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**n-Alkanes in Fresh Snow in Hokkaido, Japan: Implications for Ice Core Studies**

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**Abstract**

Plant waxes (e.g., long-chain n-alkanes) in ice cores are a promising paleovegetation proxy. However, much work needs to be done to assess how n-alkanes are transported from source areas to, and incorporated into, glacial archives. In this paper we present analyses of n-alkanes in seasonal snow and assess the information on source vegetation. n-Alkanes with carbon numbers C18 to C43 were extracted from snow samples collected at two sites in Hokkaido, northern Japan, during winter 2009–2010. Molecular distributions revealed that the majority of the n-alkanes originated from higher vegetation (ca. 65%), rather than anthropogenic sources. The distribution characteristics confirmed that the n-alkane signal had a wide regional origin, rather than a local source. We determined stable carbon and hydrogen isotopic compositions for the C27 n-alkane. The δ13C of the C27 (-28.2 to -33.0‰) was more representative of C3 than C4 vegetation, while the δD of the C27 (-169.9 to -223.1‰) indicated growth latitudes more northerly than Hokkaido. The n-alkanes in the snow preserve information about the source vegetation type (photosynthetic group, growth site), confirming that if deposited with seasonal snows that firnify to form glacial ice, they have potential to record broad, regional vegetation changes over time.

**Introduction**

Surfaces of all terrestrial higher plants are covered with protective waxes, consisting mainly of high molecular weight n-alkanes, n-alcohols, and n-fatty acids (e.g., Eglinton and Hamilton, 1967). Plant wax distributions and isotopic compositions are affected by the photosynthetic pathway employed by the source plant, hydrological and other environmental conditions, as well as the plant physiology (e.g., Collister et al., 1994; Lockheart et al., 1997; Bi et al., 2005; Liu et al., 2006; Sachse et al., 2006; Smith and Freeman, 2006; Hou et al., 2007; Vogts et al., 2009). Long-chain n-alkanes are especially resistant to biodegradation, as they lack reactive double and triple bonds, and they have no functional groups. When deposited into natural archives, n-alkanes retain information on their plant sources and can be utilized as a paleovegetation proxy dating back thousands (e.g., Jansen and Nierop, 2009) to tens or hundreds of millions of years (e.g., Tipple and Pagani, 2010; Ruhl et al., 2011).

Plant wax components are sloughed off from plant surfaces and introduced to natural archives in multiple ways. Once ablated off plants by wind and dust, they can be deflated to the atmosphere and transported over long distances as atmospheric particles. Rain and snow scavenge plant waxes from the atmosphere and deposit them on land, water, or snowfields. Plant waxes can also be deposited directly onto the ground by falling plant debris. Once on the ground, plant wax particles accumulate in soil, or are carried by rainwater into lakes, oceans, or other low-energy environments, where they finally accumulate in sedimentary archives.

Ice cores also function as plant wax archives, but so far they have been rarely utilized as such. Where seasonal snow accumulates, firnifies, and forms glaciers, plant wax particles accumulate within the ice. Long chain n-alkanes, being chemically inert, are not suspected to take any significant part in the snowpack or ice photochemistry. The difficulty of extracting plant wax molecules from glacial samples lies in their small concentrations: acquiring glacial samples is costly, large sampling volumes are necessary, and the whole process, from sampling to laboratory work, is highly sensitive to contamination. Nevertheless, n-alkanes from polar or mountainous ice archives have unrealized potential as a paleovegetation proxy.

There is little previous research on n-alkanes or other plant waxes in ice archives. A 206-m-long Greenland ice core has been analyzed for n-fatty acids of both marine and plant wax origin, and their fluctuations have been related to climatic variations (Kawamura et al., 1995, 1996). Two subsamples from the same core (dated to 1941 and 1881 A.D.) have been extracted for various lipid compounds, among them n-alkanes. Their distribution shows that at least a part of the n-alkanes originated from terrestrial vegetation (Kawamura and Suzuki, 1991). More recent n-alkane deposition has been quantified in two short cores (25.3 m and 18.7 m) acquired from the Russian Altai Mountains. Plant wax n-alkanes were found in both cores, although due to the sampling locations and the modern nature of these cores, in most samples the anthropogenic n-alkane fraction was larger than the contribution from terrestrial vegetation (Miyake et al., 2005, 2006).
Although the presence of \textit{n}-alkanes has been reported within glacial ice, and the molecular distributions of the \textit{n}-alkanes in short ice cores have been quantified, their compound-specific isotopic compositions in ice archives have, to our knowledge, not been reported. To explore the untapped potential of compound-specific isotopes to extract information from the plant waxes in ice archives, we extracted \textit{n}-alkanes from a series of seasonal snow samples and assessed the type of information they yield on their source vegetation. We set out to answer the following research questions:

(1) Do the \textit{n}-alkanes in the snow samples originate from plant surface waxes?

(2) Are the \textit{n}-alkanes of just local origin or do they arrive (and encode information) from a broader geographical region?

(3) What do the \textit{n}-alkanes reveal about their source vegetation?

