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Author(s)	Yamamoto, Shinya; Kawamura, Kimitaka; Seki, Osamu
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Long-range atmospheric transport of terrestrial biomarkers by the Asian winter  
monsoon: Evidence from fresh snow from Sapporo, northern Japan

Shinya Yamamoto<sup>a\*</sup>, Kimitaka Kawamura<sup>a</sup>, Osamu Seki<sup>a</sup>

<sup>a</sup> Institute of Low Temperature Science, Hokkaido University, N19W8, Kita-ku,  
Sapporo 060-0819, Japan.

\* Corresponding author. Tel: +81-11-706-6883; Fax: +81-11-706-7142

E-mail address: s.yamamoto@pop.lowtem.hokudai.ac.jp (S. Yamamoto)

## Abstract

Molecular distributions of terrestrial biomarkers were investigated in fresh snow samples from Sapporo, northern Japan, to better understand the long-range atmospheric transport of terrestrial organic matter by the Asian winter monsoon. Stable carbon ( $\delta^{13}\text{C}$ ) and hydrogen ( $\delta\text{D}$ ) isotope ratios of  $\text{C}_{22}\text{--}\text{C}_{28}$  *n*-alkanoic acids were also measured to decipher their source regions. The snow samples are found to contain higher plant-derived *n*-alkanes, *n*-alkanols and *n*-alkanoic acids as major components. Relative abundances of these three biomarker classes suggest that they are likely derived from higher plants in the Asian continent. The  $\text{C}_{27}/\text{C}_{31}$  ratios of terrestrial *n*-alkanes in the snow samples range from 1.3 to 5.5, being similar to those of the plants growing in the latitudes  $> 40^\circ\text{N}$  of East Asia. The  $\delta^{13}\text{C}$  values of the *n*-alkanoic acids in the snow samples ( $-33.4$  to  $-27.6\text{‰}$ ) are similar to those of typical  $\text{C}_3$  gymnosperm from Sapporo ( $-34.9$  to  $-29.3\text{‰}$ ). However, the  $\delta\text{D}$  values of the *n*-alkanoic acids ( $-208$  to  $-148\text{‰}$ ) are found to be significantly depleted with deuterium (by  $\sim 72\text{‰}$ ) than those of plant leaves from Sapporo. Such depletion can be most likely interpreted by the long-range atmospheric transport of the *n*-alkanoic acids from vegetation in the latitudes further north of Sapporo because the  $\delta\text{D}$  values of terrestrial higher plants tend to decrease northward in East Asia reflecting the  $\delta\text{D}$  of precipitation. Together with the results of backward trajectory analyses, this study suggests that the terrestrial biomarkers in the Sapporo snow samples are likely transported from Siberia, Russian Far East and northeast China to northern Japan by the Asian winter monsoon.

Keywords: stable carbon isotopes, stable hydrogen isotopes, terrestrial biomarker, snow, Asian monsoon

## 1. Introduction

Homologous series of high molecular weight *n*-alkanes, *n*-alkanols and *n*-alkanoic acids are typical biomarkers that originate from epicuticular waxes of

terrestrial higher plants (Eglinton and Hamilton, 1967). These organic compounds are easily sloughed off from the leaf surface by winds (especially by sandblasting) to result in primary organic aerosols. Alternatively, they can be emitted from decaying plant materials in soils into the atmosphere by dust storms (Simoneit et al., 1977), or injected as smoke particles by forest fires and biomass burning (Standley and Simoneit, 1987; Abas et al., 1995; Oros and Simoneit, 2001).

Chain-length distribution and stable carbon isotopic compositions ( $\delta^{13}\text{C}$ ) of terrestrial biomarkers in atmospheric aerosols are particularly important to understand their source regions because they are sensitive to the plant types (i.e.,  $\text{C}_3$  or  $\text{C}_4$ ) and changes in community composition and growing environment of their source vegetation (Hall and Jones, 1961; Poynter et al., 1989; Collister et al., 1994; Schefuß et al., 2003; Sachse et al., 2006). In addition, the hydrogen isotope ratios ( $\delta\text{D}$ ) of higher plant waxes, that primarily reflect the  $\delta\text{D}$  of precipitation waters during photosynthesis, generally show large spatial gradients between the low and high latitudes and arid and humid regions (Sachse et al., 2004, 2006; Jia et al., 2008; Rao et al., 2009) reflecting global and local hydrological cycles (West et al., 2008). Hence, combination of chain-length distribution and dual-isotope ratios ( $\delta^{13}\text{C}$  and  $\delta\text{D}$ ) of terrestrial biomarkers provides a powerful tool to access their source regions.

Previous studies on terrestrial biomarkers in marine aerosols from the North Pacific reported seasonal changes in the concentration and molecular compositions, indicating a seasonal shift in their source regions and transport pathways (Gagosian and Peltzer, 1986; Kawamura et al., 2003). More recently, the  $\delta^{13}\text{C}$  and  $\delta\text{D}$  analyses of terrestrial *n*-alkanes in aerosols from Chichi-Jima and Jeju Islands, the western North Pacific, revealed atmospheric transport of terrestrial organic materials from Southeast Asia by the Asian summer monsoon (Bendle et al., 2006; Yamamoto et al., unpublished results). However, little is known about the role of the Asian winter monsoon in the atmospheric transport of terrigenous organic matter to the Asia Pacific region.

During winter, the cold and dry air of the Asian monsoon causes intensive snowfall in the Japan sea side of the Japanese islands with the supply of the heat and moisture from warm Tsushima current over the Sea of Japan (air mass transformation). Because the airborne particles are scavenged by snow from the atmosphere efficiently, the snow in northern Japan should contain the imprint of aeolian inputs of terrestrial biomarkers. Indeed, there are worldwide reports on the occurrence of leaf lipid biomarkers in snow (Lunde et al., 1977; Meyers and Hites, 1982; Kawamura and Kaplan, 1986; Leuenberger et al., 1988; Gröllert and Puxbaum, 2000; Xie et al., 2000; Satsumabayashi et al., 2001; Miyake et al., 2006; von Schneidemesser et al., 2008), as well as in atmospheric aerosols (e.g., Simoneit et al., 1977; Gagosian et al., 1981; Fang et al., 2002; Kawamura et al., 2003).

