer during winter and spring seasons to better understand the relative contribution of marine and continental carbonaceous materials to aerosols. To evaluate air mass source
in the EA and then was measured with a thermal conductivity detector. An aliquot of CO$_2$ gas was then introduced into an isotope ratio mass spectrometer (ThermoQuest, Delta Plus) through an interface (ThermoQuest, ConFlo II). The isotopic compositions ($\delta^{13}C$) were determined using the standard isotopic conversion

$$\delta^{13}C = \frac{\left(\frac{^{13}C}{^{12}C}\right)_{\text{sample}} - 1}{\left(\frac{^{13}C}{^{12}C}\right)_{\text{standard}}} \times 1000, \quad (1)$$

where the isotope standard is Vienna PeeDee belemnite. Triplicate measurements were conducted per sample. Acetanilide and aniline were used to calibrate the TC concentrations and $\delta^{13}C$ values, respectively, and were routinely analyzed to confirm the combustion performance in the EA. The precision and the accuracy of TC measurements were about 10% whereas those of the $\delta^{13}C$ measurements were about 0.5‰. This analytical procedure has been used in previous studies [Narukawa et al., 1999; Kawamura et al., 2004].

[7] For anion and cation analyses, one eighth of the filter samples was cut in pieces and was ultrasonically extracted with Milli Q water. The extracts were filtered with a preparation filter (GL Sciences, Chromatodisk 13AI). Major anions (Cl$^-$, Br$^-$, NO$_3^-$, SO$_4^{2-}$, and methanesulfonic acid (MSA)) and cations (Na$^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$) were determined by ion chromatograph ( Dionex, DX-500). For anion analysis, Dionex-AS12A columns, 4.05 mM Na$_2$CO$_3$/0.45 mM NaHCO$_3$ eluant, and autosuppressor ARS-S1 were used. For cation analysis, Dionex-CS12A columns, 20.5 mM methanesulfonic acid eluant, and autosuppressor CSRS-ULTRA were used. The injection loop volume was 500 $\mu$L. Procedural blanks showed small peaks of Cl$^-$, SO$_4^{2-}$, and Ca$^{2+}$ in the ion chromatograms. However, they were less than 5% of those for the aerosol samples. The concentrations of the ions reported here are corrected for the procedural blanks.

3. Results and Discussion

3.1. Source Region of Air Masses

[8] Figure 2a shows a result of 10 d backward trajectory analyses (HYSPLIT4) [Draxler and Rolph, 2003; Rolph, 2003] which correspond to the aerosol sampling during winter (16–18 February). Throughout the winter campaign, most of the trajectories show that air masses were transported from Greenland, North America, and Europe. Air masses coming from the midlatitudes to the high Arctic bring primary pollutants [e.g., Hopper and Hart, 1994]. The results of our backward trajectory analyses were found to be consistent with the previous studies [Hopper and Hart, 1994], suggesting that the aerosol particles collected in winter were mainly transported from the urban areas of the midlatitudes where primary pollutants are seriously emitted.

[9] Figure 2b shows a result of 10 d backward trajectory analyses which correspond to the sampling during spring (30 April to 2 May). Throughout the spring campaign the backward trajectories are mostly characterized by a northerly air mass that traveled over the Arctic Ocean, Baffin
Figure 2
Bay, and Davis Strait. During the spring campaign a
significant O$_3$ depletion was found to occur in the Arctic
marine boundary layer [Bottenheim et al., 2002b]. Meteor-
ological analyses in the Arctic [Hopper and Hart, 1994;
Hopper et al., 1998] indicate that the air masses with
depleted O$_3$ at Alert are transported across the Arctic Ocean.
The previous studies and our backward trajectory analyses
suggest that the aerosol particles collected in spring were
transported over the Arctic Ocean and were influenced by
the emission from the ocean that is characterized by the
presence of both sea ice and leads.