\textit{n}-Alkanes in different types of snow samples (e.g. freshly fallen snow and glacial surface snow pits) have been reported before (Meyers and Hites, 1982; Kawamura and Kaplan, 1986; Leuenberger et al., 1988; Desideri et al., 1994; Gröllert et al., 1997; Desideri et al., 1998; Gröllert and Puxbaum, 2000; Xie et al., 2000; Satsumabayashi et al., 2001; Miyake et al. 2005, 2006; von Schneidemesser et al., 2008; Li et al., 2009; Yamamoto et al., 2011). However, to our knowledge, this is the first study where fresh snow was sampled throughout a whole winter season (December 2009–April 2010) and \textit{n}-alkane stable carbon and hydrogen isotopic compositions co-reported.

Yamamoto et al. (2011) recently reported stable carbon and hydrogen isotopic compositions for \textit{n}-alkanoic acids (a different chemical class to \textit{n}-alkanes) in snowfall events, and found evidence of long-range transported higher plant waxes in samples of seasonal snow. By studying \textit{n}-alkanes in a similar setting throughout the season, we provide more insights into the higher plant sources, as well as the atmospheric transport pathways. Assessing the locality vs. regionality of the plant wax signal in the seasonal snow is particularly important, as it bears much relevance to the feasibility of using \textit{n}-alkanes in glacial archives as a regional paleovegetation proxy.

\section*{Sampling and Methods}

\subsection*{SAMPLING SITES}

A total of 17 snow samples were collected at two sites in Hokkaido (Fig. 1) during December 2009–April 2010. Eight samples were acquired from a forest research site (Hokkaido Research Centre, Forestry and Forest Products Research Institute; 42°59′12″N, 141°23′7″E, 182 m a.s.l.) ca. 10 km away from the Sapporo urban center, and nine samples from a similar forest research site (Uryu Experimental Forest of Hokkaido University; 44°03′29″N, 142°01′20″E, 290 m, a.s.l.) in Moshiri, 200 km north of Sapporo. During the winter season the sites were not accessible by car, which lessened the direct anthropogenic hydrocarbon input to the snow pack.

We minimized incorporation of local wind-blown debris (e.g. small pieces of bark) by taking care to sample the snow pack where the snow was cleanest. In Moshiri snow was always sampled fresh, either immediately after or during a snowfall event. In Sapporo the snow was sampled roughly at a 10-day interval, and in some cases the sampled snow was 1–3 days old.

\subsection*{SAMPLE PREPARATION AND ANALYSIS}

Snow was collected into pre-cleaned glass jars with Teflon-lined screw caps, using a clean stainless steel scoop. A sample jar of 8 L yielded between 0.6 and 2.3 L of meltwater, depending on the snow conditions and the compaction rate. Samples were melted at +4 °C. After acidifying the meltwater with 4 M HCl to pH = 1, samples were extracted for lipids with a mixture of dichloromethane and ethyl acetate (2:1). After saponification, the neutral fraction was extracted with a mixture of \textit{n}-hexane and dichloromethane (9:1). Neutral compounds were divided into fractions of varying polarity by means of silica-gel column chromatography. The normal hydrocarbon fraction was obtained by eluting with 2.5 mL of \textit{n}-hexane. To minimize laboratory contamination, all solvents were distilled and other chemicals (e.g. KOH, HCl) were cleaned or extracted with appropriate solvents before use.

\textit{n}-Alkane abundances were determined with an Agilent 6890 gas chromatograph (GC) equipped with CPSIL-5CB fused silica capillary column (50 m × 0.32 mm i.d., film thickness 0.25 μm), on-column injector and flame ionization detector (FID). The GC oven temperature was programmed from 70 °C to 120 °C at 30 °C min$^{-1}$ and from 120 °C to 310 °C at 5 °C min$^{-1}$, and was held at 310 °C for 20 min.

A detailed procedure for the compound-specific isotopic measurements is described in Seki et al. (2010). Briefly, δ^{13}C values were acquired with a compound-specific isotopic ratio mass spectrometry (CS-IRMS) system comprising a HP 6890 GC and a Finnigan MAT Delta Plus mass spectrometer. δD values were obtained using a CS-IRMS system with a HP 6890 gas chromatograph and a ThermoQuest Finnigan MAT Delta Plus XL mass spectrometer. Separation of the \textit{n}-alkanes was achieved with a HP-5 MS fused silica capillary column (30 m × 0.32 mm i.d., film thickness of 0.25 μm) with a cooled on-column injector. δ^{13}C and δD values indicate depletion against the international standards: Vienna Pee Dee Belemnite (V-PDB) is the standard for δ^{13}C and Vienna Standard Mean Ocean Water (V-SMOW) for δD. C_{21} n-fatty acid methyl ester whose isotopic values were known was co-injected with the samples as an internal isotopic standard for δD and δ^{13}C.

A laboratory standard containing C_{16}–C_{30} \textit{n}-alkanes was analyzed daily to check the accuracy and the drift of the instrument and to normalize the data to the SMOW/SLAP isotopic scale. H^{3+} factor was measured every three days. All the laboratory work and isotope measurements were performed at the Institute of Low Temperature Science, Hokkaido University.

In addition to the laboratory analysis, a 27 member ensemble of 5-day air mass back trajectories was created for each snowfall event. Trajectories start at a height of 250 m and the ensemble is created by offsetting the starting location slightly in the x-, y-, and z-directions. Trajectories were calculated by NOAA ARL’s online HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) tool (Draxler and Rolph, 2011; Rolph, 2011). All Moshiri samples and some of the Sapporo samples were collected during
a snowfall event, in which case the sampling time was chosen as
the start of the backwards run. If a Sapporo sample was collected
after a snowfall event, the starting time was chosen with the help of
precipitation data from a weather station situated near the sampling
location.