In this study, we examined concentration and molecular composition of terrestrial biomarkers in fresh snow samples collected from urban area of Sapporo, northern Japan, to reveal atmospheric transport of terrestrial organic materials by the Asian winter monsoon. In addition, we assessed the source regions of these biomarkers by measuring the stable carbon and hydrogen isotopic composition of *n*-alkanoic acids and comparing them with those in modern plant leaves collected from East Asia.

## **2. Material and methods**

### *2.1. East Asian monsoon and meteorology in Sapporo, northern Japan*

The Asian monsoon is one of the most important atmospheric circulatory systems on Earth. In East Asia, summertime heating of the Asian continent develops low-pressure system over Siberia, which promotes the transport of relatively warm and moist air masses from the Pacific towards Siberia. In contrast, cold and dry air masses that originate from the Siberian high-pressure system create outflow towards the Pacific Ocean during winter. The East Asian monsoon has great impact on regional climate, air quality and human health in East Asian countries because they control the air mass source regions and compositions of natural and anthropogenic organic aerosols

transported to the western North Pacific regions.

In Sapporo, the capital of Hokkaido (the northernmost island of Japan), the snow usually starts to accumulate in December and continues to the end of March without melting due to low ambient temperatures; the average temperature during December to March is  $-2.1^{\circ}\text{C}$  (averages for the years 1971–2000; Japan Meteorological Agency Website at <http://www.jma.go.jp/jma/menu/report.html>, last accessed on 11 November 2010). The snow covers prevent soil particles being stirred up by winds from the ground, and dying off of deciduous foliage minimizes the emission of terrestrial biomarkers from local vegetation sources. Thus, Sapporo is a good place to track the terrestrial organic compounds that are transported by the Asian winter monsoon.

## 2.2. *Snow samples and lipid analysis*

Twelve fresh snow samples were collected on the rooftop of the three-story building of the Institute of Low Temperature Science, Hokkaido University ( $43^{\circ}05'\text{N}$ ,  $141^{\circ}20'\text{E}$ ) during intensive snowfall events in January to March 2010 and 2011. In each sampling, only the fresh snow layer was collected using a pre-cleaned stainless steel shovel into a glass jar (8L) after the surface (1~2 cm) layer was removed to avoid the possible inclusion of dry deposition of local aerosols. The glass jar was sealed with a Teflon-lined screw cap immediately after sampling, and stored in a freezer ( $-20^{\circ}\text{C}$ ) until analysis.

Prior to the extraction of organic compounds, the samples were melted at  $4^{\circ}\text{C}$  with an addition of mercuric chloride ( $\text{HgCl}_2$ ). The melted snow (0.5 to 1.0 L) was then acidified to pH  $\sim 1$  with 6M HCl, and extracted with dichloromethane (DCM) /ethyl acetate (2:1) mixture ( $\times 3$ ). The extracts were concentrated using a rotary evaporator and divided into neutral and acidic fractions after saponification with 1.0 M KOH in methanol. The neutral fraction was first separated from the solution by extraction with *n*-hexane/DCM (10:1) mixture. Aliphatic hydrocarbons and alcohols were isolated using a silica gel (deactivated with 1%  $\text{H}_2\text{O}$ ) column chromatography by elution with

*n*-hexane and DCM/methanol mixture (95:5), respectively. The remaining solution was acidified with 6M HCl, and the carboxylic acids were extracted with DCM. The acid fraction was then treated with 14% BF<sub>3</sub>/methanol to convert carboxylic acids to their methyl esters. Monocarboxylic acid methyl esters were isolated on a silica gel (deactivated with 1% H<sub>2</sub>O) column chromatography by elution with *n*-hexane/DCM (1:2) mixture.

All the fractions were analyzed using a gas chromatography (GC) and GC/mass spectrometry (MS). The alcohol fraction was silylated with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) to derive trimethyl silyl (TMS) ethers prior to GC injection. GC analysis was performed using a Hewlett-Packard 6890 gas chromatograph equipped with an on-column injector, CP-Sil 5 CB fused silica capillary column (60 m × 0.32 mm i.d., 0.25 μm film thickness) and a flame ionization detector (FID). Helium was used as a carrier gas. The GC oven temperature was programmed from 50 to 120 °C at 30 °C/min, then to 310 °C (held 15.5 min) at 5 °C/min. GC/MS analysis was performed using a Hewlett-Packard 5973 Mass Selective Detector (quadrupole mass spectrometer) coupled to a Hewlett-Packard 6890 GC equipped with a HP-5MS fused silica column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The temperature program was the same as for GC analysis. The components were identified by the comparison of their GC retention times and mass spectra with those of reference compounds.

In order to assure the quality of our experiments, a recovery test was performed for three times by using a 500 ml of organic-free deionized water, to which 0.13 to 1.0 ng of C<sub>27</sub>, C<sub>29</sub> and C<sub>30</sub> *n*-alkanes, C<sub>20-22</sub>, C<sub>26</sub>, C<sub>28</sub> and C<sub>30</sub> *n*-alkanols and C<sub>24</sub> and C<sub>30</sub> *n*-alkanoic acids were spiked. The average recoveries of the *n*-alkanes, *n*-alkanols and *n*-alkanoic acids were 92±8%, 99±2% and 93±4%, respectively. The analytical error averages 8.7% for the *n*-alkanes, 5.8% for the *n*-alkanols and 4.1% for the *n*-alkanoic acids. Blank test showed no laboratory contamination of any target compounds.

### 2.3. Lipid analysis of plant leaf samples

Five plant leaf samples were collected from typical C<sub>3</sub> gymnosperm species (conifers) growing in Sapporo near the Institute of Low Temperature Science, Hokkaido University (43°05'N, 141°20'E) on 3 March 2010 and 31 January 2011. The samples were collected using pre-cleaned scissors into plastic bags and stored in a freezer (−20°C) until analysis. The surface of leaves were cleaned with distilled water to remove contaminants and dried in an oven (60°C) before use. Two plant leaf samples of C<sub>3</sub> gymnosperm (larch trees) were also collected near Yakutsk, Russia (62°02'N, 129°44'E) on 18 June 2005, which were freeze-dried and stored in glass vials until analysis. Plant leaf samples were ultrasonically extracted with DCM/methanol (95:5) mixture (15 min × 3) and then analyzed by the method described above for the snow analysis.