3.2. Total Carbon and Inorganic Ions

Table 1 shows a summary of the analyses of total
carbon and inorganic ions in the aerosol samples collected
during the winter and spring campaigns. Figures 3a and 3b
show the time variations of TC and Na$^+$ concentrations,
respectively. The concentrations of TC seem to decrease
from winter to spring. The concentrations of the spring
aerosols were about half of the winter aerosols. This
decline in TC concentrations is consistent with the previ-
sous studies [Sirois and Barrie, 1999]. In the Arctic winter,
hazy aerosols are quite often observed in the North Amer-
ican Arctic [Barrie, 1986]. They are mainly caused by long-
range atmospheric transport of anthropogenic aerosols and
their precursors from the midlatitudes and are characterized
by significantly enhanced concentrations of sulfate and
carbon [Sirois and Barrie, 1999; Polissar et al., 1999;
Quinn et al., 2002]. Black carbon concentrations in Cana-
dian Arctic aerosols show a maximum during winter and
decrease toward spring [Sharma et al., 2004]. During the
spring campaign, secondary organic aerosols (SOAs) were
formed by enhanced photochemical reactions in the high
Arctic [Narukawa et al., 2002]. Our data for TC and the
previous studies suggest that winter aerosols were strongly
influenced by anthropogenic sources whereas spring aero-
sols were influenced by both primary marine-derived mate-
rials and secondary formation of organic aerosols
[Kawamura et al., 1996].

Concentrations of marine constituents (Na$^+$, Cl$^-$, Br$^-$, and MSA) increased from winter to spring (see Table 1 and Figure 3b), indicating that the spring aerosols were more influenced by sea salts than were the winter aerosols. The increase in MSA may suggest an increased phytoplank-
on activity in spring. It is indicated that marginal sea ice zones are the source regions of the air masses in which O$_3$
and NO$_3$ are depleted [Bottenheim and Chan, 2006]. In these source regions the sea-salt particles enriched with Br$^-$ are more significantly produced through the emission of sea spray and/or frost flowers in polynyas, leads, and coasts in the Arctic Ocean [Domine et al., 2004; Simpson et al., 2005].

Non-sea-salt sulfate (NSS-SO$_4^{2-}$) concentrations of the winter aerosols were somewhat higher than those of the spring samples (see Table 1). This is consistent with the
denuder/filter measurement of particulate SO$_4^{2-}$ conducted
during the same campaigns (winter, 1110 ± 440 ng m$^{-3}$; spring, 750 ± 340 ng m$^{-3}$) [Ianniello et al., 2002]. Ianniello
et al. [2002] also reported that gaseous SO$_2$ concentrations in winter were about 5 times higher than in spring (winter, 1490 ± 880 ng m$^{-3}$; spring, 280 ± 240 ng m$^{-3}$). Our results are also consistent with previous observations by Barrie and Hoff [1984] and Barrie et al. [1994], which demonstrated that the oxidation rate of SO$_2$ transported from the midlatitudes increases in spring when the Sun rises [Ianniello et al., 2002]. Concentrations of NSS-SO$_4^{2-}$ that are produced by photochemical reactions in the Arctic show
a maximum in spring whereas those of NSS-SO$_4^{2-}$ that are long-range transported from the midlatitudes as primary pollutants show a maximum in winter [Sirois and Barrie, 1999].

Nitrate concentrations of the spring aerosols were
higher than those of the winter aerosols (see Table 1). Using
denuder/filter sampling techniques during the same cam-
paigns, Ianniello et al. [2002] reported that gaseous HNO$_3$
concentrations increased in spring (winter, 15 ± 21 ng m$^{-3}$; spring, 55 ± 59 ng m$^{-3}$), and particulate NO$_3$ concentrations also increased (winter, 81 ± 26 ng m$^{-3}$; spring, 140 ± 30 ng m$^{-3}$), suggesting that a photochemical production of HNO$_3$ via the reaction of OH with NO$_2$ was enhanced in spring. In the Arctic, gaseous HNO$_3$ is incorporated into
sea-salt particles, forming an internally mixed condition
[Hara et al., 1999]. Increased concentrations of NO$_3$ were also reported in the supermicrometer aerosol fractions collected by a size-segregated 11-stage impactor sampler at Alert [Kawamura et al., 2007]. Therefore higher concentrations of NO$_3$ in our spring samples should be caused by the adsorption of gaseous HNO$_3$ on sea-salt particles following the enhanced photochemical oxidation of NO$_x$
in spring.