ACCURACY

Recovery of the \( n \)-alkanes was assessed with a series of 3
recovery tests performed for the C\(_{27} \) \( n \)-alkane, yielding a recovery
of 93 ± 5%. Results are corrected for the blank levels, but not for
recovery. Variation of the recovery rate incorporates the various
errors associated with extraction, silica gel chromatography, and
other procedures preceding the GC-FID measurement. Since the
errors resulting from the GC-FID measurement are <5%, the error
margin of 5% is used as the comprehensive error margin for the
total concentrations.

Blank concentrations of the \( n \)-alkanes were obtained by labo-
atory blank runs performed at the beginning and at the end of
the laboratory working period. Averaging these, a total \( n \)-alkane
contamination level of 20 ng L\(^{-1} \) was obtained. This is 6% of
the lowest total \( n \)-alkane concentration (331 ng L\(^{-1} \)) and 0.4% of
the highest total concentration (5290 ng L\(^{-1} \)). Blanks contained individual homologue contamination ranging from C\(_{25} \) to C\(_{37} \), C\(_{27} \) hav-
ing the largest concentration (4 ng L\(^{-1} \) on average). As C\(_{27} \) was
the most abundant \( n \)-alkane in the majority of the actual samples,
blank contamination levels may reflect some residue from the pre-
viously processed samples, instead of originating from e.g. labora-
tory chemicals.

We base our isotopic precision (and error bars in Figs. 8 and
9) on repeated injections of an external standard of \( n \)-alkanes (mix-
ture of various carbon numbers from C\(_{15} \) to C\(_{33} \)) of known isotopic
composition and replicates of the samples in this study (\( \delta^{13} \)C values
are based on 2–5 measurements each, and \( \delta^{15} \)N values on 1–2
measurements each). These two methods gave a reproducibility of
±0.5‰ for \( \delta^{13} \)C and ±5‰ for \( \delta^{15} \)N.

Results and Discussion

CONCENTRATIONS

\( n \)-Alkanes from C\(_{18} \) to C\(_{43} \) were detected in the snow samples.
For each sample the molecular distributions are presented alongside
air mass back-trajectories (for the sample snowfall event) in Figure
2 (Sapporo samples) and Figure 3 (Moshiri samples). The air mass
back-trajectories point to the potential vegetation source areas of
the \( n \)-alkanes atmospherically transported to the snowfield sam-
ples. Sample information and distribution parameters are
listed in Table 1.

Total \( n \)-alkane concentrations ranged between 393 and 5290
ng L\(^{-1} \) in Sapporo (Fig. 4), and between 331 and 4881 ng L\(^{-1} \) in
Moshiri (Fig. 5). This range of concentrations is comparable with
previous studies of \( n \)-alkanes in snow, especially with Meyers and
Hites (1982), Kawamura and Kaplan (1986), Leuenberger et al.
(1988), Satsumabayashi et al. (2001), and Yamamoto et al. (2011),
who have also sampled seasonal snow. \(n\)-Alkane concentrations reported in glacial surface snow and snow pits are typically somewhat lower, due to the remoteness of the sampling locations (Desideri et al., 1994, 1998; Xie et al., 2000; Miyake et al., 2005, 2006; von Schneidemesser et al., 2008; Li et al., 2009).

No trend in the total \(n\)-alkane concentration was detected at either site from late autumn to spring. Both the concentrations and the distributions of the \(n\)-alkanes varied significantly from one snowfall event to another, and this variability persisted throughout the season. The predominant weather type causing snow in Hokkaido is wind from the north or the northwest, bringing cold air from the Siberian landmass. This is illustrated by the 5-day back-trajectories for each sampling event presented in Figures 2 and 3. Snow sampling studies are generally limited to looking at snow-bearing air masses coming from a specific direction. This may also be the case with a glacial sampling site, and should be borne in mind when interpreting a plant wax signal from within an ice core.

**CARBON PREFERENCE INDEX AND PLANT WAX PERCENTAGE**

Carbon Preference Index (CPI) quantifies the odd-over-even-predominance over a range of \(n\)-alkanes in a sample. We have calculated the CPIs for the range \(C_{23}\) to \(C_{35}\):

\[
\text{CPI} = \frac{1}{2} \left[ \frac{\sum C_{23} \ldots C_{35}}{\sum C_{22} \ldots C_{34}} + \frac{\sum C_{23} \ldots C_{35}}{\sum C_{24} \ldots C_{36}} \right]
\]

\(C_{22}, C_{23}, \ldots\) refer to the concentrations of the \(n\)-alkanes. Generally a low CPI (~1) indicates that the \(n\)-alkanes originate predominantly from anthropogenic sources, whereas a higher CPI signifies vascular plant input (e.g. Simoneit, 1986). There is some evidence that individual plants can produce waxes with low CPI (~2) values (Liebezeit and Wöstmann, 2009), but this is expected to have limited influence in our samples, which likely integrate a diverse mixture of vegetation types, via regional-scale atmospheric transport processes.

In the Sapporo samples, CPI ranged from 1.4 to 27.9, with an average of 8.7. CPI for the Moshiri samples ranged from 1.2 to 7.5, with an average of 3.2. CPI also varied considerably between individual snowfall events, and the much higher average CPI in the Sapporo samples is largely due to the first two samples (S1 and S2) having a high CPI. All CPI values are listed in Table 1.