### 2.4. Compound-specific stable isotope analyses

<sup>13</sup>C/<sup>12</sup>C ratios of *n*-alkanoic acid methyl esters (FAMES) were determined using a HP 6890 GC coupled to a Finnigan MAT Delta Plus isotope ratio mass spectrometer via a Finnigan MAT combustion furnace maintained at a temperature of 850 °C. The GC was equipped with CP-Sil 8CB fused silica column (60 m × 0.32 mm i.d., 0.25 μm film thickness). The GC oven was programmed from 50 to 120 °C at 30 °C/min, and to 310 °C (held 45 min) at 5 °C/min. One to two μl of sample solution were injected into the GC via an on-column injector with an internal standard of known isotopic composition (C<sub>13</sub> *n*-alkane; δ<sup>13</sup>C = −27.24‰). The δ<sup>13</sup>C values are expressed as per mil (‰) relative to the Pee Dee Belemnite (PDB).

D/H ratios for *n*-alkanoic acid methyl esters (FAMES) were determined using a Hewlett-Packard GC (HP 6890) interfaced to a Finnigan MAT Delta Plus XL mass spectrometer via a Finnigan MAT thermal conversion unit with a ceramic tube that was maintained at 1450 °C. The GC was equipped with an on-column injector and DB-5MS



fused silica capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness). The GC oven temperature was programmed from 50 to 120 °C at 10 °C/min, and to 310 °C (held 20 min) at 4 °C/min. Helium was used as a carrier gas at a flow rate of 1.5 ml/min. One to two μl of samples were injected with an internal standard (selected from C<sub>27</sub>, C<sub>29</sub> and C<sub>32</sub> *n*-alkanes to avoid co-elution with sample peaks). The δD values are expressed as per mil (‰) relative to the Standard Mean Ocean Water (SMOW).

The measured δ<sup>13</sup>C and δD values of FAMEs were corrected for the contribution of carbon and hydrogen (δ<sup>13</sup>C = -46.3‰; δD = -225‰) added during methyl esterification using the mass balance equation of Fang et al. (2002). An external standard consisting of C<sub>16</sub> to C<sub>30</sub> *n*-alkanes of known isotopic compositions was daily injected into the GC/IRMS system to check the data quality and to ensure the analytical error to be ±0.5‰ for δ<sup>13</sup>C and ±5‰ for δD during the analyses. Most measurements were duplicated and the averaged value was reported.

In this study, snow and plant leaf samples were extracted using two different methods because the type of samples is different. However, the δ<sup>13</sup>C and δD values of authentic standards (C<sub>21</sub>, C<sub>27</sub>, C<sub>29</sub> and C<sub>30</sub> *n*-alkanes) that are treated with the both methods are identical within the range of analytical errors, meaning that the results of the snow and plant samples are comparable in spite of a difference in the extraction methods.

### *2.5. Air mass trajectory analysis*

Ten-day back air mass trajectories were calculated for each of the samples using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Draxler and Rolph, 2003; Rolph, 2003). The trajectories were calculated for air masses starting from the sampling site at 500, 3000 and 6000 m height using the model vertical velocity with the data from the GDAS archives.

## **3. Results and discussion**

### 3.1. Molecular distributions of lipid class compounds in fresh snow from Sapporo

#### 3.1.1. *n*-Alkanes

Homologous series of *n*-alkanes (C<sub>19</sub> to C<sub>36</sub>) were detected in the Sapporo snow samples (Fig. 2a). The low molecular weight (LMW: C<sub>19</sub>–C<sub>24</sub>) *n*-alkanes showed a weak odd/even carbon number predominance (CPI<sub>LMW *n*-alkanes</sub> = ~1.9; Table 1; Fig. 2a), suggesting that they originate mainly from vehicular exhausts and fossil fuel combustion residues (Simoneit, 1984; Wang and Kawamura, 2005; Simoneit, 2006). In contrast, high molecular weight (HMW: C<sub>25</sub>–C<sub>36</sub>) *n*-alkanes showed a strong odd/even carbon number predominance (CPI<sub>HMW *n*-alkanes</sub> = ~18.1; Table 1; Fig. 2a), suggesting that they are derived from terrestrial higher plant waxes (Eglinton and Hamilton, 1967). The C<sub>27</sub> *n*-alkane is found as the most abundant homologue except for the SP10-5 and SP11-1 samples, in which the C<sub>31</sub> and C<sub>29</sub> *n*-alkanes dominate, respectively. Total concentrations of the *n*-alkanes range from 0.4 to 14.8 µg L<sup>-1</sup> (Table 1). The concentrations are generally similar to those reported in snow samples from Nagano, Japan (0.1–2.2 µg L<sup>-1</sup> for C<sub>17</sub>–C<sub>33</sub> *n*-alkanes; Satsumabayashi et al., 2001) and mountain sites near Los Angeles, USA (0.2–2.6 µg L<sup>-1</sup> for C<sub>17</sub>–C<sub>35</sub> *n*-alkanes; Kawamura and Kaplan, 1986), except for the SP10-1 sample that contains extraordinarily high concentrations of HMW *n*-alkanes (13.3 µg L<sup>-1</sup>).

#### 3.1.2. *n*-Alkanols

Homologous series of *n*-alkanols (C<sub>14</sub>–C<sub>30</sub>) were detected in Sapporo snow samples, with C<sub>22</sub>, C<sub>24</sub>, C<sub>26</sub> and C<sub>28</sub> being dominant species (Fig. 2b). Total concentrations of the *n*-alkanols range from 0.4 to 11.4 µg L<sup>-1</sup> (Table 1). The most abundant *n*-alkanol homologue was generally C<sub>22</sub> or C<sub>24</sub>, however, C<sub>26</sub> *n*-alkanol was found as the most abundant species in the SP10-1, SP11-1 and SP11-3 samples. High molecular weight *n*-alkanols (HMW: > C<sub>24</sub>) showed a strong even/odd carbon number predominance with CPI<sub>HMW *n*-alkanols</sub> > 2.4, suggesting that they originate from terrestrial higher plant waxes (Eglinton and Hamilton, 1967). In contrast, low molecular weight

*n*-alkanols (LMW: < C<sub>20</sub>) may be derived from microbial/marine sources because they are not major constituents of plant waxes (Simoneit, 1977).