3.3. Stable Carbon Isotopic Composition of Aerosols

Figure 3a shows time variations of the $\delta^{13}$C values of TC in the Arctic aerosols. The average $\delta^{13}$C values ($-25.7 \pm 0.7\%$) of the winter aerosols were found to be lower than those ($-23.7 \pm 0.8\%$) of the spring aerosols (Table 1). As discussed in section 3.2, our data in the present study and data in previous studies suggest that winter samples were strongly influenced by the primary pollutants transported from the midlatitudes whereas spring samples were more influenced by the sea-to-air emission of marine organic matter as well as the SOAs. Figure 4 compares the $\delta^{13}$C values measured in our Arctic aerosol samples with those reported for the potential sources. The $\delta^{13}$C values of TC in urban Tokyo aerosols were measured to be $-25.0 \pm 0.8\%$ (K. Kawamura et al., unpublished data, 2003). Those of traffic tunnel aerosols in Vancouver affected by motor vehicular emissions were reported to be $\sim -27.3\%$ with no significant difference between OC and EC [Huang et al., 2006].
suggest that the δ13C values of the SOAs formed in the atmosphere should be lighter than those of the precursor compounds emitted in the source regions. It should be noted that the faster VOC oxidation in spring would result in a more complete precursor oxidation, which then can cause heavier (closer to anthropogenic emissions) carbon in aerosols. As a result, the δ13C values of the SOAs formed in the spring would be lighter than and/or closer to those formed in the ocean.

[15] Previous studies on particulate organic matter (POM) in the oceans show the δ13C values ranging from −35‰ to −16‰ [Goericke and Fry, 1994]. In the Beaufort Sea the δ13C values of plankton were −22‰ [Rau et al., 1982] (see Figure 4). Sea ice algae in the Arctic Ocean can influence isotopic values of POM. The ice algae growing within sea ice brines are significantly enriched in 13C relative to marine phytoplankton in high-latitude waters because of carbon limitation and physiological properties, including carbon-concentrating mechanisms and/or bicarbonate uptake [Gleitz et al., 1996; Gibson et al., 1999; Villinski et al., 2000]. Such an enrichment of 13C in ice algae and suspended POM (−17.7‰ versus −22.3‰) has been confirmed in the North Water Polynya, the largest polynya in the Canadian Arctic [Hobson et al., 2002]. Similar 13C enrichment was reported between ice algae and suspended POM (−18.6‰ versus −27.9‰) in the Northeast Water Polynya [Hobson et al., 1995] and between ice POM and suspended POM (−20.3‰ versus −24.8‰) in the Barents Sea [Tamelaander et al., 2006] (see Figure 4). These comparisons suggest that δ13C values of Arctic marine organisms are heavier than those of anthropogenic aerosols (−26‰).

[16] The δ13C values of the SOAs formed in the atmosphere should be lighter than the volatile precursor compounds since the δ13C values of SOAs formed by OH radical-induced reactions of toluene are 0.6 ± 0.2‰ lighter than those of the precursor [Ivre et al., 2006]. In general, the δ13C values of volatile organic compounds (VOCs) that can form SOAs in the atmosphere should become lighter through long-range transport processes since the kinetic isotope effects for the reactions of hydrocarbons with OH radicals are positive [Rudolph et al., 2000]. These studies suggest that the δ13C values of the SOAs formed in the atmosphere should be lighter than those of the precursor compounds emitted in the source regions. It should be noted that the faster VOC oxidation in spring would result in a more complete precursor oxidation, which then can cause heavier (closer to anthropogenic emissions) carbon in aerosols. As a result, the δ13C values of the SOAs formed in the spring would be lighter than and/or closer to those formed in the ocean.