CPI values indicate that both vascular plant and anthropogenic \(n\)-alkanes are present in the samples. The plant wax contribution can be estimated by subtracting from each homologue the average of the adjacent members (Simoneit et al., 1991):

\[
\text{WaxC}_n = \frac{C_n - C_{n+1} + C_{n-1}}{2}
\]

\(C_n\) again refers to the concentration of the \(n\)-alkanes. The ratio \(\text{WaxC}_n/C_n\) multiplied by 100 gives a percentage value (Wax%) that estimates the contribution from terrestrial plant waxes (assuming \(n\)-alkanes in a sample originate from either terrestrial vegetation or anthropogenic sources, and the CPI of the anthropogenic \(n\)-alkanes is taken to be exactly 1). Wax% for the range \(C_{23}\)–\(C_{35}\) is obtained by calculating the individual Wax% for each odd homologue in the range and taking a weighted average.
The plant wax contribution for the odd \( n \)-alkanes in the range \( C_{23} - C_{35} \) is 28–96% in the Sapporo samples, and 15–87% in the Moshiri samples. In 13 out of 17 samples, the vascular plant input for \( C_{23} - C_{35} \) is higher than 50%. For the \( C_{27} \) \( n \)-alkane the wax input is even higher: 48–98% in Sapporo, 20–91% in Moshiri, and more than 50% in 14 out of 17 samples. Thus the \( n \)-alkanes in the snow samples, and \( C_{27} \) in particular, originate predominantly from plant waxes.

The wax% values also address the locality versus regionality of the \( n \)-alkane signal. Although the Sapporo sampling campaign took place in a research forest with no vehicle access, the site was fairly close to the Sapporo urban area. It is a concern that anthropogenic input from the nearby city center might dominate the Sapporo samples. From the generally high Wax% values, we conclude that this did not happen. In comparison, plant wax contributions to urban-site aerosol particles collected in Taiwan ranged from 4.8% to 32% (Lin and Lee, 2004). Evidently, the origin of the \( n \)-alkanes in our snow samples is not restricted to the nearby areas, i.e. if the Sapporo urban area inputs were stronger, we would see smaller plant wax percentages, as well as less Wax% variability in the Sapporo samples.

Air mass back-trajectories, shown in Figures 2 and 3, serve to illustrate the prevailing wind directions that bring snowfall to Hokkaido. It might be expected that samples with the smallest plant wax percentages would be accompanied by back-trajectories crossing the most densely populated areas (see Fig. 6, part a). However, a comparison of the urban area extent in Asia with the relevant 5-day back-trajectories does not lead to any obvious conclusions.

As well as anthropogenic and freshly ablated plant waxes, fossil/soil \( n \)-alkanes contributed to our samples. Specifically, the last sample acquired from Sapporo (S8) was collected shortly after a yellow dust storm occurred in China and westerly winds brought yellow dust particles ("Kosa") to Japan. \( n \)-Alkanes originating from loess can have a lower odd-over-even preference than ones freshly scoured off from vegetation; for example, Liu and Huang (2005) report CPI values ranging from 2.0 to 9.9 for \( n \)-alkanes in the Chinese Loess Plateau. The snow sample S8 has the lowest CPI (1.4) and Wax% (28%) of all the Sapporo samples, along with a high total \( n \)-alkane concentration (4648 ng L\(^{-1}\)). This is likely due to the contribution of the \( n \)-alkanes associated with the yellow dust (i.e. including fossil \( n \)-alkanes deflated from the soil reservoir).
### TABLE 1
Sample information and \( n \)-alkane ranges, concentrations, and distributions in the Sapporo and Moshiri samples. ACL = average chain length, CPI = carbon preference index.