### 3.1.3. *n*-Alkanoic acids

Homologous series of C<sub>12</sub>–C<sub>34</sub> *n*-alkanoic acids were detected as the most abundant lipid compound class in Sapporo snow samples. The *n*-alkanoic acids exhibit a bimodal distribution with maxima at C<sub>16</sub> and C<sub>24</sub> (Fig. 2c). A strong even/odd carbon number predominance in the molecular distributions of *n*-alkanoic acids (CPI<sub>*n*-alkanoic acids</sub> > 3.6; Table 1) suggests that they originate from biological sources (Fig. 2c). Lower molecular weight (LMW: C<sub>12</sub>–C<sub>19</sub>) *n*-alkanoic acids are generally attributed to various organisms including marine phytoplankton and bacteria as well as terrestrial higher plants, however, their high molecular weight homologues (HMW: > C<sub>24</sub>) exclusively originate from terrestrial higher plant waxes (Simoneit, 1977; Gagosian et al., 1981). Total concentration of the *n*-alkanoic acids ranged from 0.8 to 38.8 µg L<sup>-1</sup> (Table 1), being similar to those reported in snow samples from Nagano, Japan (4.2–19 µg L<sup>-1</sup> for C<sub>12</sub>–C<sub>23</sub> *n*-alkanoic acids; Satsumabayashi et al., 2001) and mountain sites near Los Angeles (1.4–8.3 µg L<sup>-1</sup> for C<sub>12</sub>–C<sub>30</sub> *n*-alkanoic acids; Kawamura and Kaplan, 1986) and Indiana (6–46 µg L<sup>-1</sup> for C<sub>12</sub>–C<sub>28</sub> *n*-alkanoic acids; Meyers and Hites, 1982), USA.

### 3.1.4. Contribution of anthropogenic hydrocarbons to HMW *n*-alkanes

The carbon preference index (CPI) of *n*-alkanes is often used to estimate relative contributions from higher plant waxes and fossil fuel hydrocarbons to these homologues. This is because the CPI values of higher plant wax *n*-alkanes are generally > 5 when there is no serious input from pollutant, but the values tend to decrease down to 1.0 with an increase of contribution from anthropogenic sources.

In Table 1, the CPI values of HMW *n*-alkanes (CPI<sub>HMW *n*-alkane</sub>) are given for the fresh snow samples from Sapporo. Their CPI<sub>HMW</sub> values range from 2.5 to 18.1 (Table 1). Relatively low CPI values for the samples SP10-5, SP11-2, -3 and -6 can be

partly interpreted by a contribution from anthropogenic *n*-alkanes. However, the concentrations of HMW *n*-alkanes are strongly correlated with the HMW *n*-alkanols ( $r = 0.94, p < 0.01$ ) and *n*-alkanoic acids ( $r = 0.85, p < 0.01$ ). Because the HMW *n*-alkanols and *n*-alkanoic acids are exclusively originated from terrestrial higher plant waxes, the strong positive correlations suggest that the HMW *n*-alkanes should also be derived from similar vegetation sources that supply the HMW *n*-alkanols and *n*-alkanoic acids.

### 3.1.5. Relative abundances of three terrestrial biomarker classes

Relative abundances of HMW *n*-alkanes, HMW *n*-alkanols and HMW *n*-alkanoic acids are often used to distinguish the source regions of terrestrial biomarkers. Previous studies in marine sediments and atmospheric aerosols suggest that terrestrial biomarkers transported from Central and South Americas by trade winds are characterized by relatively high abundances of the *n*-alkanoic acids (Group A in Fig. 3; Ohkouchi et al., 1997), whereas those transported from the Asian continent by the westerly winds are characterized by lower abundance of the *n*-alkanoic acids than those in the trade wind regime (Groups B, C, D and E in Fig. 3; Ohkouchi et al., 1997; Kawamura et al., 2003, Bendle et al., 2007; Fu et al., 2008).

In Fig. 3, we plotted relative abundances of three terrestrial biomarker classes in the Sapporo snow samples. Relative abundances of the HMW *n*-alkanes, *n*-alkanols and *n*-alkanoic acids in the Sapporo snow range from 21.2–65.8%, 14.7–42.1% and 6.5–59.1%, respectively. The distribution of Sapporo snow samples closely fall in the area of aerosol samples from the westerly regime (Groups B, C, D and E) (Fig. 3), suggesting that they likely originated from higher plants in the Asian continent. The results of back trajectory analysis of the snow fall events, however, showed that the air masses are transported from the northern part of the Asian continent by low-elevation winds (< 3000 m) of the Asian monsoon rather than upper tropospheric channel of the westerlies (Fig. 4). Hence, we consider that the similarities in the distribution are more

likely attributed to their identical source regions, not transport pathways.

### 3.2. Chain-length distributions of the *n*-alkanes in fresh snow samples from Sapporo

The chain-length distribution of terrestrial higher plant *n*-alkanes can vary significantly depending on the latitude in East Asia where their source vegetations grow (Kawamura et al., 2003; Rao et al., 2009). For example, Kawamura et al. (2003) reported that the average chain length (ACL) value in plant leaves from the northern latitude (43.1°N) is higher than those in the lower latitudes (27.4°N–6°S). Likewise, Simoneit et al. (1991) reported higher relative abundance of C<sub>31</sub> *n*-alkane in the aerosols of the warmer climate in southern China. Because plants generally alter the chain-length distribution of leaf waxes to minimize the loss of water vapor from their leaves (Sachse et al., 2006), or to maintain the hardness of the leaf surfaces following the changes in the ambient temperature (Kawamura et al., 2003), the changes in the chain-length distribution of the *n*-alkanes should be the plant physiological responses to their growing environments.

Fig. 5 shows latitudinal variations of the C<sub>27</sub>/C<sub>31</sub> ratios of terrestrial higher plant-derived *n*-alkanes in surface soils from eastern China (18°N–50°N; Rao et al., 2009), together with those in modern conifer leaves and snow samples from Sapporo. The C<sub>27</sub>/C<sub>31</sub> ratios of the soil *n*-alkanes in the latitudes < 40°N are generally less than 1 with the exception of a few outliers at around 20°N, whereas the values of the soil *n*-alkanes in the latitudes > 40°N and plant leaves from Sapporo (43°N) exhibit large variations from 0.8 to 4.1 and 0.4 to 6.3, respectively (Fig. 5). In contrast, the C<sub>27</sub>/C<sub>31</sub> ratios of snow samples from Sapporo (43°N) ranged from 1.3 to 5.5 (Fig. 5), being similar to those in the latitudes > 40°N in East Asia including Japanese Islands. The results of backward trajectory analyses demonstrated that the air masses in the lower troposphere predominantly originated from the northern latitudes (> 40°N) of the Asian continent (Fig. 4) during the snow fall events, suggesting that relatively high C<sub>27</sub>/C<sub>31</sub> ratios (> 1) found in the Sapporo snow samples are most likely interpreted by the

long-range atmospheric transport of terrestrial *n*-alkanes from the northern regions of the continent.