Figure 3. Temporal variations of (a) stable carbon isotopic composition (δ13C) in the Arctic aerosol samples and their total carbon (TC) concentrations (ng m$^{-3}$) and (b) Na$^+$ concentrations.
and g, this work.

3.4. Contributions of Marine and Continental Carbon in the Spring Arctic Aerosols

The Na+/TC ratio in the marine aerosols over the Arctic Ocean is 2.3 as expected; namely, the Na+/TC ratio in the marine aerosols over the North Atlantic was reported to be 2.3 [Cavalli et al., 2004]. Assuming that the Na+/TC ratio in the marine aerosols over the Arctic Ocean is 2.3 as well, one can obtain the δ13C value at the ratio of 2.3 on the regression line in Figure 5. This δ13C value coincides with those of marine organic matter reported in the Arctic (Figure 4).

Table 2 shows the calculated average concentrations of TC from marine and continental sources using the relative contribution. These estimates clearly indicate that marine carbon increased from winter to spring and that continental carbon decreased inversely. The present study demonstrates that an enrichment of 13C in the Arctic spring aerosols is mainly caused by the enhanced sea-to-air emis-

δ13C values in Figure 4 were applied using the following equations:

\[ \delta^{13}C_{aerosol} = f_{marine}\delta^{13}C_{marine} + f_{continental}\delta^{13}C_{continental} \]  

\[ f_{marine} + f_{continental} = 1, \]  

where \( f_{marine} \) and \( f_{continental} \) are the fractions of marine and continental carbon, respectively, and \( \delta^{13}C_{marine} \) and \( \delta^{13}C_{continental} \) are the reported isotopic values for marine and continental carbon, respectively. To estimate the uncertainties in differentiating the marine and continental contributions associated with the range in δ13C values for the different sources, we used three sets of calculations for each sample. Our reasonable estimates are based on the δ13C values for the Arctic marine aerosols (−21%) and continental aerosols (−26%) as discussed in section 3.3. The upper limit for the contribution of marine carbon is calculated using δ13Cmarine of −22.0‰ and δ13Ccontinental of −27.3‰. The lower limit for the contribution of marine carbon is calculated using δ13Cmarine of −17.7‰ and δ13Ccontinental of −25.0‰. These δ13C values for the limit are derived from Figure 4. The contribution from marine carbon to spring Arctic aerosols is estimated to be 45% (upper and lower estimate of 67% and 0%, respectively). Our estimate (45%) is a little higher than that (38%) reported at Bermuda [Turekian et al., 2003], where the marine aerosols are more affected by the anthropogenic sources than the Arctic.

Table 2 shows the calculated average concentrations of TC from marine and continental sources using the relative contribution. These estimates clearly indicate that marine carbon increased from winter to spring and that continental carbon decreased inversely. The present study demonstrates that an enrichment of 13C in the Arctic spring aerosols is mainly caused by the enhanced sea-to-air emis-

[19] Table 2 shows the calculated average concentrations of TC from marine and continental sources using the relative contribution. These estimates clearly indicate that marine carbon increased from winter to spring and that continental carbon decreased inversely. The present study demonstrates that an enrichment of 13C in the Arctic spring aerosols is mainly caused by the enhanced sea-to-air emis-