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>Code</th>
<th>Meltwater volume (1)</th>
<th>Total n-alkane concentration (ng/L)</th>
<th>( C_{\text{range}} )</th>
<th>( C_{\text{max}} ) concentration (ng/L)</th>
<th>ACL for ( C_{23} - C_{35} )</th>
<th>CPI for ( C_{23} - C_{35} )</th>
<th>Wax % for ( C_{23} - C_{35} )</th>
<th>Wax % for ( C_{27} )</th>
<th>( C_4 ) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapporo</td>
<td>29 Dec 2009</td>
<td>S1</td>
<td>1.2</td>
<td>3907</td>
<td>( C_{20} - C_{38} )</td>
<td>1650</td>
<td>26.4</td>
<td>27.9</td>
<td>96</td>
<td>98</td>
<td>24</td>
</tr>
<tr>
<td>Sapporo</td>
<td>7 Jan 2010</td>
<td>S2</td>
<td>1.0</td>
<td>3993</td>
<td>( C_{21} - C_{39} )</td>
<td>1433</td>
<td>27.6</td>
<td>17.4</td>
<td>94</td>
<td>96</td>
<td>19</td>
</tr>
<tr>
<td>Sapporo</td>
<td>19 Jan 2010</td>
<td>S3</td>
<td>1.2</td>
<td>1051</td>
<td>( C_{21} - C_{42} )</td>
<td>248</td>
<td>27.8</td>
<td>2.9</td>
<td>66</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Sapporo</td>
<td>29 Jan 2010</td>
<td>S4</td>
<td>1.0</td>
<td>5290</td>
<td>( C_{19} - C_{43} )</td>
<td>1109</td>
<td>27.6</td>
<td>4.6</td>
<td>78</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>Sapporo</td>
<td>10 Feb 2010</td>
<td>S5</td>
<td>2.0</td>
<td>5132</td>
<td>( C_{18} - C_{44} )</td>
<td>1521</td>
<td>27.8</td>
<td>8.6</td>
<td>88</td>
<td>91</td>
<td>20</td>
</tr>
<tr>
<td>Sapporo</td>
<td>23 Feb 2010</td>
<td>S6</td>
<td>2.2</td>
<td>2266</td>
<td>( C_{18} - C_{42} )</td>
<td>482</td>
<td>27.4</td>
<td>4.8</td>
<td>79</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>Sapporo</td>
<td>5 Mar 2010</td>
<td>S7</td>
<td>2.1</td>
<td>393</td>
<td>( C_{18} - C_{40} )</td>
<td>50</td>
<td>27.1</td>
<td>2.1</td>
<td>52</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>Sapporo</td>
<td>25 Mar 2010</td>
<td>S8</td>
<td>2.3</td>
<td>4648</td>
<td>( C_{20} - C_{42} )</td>
<td>473</td>
<td>28.4</td>
<td>1.4</td>
<td>28</td>
<td>48</td>
<td></td>
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<tr>
<td>Moshiri</td>
<td>9 Dec 2009</td>
<td>M1</td>
<td>1.0</td>
<td>4881</td>
<td>( C_{19} - C_{43} )</td>
<td>790</td>
<td>27.9</td>
<td>2.3</td>
<td>55</td>
<td>54</td>
<td></td>
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<tr>
<td>Moshiri</td>
<td>17 Dec 2009</td>
<td>M2</td>
<td>0.6</td>
<td>884</td>
<td>( C_{21} - C_{40} )</td>
<td>103</td>
<td>28.9</td>
<td>1.2</td>
<td>20</td>
<td>30</td>
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<tr>
<td>Moshiri</td>
<td>15 Jan 2010</td>
<td>M3</td>
<td>0.9</td>
<td>331</td>
<td>( C_{22} - C_{43} )</td>
<td>54</td>
<td>28.4</td>
<td>1.8</td>
<td>44</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>Moshiri</td>
<td>22 Jan 2010</td>
<td>M4</td>
<td>0.9</td>
<td>1388</td>
<td>( C_{22} - C_{42} )</td>
<td>172</td>
<td>29.7</td>
<td>1.2</td>
<td>15</td>
<td>20</td>
<td></td>
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<tr>
<td>Moshiri</td>
<td>4 Feb 2010</td>
<td>M5</td>
<td>1.7</td>
<td>704</td>
<td>( C_{19} - C_{44} )</td>
<td>87</td>
<td>27.5</td>
<td>2.5</td>
<td>59</td>
<td>73</td>
<td></td>
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<tr>
<td>Moshiri</td>
<td>23 Feb 2010</td>
<td>M6</td>
<td>1.3</td>
<td>2362</td>
<td>( C_{18} - C_{41} )</td>
<td>364</td>
<td>27.1</td>
<td>2.5</td>
<td>59</td>
<td>70</td>
<td></td>
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<tr>
<td>Moshiri</td>
<td>15 Mar 2010</td>
<td>M7</td>
<td>1.4</td>
<td>2639</td>
<td>( C_{19} - C_{39} )</td>
<td>624</td>
<td>27.0</td>
<td>5.3</td>
<td>81</td>
<td>87</td>
<td></td>
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<tr>
<td>Moshiri</td>
<td>18 Mar 2010</td>
<td>M8</td>
<td>1.2</td>
<td>1884</td>
<td>( C_{19} - C_{39} )</td>
<td>400</td>
<td>27.3</td>
<td>4.3</td>
<td>76</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>Moshiri</td>
<td>7 Apr 2010</td>
<td>M9</td>
<td>2.1</td>
<td>2273</td>
<td>( C_{18} - C_{38} )</td>
<td>638</td>
<td>27.3</td>
<td>7.5</td>
<td>87</td>
<td>91</td>
<td>11</td>
</tr>
</tbody>
</table>

### AVERAGE CHAIN LENGTH

Average chain length was calculated for the range \( C_{23} \) to \( C_{35} \):

\[
ACL = \frac{23C_{23} + 25C_{25} + \ldots + 35C_{35}}{\text{odd}}
\]  

(3)

ACL for each sample is given in Table 1, along with the most abundant homologue (\( C_{\text{max}} \)). ACL ranged from 26.4 to 28.4 in the Sapporo samples, averaging 27.5 for the whole season. ACL for the Moshiri samples was somewhat higher, ranging from 27.0 to 29.7 and averaging 27.9. Similar ACL values are reported for \( C_3 \) trees (e.g. birch, beech, oak, alder) growing in the latitude band 42°–67° (Sachse et al., 2006). The ACL of the \( n \)-alkanes extracted from the Hokkaido snow most likely reflects a large input of plant waxes from \( C_3 \) trees, which make up a large portion of the Siberian vegetation (see Fig. 6, parts b and c).