### 3.3. Stable carbon and hydrogen isotope ratios of *n*-alkanoic acids in fresh snow samples from Sapporo

To further verify the above idea, that is, the terrigenous biomarkers in Sapporo snow samples are originated from the vegetations in the northern regions of the Asian continent, we measured stable carbon ( $\delta^{13}\text{C}$ ) and hydrogen ( $\delta\text{D}$ ) isotope ratios of  $\text{C}_{22}$ – $\text{C}_{28}$  even carbon-numbered *n*-alkanoic acids in the Sapporo snow samples and compared them with those in typical  $\text{C}_3$  gymnosperms from Sapporo and larch trees (*Larix*), one of the most dominant  $\text{C}_3$  gymnosperms in Siberian forest (Tchebakova et al., 2005), collected near Yakutsk, Russia (Fig. 1). We chose the long-chain *n*-alkanoic acids because they are the major components of higher plant waxes (Eglinton and Hamilton, 1967; Simoneit and Mazurek, 1982) but are not produced by human activities (e.g., the use of fossil fuels and cooking operations; Rogge et al., 1991, 1993) unlike *n*-alkanes.

In Fig. 6, we present the  $\delta^{13}\text{C}$ - $\delta\text{D}$  diagram of the *n*-alkanoic acids in the snow samples from Sapporo and the plant leaves from Sapporo and Yakutsk. The  $\delta^{13}\text{C}$  and  $\delta\text{D}$  values of  $\text{C}_3$  gymnosperm from Sapporo range from  $-34.9$  to  $-29.3\text{‰}$  and  $-158$  to  $-96\text{‰}$ , respectively. In contrast, those in *Larix* leaves from Yakutsk showed higher  $\delta^{13}\text{C}$  ( $-30.1$  to  $-27.9\text{‰}$ ) and lower  $\delta\text{D}$  ( $-223$  to  $-191\text{‰}$ ) values. On the other hand, the  $\delta^{13}\text{C}$  and  $\delta\text{D}$  values in the Sapporo snow samples showed intermediate values ranging from  $-33.4$  to  $-27.6\text{‰}$  and  $-208$  to  $-148\text{‰}$ , respectively. These values are plotted in the middle of the negative trend line between the plant leaves from Sapporo and Yakutsk (Fig. 6) though the relation is not statistically significant.

It is noteworthy that the  $\delta\text{D}$  values of the *n*-alkanoic acids in Sapporo snow samples are found more depleted with D by up to  $72\text{‰}$  than those of local vegetation (plant leaves) from Sapporo despite the  $\delta^{13}\text{C}$  values of the *n*-fatty acids in Sapporo snow

samples are in a similar range of those in plant leaves from Sapporo (Fig. 6). Although we collected the snow and plant samples in different days in the 2010 sampling, the  $\delta D$  values of plant leaves are generally constant in an order of weeks even in the growing season (Sachse et al., 2009). Further, quite similar isotope values between plant leaves collected from Sapporo in March 2010 and January 2011 (Fig. 6) also suggest that a time lag in collection of the samples is not responsible for differences in the stable isotope values between the snow and plant samples. Large differences in the  $\delta D$  values between the Sapporo snow and plant samples (Fig. 6), therefore, suggest that the *n*-alkanoic acids in the Sapporo snow samples should be, at least in part, derived from the vegetation whose isotopic compositions are distinct from those of the local plants in Sapporo.

Previous study reported that the  $\delta D$  values of terrestrial higher plant *n*-alkanes in East Asia decrease northwards as a function of latitude (Rao et al., 2009), reflecting the  $\delta D$  values of precipitation (IAEA/WMO, 2006). Given that the  $\delta D$  values of terrestrial *n*-alkanoic acids generally track those of the corresponding carbon-numbered *n*-alkanes with systematic offset (ca. 25‰; Chikaraishi and Naraoka, 2007), the lower  $\delta D$  values of *n*-alkanoic acids in Sapporo snow samples most likely suggest that they originate from vegetation in the latitudes further north of Sapporo. Indeed, we found D-depletion of by up to 95‰ in the  $\delta D$  values of plant leaves from Yakutsk compared to those in Tokyo and Sapporo (Fig. 6). As we mentioned in section 3.2, the backward trajectories demonstrated that the air masses were predominantly transported over Siberia, Russian Far East and northeast China during the snowfall events (Fig. 4). Hence, our results consistently suggest that the terrestrial biomarkers are long-range transported from the higher latitudes of the Asian continent to northern Japan by the Asian winter monsoon.

#### **4. Summary and conclusions**

In this study, we measured the molecular distributions of terrestrial

biomarkers and the stable carbon and hydrogen isotopic compositions of the HMW *n*-alkanoic acids in the snow samples collected from Sapporo, northern Japan, to better understand the source regions and transport pathways of the terrestrial biomarkers by the Asian monsoon. Our results showed that terrestrial organic matter is transported to the margin of the Asian continent including Japanese islands by the Asian winter monsoon, whereas the westerlies play an important role in the long-range transport of terrestrial organic matter to the remote sites in the North Pacific. This finding suggests that we need to pay more attention not only to the changes in the emission source strength but also the changes in the winter monsoon strength to better understand the transport of terrestrial organic matter to the western North Pacific. In addition, the airborne particles containing terrestrial biomarkers are eventually deposited over ice sheet and ocean floor without suffering major modification due to their refractory nature. Hence, our results also suggest that the molecular and stable isotope analyses of terrestrial biomarkers in marine sediments and ice cores provide a useful tool to reconstruct their source regions and transport pathways in the geological past.