Figure 5. Relationship between stable carbon isotopic compositions (δ13C) (mean ± 1σ) and concentration ratios of Na+/total carbon (TC) in the winter and spring aerosol samples collected in the Arctic in the year 2000. Regression line is presented as a solid line. Na+/TC of 2.3 was taken for marine aerosols from Cavalli et al. [2004]. See the text for more details.
ension of marine organic matter in the Arctic Ocean. The emission of marine organic matter from the Arctic Ocean is also supported by halogenated dicarboxylic acids (see Table 1), which were detected in the spring samples but not in the winter samples [Narukawa et al., 2003]. Organic-halogen compounds that can serve as precursors of halogenated diacids are produced by macroalgae and ice microalgae in the Arctic [Lauterbur, 1996; Cota and Sturges, 1997]. This evidence supports the idea that the spring aerosol samples are more influenced by the enhanced biological activity in the Arctic Ocean.

[20] It is of interest to note that Kawamura et al. [1996] analyzed homologous series of dicarboxylic acids (C$_2$–C$_{10}$) in the Arctic aerosols and reported their seasonal variations. They found that the abundances of azelaic acid (C$_9$) started to increase in May toward summer. Azelaic acid is produced by a photooxidation of unsaturated fatty acids that are produced by marine phytoplankton and are emitted to the atmosphere via the marine microlayer [Kawamura and Gagosian, 1987; Stephanou and Straitagakis, 1993]. The changes in the $\delta^{13}$C values obtained for the spring aerosol samples are consistent with the increased concentrations of azelaic acid in the Arctic aerosols, again suggesting that the Arctic organic aerosols in spring are affected by sea-to-air emission of marine organic matter.

4. Summary and Conclusions

[21] Stable carbon isotopic measurements of the aerosol total carbon (TC) in the high Arctic showed a significant change in the $\delta^{13}$C values from lighter values ($-25.7 \pm 0.7 \%_\text{oo}$) in winter to heavier values ($-23.7 \pm 0.8 \%_\text{oo}$) in spring. The $\delta^{13}$C values were found to strongly correlate with Na/TC ratios in the aerosol samples ($r^2 = 0.92$, $p < 0.001$), indicating an enhanced sea-to-air emission of marine organic matter from the Arctic Ocean and the surrounding seas in spring. We estimated a contribution of marine organic matter to the aerosol TC to be 45% in late spring. The changes in the source strength are also caused by a decreased anthropogenic input from the midlatitudes; a meridional transport of organic pollutants to the Arctic is decreased after the Arctic sunrise. The present study demonstrates that the changes in the source strength of aerosol carbon in the high Arctic are closely linked to the Arctic sunrise and subsequent oceanic changes in the Arctic Ocean and surrounding seas. We presented an example where the melting of sea ice and expansion of leads are significantly accelerated these days, probably as a result of global warming (e.g., http://www.realclimate.org/index.php/archives/2007/08/arctic-sea-ice-watch/, http://www.jaxa.jp/press/2007/08/20070816_arctic_e.html).

[22] Acknowledgments. We thank L. A. Barrie, A. Gaudenzi, A. Leithad, and D. Toom for their support in collecting samples and T. Nakatsuka for his help in the isotope analysis. We also acknowledge H. Narita, M. Watanabe, and S. Matoba for their help in the ion analysis. This study was supported in part by the Japanese Ministry of Education, Science and Culture through grant-in-aid 10144101. NOAA Air Resources Laboratory (ARL) is acknowledged for the provision of the HYSPLIT transport and dispersion model and the READY Web site (http://www.arl.noaa.gov/ready.html) used in this publication.

References


J. W. Bottenheim and S.-M. Li, Air Quality Research Division, Atmospheric Science and Technology Directorate, Science and Technology Branch, Environment Canada, 4905 Dufferin Street, Toronto, ON, Canada M9H 5T4 (jan.bottenheim@ec.gc.ca; shao-meng.li@ec.gc.ca)

K. Kawamura and M. Narukawa, Institute of Low Temperature Science, Hokkaido University, N19W18 Kita-ku, Sapporo 060-0819, Japan. (masahiro_narukawa@ihi.co.jp; kawamura@lowtem.hokudai.ac.jp)