Comparison of the ACL and Wax% gives insights to the regionality of the \( n \)-alkane signal in the snow. Jeng (2006) has reported a positive correlation between \( n \)-alkane CPI/Wax% and ACL in polluted riverine and marine sediments in southwestern Taiwan. Because the petrogenic \( n \)-alkanes produced by human activities have a lower ACL than those originating from terrestrial vegetation, their addition to plant \( n \)-alkanes lowers the ACL as well as Wax%. However, as Jeng (2006) points out, this correlation happens in a setting where the terrigenous \( n \)-alkanes in the sediment originate from the local vegetation, and thus ACL does not vary greatly. ACL generally increases with decreasing latitude (e.g. Simoneit et al., 1991; Kawamura et al., 2003; Sachse et al., 2006; Bendle et al., 2007), thus a regional, broad-scale, plant wax signal...
FIGURE 6. (a) Urban area extent in Asia, as the percentage of urban 0.5 × 0.5 km pixels in 5 × 5 km bins. (b) Land use classes and urban areas in Asia. Data for both parts a and b are from the MODIS 500-m global map of urban extent (Schneider et al., 2009, 2010). In part b, several land use classes are combined: forest includes all forest types (1–5); shrub- and grasslands include open and closed shrublands, savannas, and grasslands (6–10); and a land use class defined as a mosaic of crops and other land cover types is included in croplands (12, 14). Numbers refer to the International Geosphere-Biosphere Programme (IGBP) scheme of 17 land use classes. (c) Distribution of C₄ vegetation in Asia (Still et al., 2009).
mixed with a petrogenic \( n \)-alkane signal might not lead to a similar correlation.

The above is of immediate interest for this study, because in the Moshiri data set, just the opposite correlation is found. For the Moshiri samples, ACL and Wax\% have a clear negative Pearson’s correlation of \( r = -0.94 \), with \( p = 0.0001 \) (Fig. 7). In this case lower ACL values coincide with higher plant wax contribution. No statistically significant correlation between the two is found in the Sapporo samples.

The urban area extent map of northern Asia (Fig. 6, part a) offers a possible mechanism for the negative correlation between ACL and Wax\%. As noted before, individual back-trajectories have a limited explanation power as to why the Wax\% varies from one sample to another. However, in northern Asia the urban area extent diminishes with latitude as well. \( n \)-Alkanes originating from further north are likely to have a smaller petrogenic contribution and therefore bigger plant wax percentage, and at the same time lower ACL.

An alternative explanation for the negative correlation between Wax\% and ACL is varying input from forested areas and grasslands. Plant waxes originating from trees tend to have lower ACL than plant waxes of shrubs and grasses (e.g. Vogts et al., 2009). Figure 6, part b, shows the distribution of forested areas and grasslands in northern Asia (Schneider et al., 2009, 2010). If air masses originating from forested areas carried more plant wax \( n \)-alkanes than air masses originating from grasslands, a negative correlation between ACL and plant wax contribution would pertain.

Whichever explanation is valid, a negative correlation between ACL and Wax\% further supports the conclusion that the \( n \)-alkane signal in the Moshiri samples originates from a broad region rather than the local area. If both plant wax \( n \)-alkanes and anthropogenic \( n \)-alkanes found in these samples originated from local sources only, then a result similar to that of Jeng (2006) would be expected: events with a higher local anthropogenic input would coincide with lower rather than higher ACL. Our finding is similar to that of Yamamoto et al. (2011), who also sampled seasonal snow in Hokkaido, but focused on \( n \)-alkanoic acids rather than \( n \)-alkanes (which have significantly different chemical properties); they concluded that \( n \)-alkanoic acids in seasonal Hokkaido snow portrayed evidence of long-range atmospheric transport by the Asian winter monsoon.

The fact that no significant correlation is found between ACL and Wax\% in Sapporo, and a strong correlation is found in Moshiri, likely arises from the different sampling conditions at the two sites. At Moshiri, snowfall was generally heavy and fresh snow could be sampled. In such conditions it is more likely that each sample reflects the characteristics of just the one snowfall event. In Sapporo the snow was sampled at a 10-day interval, and snowfall was generally more sparse than in Moshiri. It is probable that some mixing occurred among the Sapporo snowfall events.

### STABLE CARBON ISOTOPIC COMPOSITION

\( \delta^{13}C \) values for different homologues are presented in Table 2. We prioritized acquiring both stable carbon and hydrogen isotope compositions when possible, which often left little plant wax material for the \( \delta^{13}C \) measurement. As a result, \( C_{27} \) was the only homologue for which \( \delta^{13}C \) was acquired for both sites throughout the whole season.

Terrestrial higher plants with different photosynthetic pathways (\( C_3 \), \( C_4 \), CAM) show differing levels of \( ^{13}C \) depletion both in their bulk tissue and individual compounds (e.g. Smith and Epstein, 1971; O’Leary, 1981; Rieley et al., 1993). Compound-specific \( \delta^{13}C \) for \( C_{27} \) ranged from \(-30.6\%e\) to \(-32.3\%e\) in Sapporo, while in Moshiri the range was broader, from \(-28.2\%e\) to \(-33.0\%e\) (Figs. 8 and 9). These values are more representative of \( C_3 \) than \( C_4 \) vegetation.