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**Table 1.** Concentrations of lipid class compounds in snow from Sapporo, northern Japan

Sample	SP10-1	SP10-2	SP10-3	SP10-4	SP10-5	SP10-6	SP11-1	SP11-2	SP11-3	SP11-4	SP11-5	SP11-6
Date	14 Jan. 2010	16 Jan. 2010	17 Jan. 2010	1 Mar. 2010	5 Mar. 2010	22 Mar. 2010	6 Jan. 2011	7 Jan. 2011	14 Jan. 2011	17 Jan. 2011	31 Jan. 2011	1 Feb. 2011
Sampling time	13:15	15:50	16:10	13:30	14:35	11:15	16:00	11:00	18:20	17:15	10:30	10:30
Air temperature <sup>a</sup>	-3.7°C	-5.2°C	-2.4°C	-1.8°C	2.8°C	0.2°C	-7.5°C	-9.4°C	-7.0°C	-2.0°C	-4.6°C	-3.9°C
Snowfall	18 cm	9 cm	22.5 cm	3 cm	8 cm	5 cm	12.5 cm	12 cm	16 cm	30 cm	6 cm	31 cm
<i>n-Alkanes</i>												
LMW (C <sub>19</sub> -C <sub>24</sub> ) (µg L <sup>-3</sup> )	1.5	1.4	0.3	1.3	0.1	0.9	3.3	1.3	4.1	0.7	0.8	1.9
HMW (C <sub>25</sub> -C <sub>36</sub> ) (µg L <sup>-3</sup> )	13.3	2.7	0.6	3.4	0.3	3.5	4.0	3.9	4.6	2.9	1.0	3.0
Total	14.8	4.0	1.0	4.7	0.4	4.4	7.3	5.2	8.7	3.5	1.8	4.9
CPI <sub>LMW n-alkanes</sub> <sup>b</sup>	1.9	1.1	1.0	1.1	0.9	1.3	1.0	1.0	1.0	1.1	1.0	0.9
CPI <sub>HMW n-alkanes</sub>	18.1	5.9	4.3	4.9	2.5	7.5	3.2	2.9	2.9	4.4	3.4	2.9
<i>n-Alkanols</i>												
LMW (C <sub>14</sub> -C <sub>23</sub> ) (µg L <sup>-3</sup> )	4.1	1.3	0.3	1.6	0.2	2.0	2.3	1.3	1.2	0.4	0.7	1.3
HMW (C <sub>24</sub> -C <sub>30</sub> ) (µg L <sup>-3</sup> )	7.4	1.9	0.2	2.3	0.2	2.9	3.2	2.0	1.4	0.6	0.8	2.5
Total	11.4	3.2	0.4	3.8	0.4	4.9	5.5	3.3	2.7	1.0	1.5	3.8
CPI <sub>HMW n-alkanols</sub>	8.2	6.9	8.7	8.8	8.4	5.1	6.8	3.9	7.1	2.4	7.3	7.7
<i>n-Alkanoic acids</i>												
LMW (C <sub>12</sub> -C <sub>23</sub> ) (µg L <sup>-3</sup> )	20.0	21.6	2.0	19.4	3.1	15.6	1.8	1.6	0.5	0.5	2.2	7.5
HMW (C <sub>24</sub> -C <sub>34</sub> ) (µg L <sup>-3</sup> )	18.8	8.9	0.5	10.5	0.7	7.7	1.3	1.2	0.3	0.5	1.0	4.1
Total	38.8	30.5	2.5	29.8	3.7	23.3	3.1	2.8	0.8	1.0	3.3	11.6
CPI <sub>n-alkanoic acids</sub>	8.2	5.6	5.7	5.9	5.7	7.3	3.9	5.0	3.6	4.6	4.8	4.6

<sup>a</sup>Data from Japan Meteorological Agency Website, <http://www.data.jma.go.jp/obd/stats/etrn/index.php> (retrieved 1 Feb. 2011).

<sup>b</sup>CPI: carbon preference index: (C<sub>19</sub> + C<sub>21</sub> + C<sub>23</sub>)/(C<sub>20</sub> + C<sub>22</sub> + C<sub>24</sub>) for LMW *n*-alkanes; (C<sub>25</sub> + C<sub>27</sub> + C<sub>29</sub> + C<sub>31</sub> + C<sub>33</sub> + C<sub>35</sub>)/(C<sub>26</sub> + C<sub>28</sub> + C<sub>30</sub> + C<sub>32</sub> + C<sub>34</sub> + C<sub>36</sub>) for HMW *n*-alkanes; (C<sub>24</sub> + C<sub>26</sub> + C<sub>28</sub> + C<sub>30</sub>)/(C<sub>25</sub> + C<sub>27</sub> + C<sub>29</sub>) for HMW *n*-alkanols; (C<sub>12</sub> + C<sub>14</sub> + C<sub>16</sub> + C<sub>18</sub> + C<sub>20</sub> + C<sub>22</sub> + C<sub>24</sub> + C<sub>26</sub> + C<sub>28</sub> + C<sub>30</sub> + C<sub>32</sub> + C<sub>34</sub>)/(C<sub>13</sub> + C<sub>15</sub> + C<sub>17</sub> + C<sub>19</sub> + C<sub>21</sub> + C<sub>23</sub> + C<sub>25</sub> + C<sub>27</sub> + C<sub>29</sub> + C<sub>31</sub> + C<sub>33</sub>) for *n*-alkanoic acids.

## Figure captions

Fig. 1. Map showing the location of Sapporo, northern Japan.

Fig. 2. Molecular composition of (a) *n*-alkanes, (b) *n*-alkanols and (c) *n*-alkanoic acids in snow samples from Sapporo.

Fig. 3. Ternary plots of relative abundances of terrestrial biomarker in Sapporo snow. Areas surrounded by solid and dotted lined ellipses indicate the distribution of relative abundances of terrestrial biomarkers in the marine surface sediments from (A) low latitudes (12°S–12°N) and (B) high latitudes (15°N–48°N) of the central Pacific (Ohkouchi et al., 1997), (C) the marine aerosols collected from Chichi-Jima Island, western North Pacific in November–June, 1990–1993 (Kawamura et al., 2003), (D) the mountain aerosols collected at Mt. Tai, North China Plain in May–June, 2006 (Fu et al., 2008) and (E) the marine aerosols from the western Pacific (Bendle et al., 2007).

Fig. 4. Ten-day back air mass trajectories at (a) 500 m, (b) 3000 m, (c) 6000 m AGL (above ground level) during the snowfall events.

Fig. 5. Latitudinal distribution of  $C_{27}/C_{31}$  ratios of terrestrial higher plant-derived *n*-alkanes in surface soils from eastern China and snow and plant leaves from Sapporo, northern Japan.