Assuming that both vegetation groups contribute to the \( n \)-alkanes in the snow, the \( C_4 \) contribution is obtained from (Chesselet et al., 1981):

\[
\frac{C_4}{C_{alk}} = \frac{\delta^{13}C_{alk} - \delta^{13}C_3}{\delta^{13}C_{C_4} - \delta^{13}C_3}
\]

A possible contribution from CAM plants (e.g. cacti) is not considered, as they are restricted to areas remote from our sampling sites. Here \( C_{alk} \) is the total concentration of \( C_{27} \) in a given sample, \( C_4 \) is the contribution from \( C_4 \) plants, and \( \delta^{13}C_{alk} \) is the measured \( \delta^{13}C \) for \( C_{27} \). \( \delta^{13}C_3 \) and \( \delta^{13}C_4 \) are obtained from literature. This method is only valid if the bulk of the \( n \)-alkanes originates from terrestrial vegetation. We take a conservative approach and estimate the \( C_4 \) contribution for only those samples with the \( C_{27} \) plant wax proportion exceeding 90%. This criterion is fulfilled by 4 samples: 3 from Sapporo (S1, S2, S5) and 1 from Moshiri (M9).

\( \delta^{13}C \) for the \( C_{27} \) \( n \)-alkane has been reported in several studies of one or more plant species (e.g. Collister et al., 1994; Lichtfouse et al., 1994; Huang et al., 1997; Lockheart et al., 1997; Chikaraishi and Naraoka, 2003; Bi et al., 2005; Rommerskirchen et al., 2006; Pedentchouk et al., 2008; Vogts et al., 2009). We have chosen to use \( \delta^{13}C_3 \) and \( \delta^{13}C_4 \) as obtained by Chikaraishi and Naraoka (2003), because they have sampled plants growing in their natural habitats in Japan and Thailand, fairly close to our study region. Based on their results, \( \delta^{13}C \) for \( C_{27} \) is \(-34.6\%e\) for \( C_3 \) plants (average of 22 species) and \(-20.1\%e\) for \( C_4 \) plants (average of 6 species).

Using the above method, the contribution of \( C_4 \) plants varies from 11% to 24% in the 4 selected samples. Any comparison be-
TABLE 2
Stable carbon and hydrogen isotopic composition of the n-alkanes in the Sapporo and Moshiri samples. V-SMOW = Vienna Standard Mean Ocean Water, and V-PDB = Vienna Pee Dee Belemnite.

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<td>δD, ‰ (against V-SMOW)</td>
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<td>C&lt;sub&gt;20&lt;/sub&gt;</td>
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<td>C&lt;sub&gt;21&lt;/sub&gt;</td>
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<td>-202.3</td>
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<td>-200.0</td>
<td>-176.3</td>
<td>-196.9</td>
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<td>C&lt;sub&gt;23&lt;/sub&gt;</td>
<td>-211.3</td>
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<td>C&lt;sub&gt;24&lt;/sub&gt;</td>
<td>-224.0</td>
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<td>C&lt;sub&gt;25&lt;/sub&gt;</td>
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| δ<sup>13</sup>C, ‰ (against V-PDB) |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| C<sub>20</sub> | -32.0 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| C<sub>21</sub> | -32.0 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| C<sub>22</sub> | -29.1 | -25.6 | -28.2 | -29.0 | -29.3 | -27.3 | -30.2 | -28.3 | -27.5 | -30.6 | -29.3 | -36.9 |
| C<sub>23</sub> | -29.7 | -29.8 | -28.5 | -29.3 | -27.2 | -30.8 | -32.4 | -32.8 | -28.8 | -30.9 | -32.8 |     |     |     |     |     |
| C<sub>24</sub> | -31.2 | -32.2 | -31.0 | -31.3 | -32.4 | -32.3 | -31.1 | -29.5 | -32.3 | -31.9 | -33.4 | -28.8 | -30.9 | -32.8 |     |     |
| C<sub>25</sub> | -31.3 | -32.4 | -31.5 | -32.0 | -29.7 | -29.2 | -30.3 | -32.0 | -31.3 | -32.7 | -31.9 | -33.0 | -28.8 | -30.9 | -32.8 |     |
| C<sub>26</sub> | -31.1 | -31.9 | -30.6 | -31.5 | -31.7 | -32.1 | -31.7 | -32.3 | -28.2 | -32.7 | -30.3 | -32.0 | -31.3 | -32.7 | -31.9 | -33.0 |
| C<sub>27</sub> | -31.8 | -29.9 | -31.0 | -29.4 | -29.6 | -32.5 | -31.7 | -32.7 | -34.4 | -32.7 | -29.5 | -28.2 | -30.6 | -29.3 | -36.9 |     |
| C<sub>28</sub> | -32.2 | -32.5 | -31.9 | -32.2 | -32.6 | -32.5 | -29.9 | -32.7 | -32.8 | -29.6 | -32.5 | -31.7 | -32.7 | -34.4 | -32.7 | -29.5 |
| C<sub>29</sub> | -32.5 | -32.0 | -32.4 | -32.4 | -33.3 | -32.5 | -29.6 | -33.2 | -31.1 | -32.6 | -33.0 | -29.5 | -28.2 | -30.6 | -29.3 | -36.9 |

Between Sapporo and Moshiri sampling sites is not feasible with such a small selection of suitable samples. A comparison between air mass back-trajectories presented in Figures 2 and 3 and the global distribution map of C₄ vegetation in Figure 6, part c (Still et al., 2009), implies that a C₄ contribution of 11–24% is reasonable. However, it should be borne in mind that the n-alkanes originating from C₃ gymnosperms are isotopically heavier than those originating from C₃ angiosperms (e.g. Chikaraishi and Naraoka, 2003). Relatively heavy δ¹³C values within an individual sample may also signify a larger input from gymnosperms, instead of a larger input from C₄ vegetation.