Fig. 6. Cross plot of weighted mean  $\delta^{13}C$  and  $\delta D$  values of  $C_{22}$ – $C_{28}$  even carbon-numbered *n*-alkanoic acids in snow and plant leaves from Sapporo and Tokyo, Japan and Yakutsk, Russian Far East. Error bars indicate a standard deviation. <sup>a</sup>Data from Chikaraishi and Naraoka (2007).

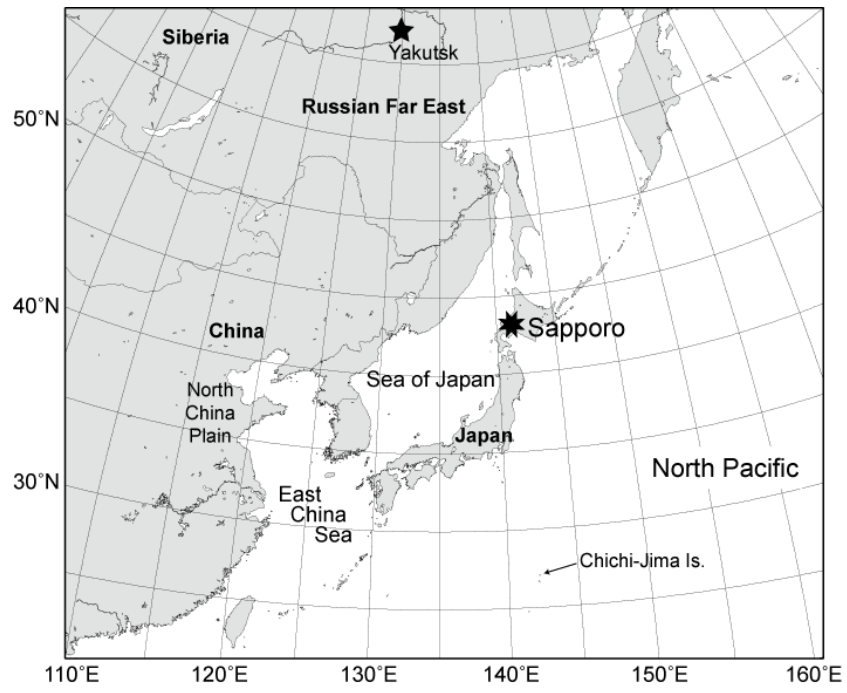


Fig. 1



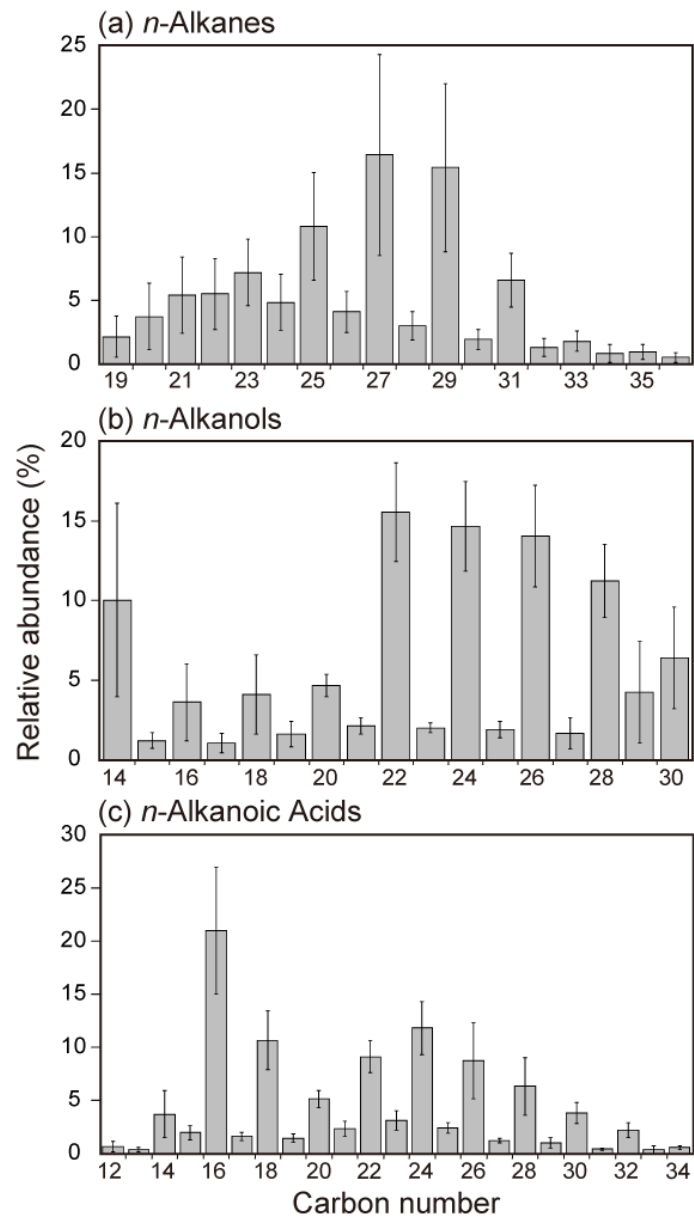


Fig. 2

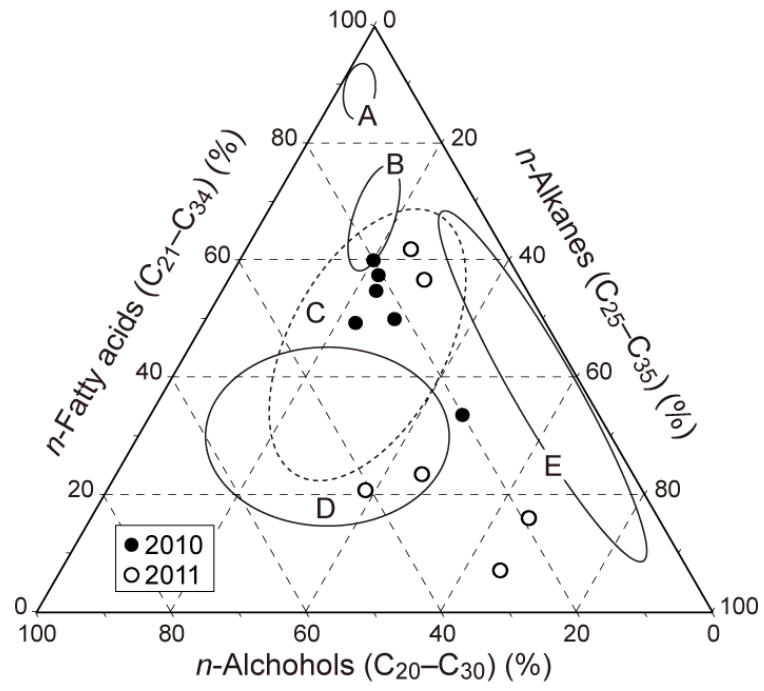


Fig. 3

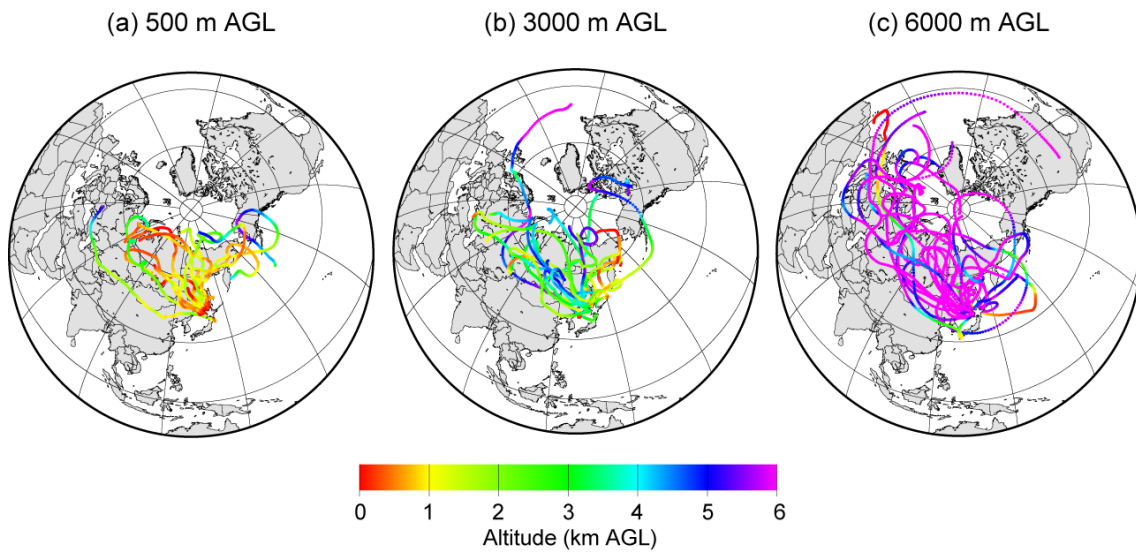


Fig. 4

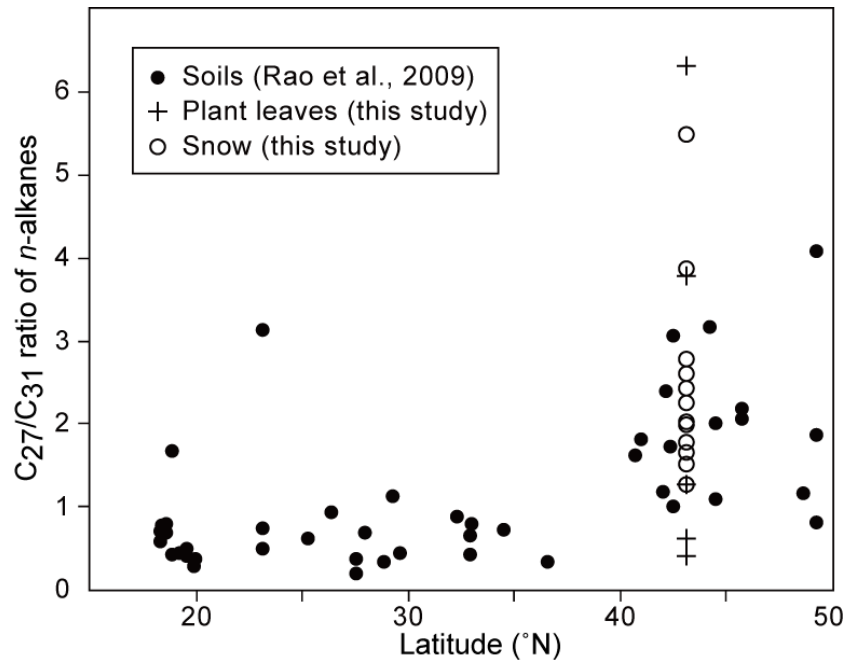


Fig. 5

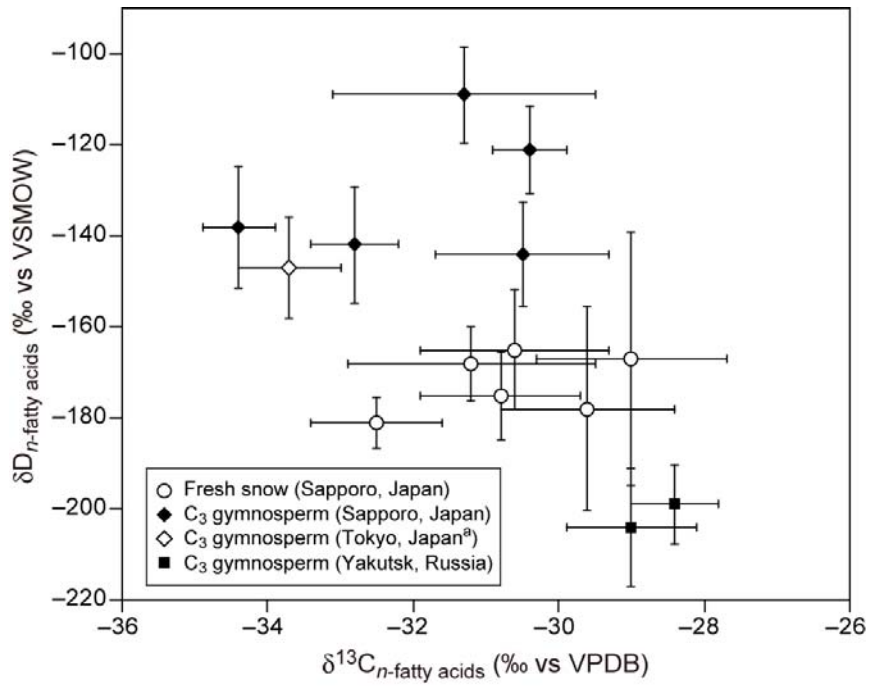


Fig. 6