Both the Sapporo and the Moshiri samples show a trend towards lighter values of δ¹³C through the season (Figs. 8 and 9). In Sapporo the overall decline is approximately 1‰ from late December to late March. In Moshiri the overall decline is approximately 3‰ from early December to early April. Bendle et al. (2006) also found a seasonal trend in δ¹³C when studying n-alkanes in aerosol samples in the western North Pacific. They attributed this seasonality in part to seasonal changes within individual source areas, but mainly to seasonal variability in atmospheric conditions, leading to varying proportions of C₃ and C₄ plant material being transported to the sampling site.
The δ¹³C trend in our samples can also be explained by diminishing C₄ plant contribution during the winter season. C₄ crops such as maize are harvested before the winter, and where it snows, C₄ grasses are wholly or partially covered with snow. For C₃ vegetation, trees are rarely wholly covered with snow, and gymnosperms generally retain their needles throughout the winter. Plant wax molecules have a residence time in the atmosphere, so a diminution in C₄ plant mass surface exposed to wind abrasion may be communicated into our results with a time lag. Seasonal changes within the isotopic composition of the individual plants themselves may also contribute the seasonality of the carbon isotopic signal (Lockheart et al., 1997; Chikaraishi et al., 2004; Pedentchouk et al., 2008). In the context of ice core research, the question of seasonality may not arise, as the sampling resolution would typically integrate multiple seasons and years.

HYDROGEN ISOTOPIC COMPOSITION

Compound-specific δD values for C₂₇ were obtained for 7 Sapporo snow samples and 5 Moshiri snow samples (Table 2). δD ranged from −191.7‰ to −215.8‰ in Sapporo and from −169.9‰ to −223.1‰ in Moshiri (Figs. 8 and 9).

Several studies have reported compound-specific δD values for C₂₇ n-alkane from plant samples (e.g. Chikaraishi and Naraoka, 2003; Bi et al., 2005; Liu et al., 2006; Sachse et al., 2006; Smith and Freeman, 2006; Hou et al., 2007; Pedentchouk et al., 2008). Plant wax hydrogen isotopic composition reflects both local and global hydrology and ecology, and plant waxes are generally more depleted in deuterium at higher latitudes. Because of this correlation, the n-alkanes in the snow may also retain information about the growth latitude of their source vegetation. However, large δD variations occur between plant species, even at the same geographic location, adding noise to the latitudinal trend.

Figure 10 shows δD values for C₂₇ in individual plant samples as a function of latitude. Measurements from Bi et al. (2005), Chikaraishi and Naraoka (2003), Sachse et al. (2006), and Smith and Freeman (2006) include plant samples from various photosynthetic groups (C₃, C₄, CAM) and vegetation types (trees, grasses, moss). Additional δD measurements by Sankelo and Seki are previously unpublished: Sankelo sampled *Pinus parviflora* (−195‰) and *Sasa kurilensis* (−226‰) in Sapporo (year 2010); Seki sampled *Betula platyphylla* (−156‰), *Magnolia obovata* (−157‰), *Metasequoia glyptostroboides* (−170‰), and a type of *Pinus* (−170‰), also in Sapporo (year 2004). The gray area represents the range of δD values for C₂₇ in the Hokkaido snow samples. As illustrated by Figure 10, it proves difficult to trace the origin of plant waxes in Hokkaido snow by comparison with individual plant samples from various latitudes, because of the large variation of δD between individual plant specimens.

In an alternative approach we compare our δD data with a study by Rao et al. (2009) where n-alkanes in soil samples were examined along a transect in eastern China (Fig. 11). The high CPI values of the n-alkanes indicated that they originated from terrestrial vegetation (Rao et al., 2009). Vegetation type at the sampling sites was either forest or grassland, both highly representative for vegetation in northeast Asia (see Fig. 6, part b). Soil n-alkane data are an appropriate point of comparison, because the characteristics of the n-alkanes in both snow and soil samples integrate an average of multiple species from the local or regional area, thus, smoothing out the variability between plant species.

Figure 11 shows δD values for C₂₇ measured by Rao et al. (2009) as a function of latitude. δD values for C₂₇ in the Hokkaido snow samples are plotted against the Sapporo and Moshiri latitudes. Our snowpack δD values for C₂₇ are significantly lighter than predicted for plant waxes originating solely from soils at the same latitudes as Hokkaido, between 42°N and 46°N (confirmed with a
t-test at the 95% confidence level: P-value 0.2). n-Alkanes in our snow samples therefore likely originate from further north. This conclusion is not surprising, as Hokkaido snowfall often coincides with air masses arriving from the north or west, but illustrates that plant waxes in snow and ice archives do retain information about the source vegetation. Yamamoto et al. (2011) reached a similar conclusion in their study of n-fatty acids in the Hokkaido snow.

A more surprising result is that the compound-specific δ13C and δD values for C27 are correlated in the Hokkaido samples (Figs. 8 and 9). If the anomalous measurement S8 is not included, a correlation of r = 0.87 is obtained for the Sapporo measurement series (p = 0.025). The δD data set from the Moshiri time series is not large enough to draw conclusions about the whole winter, but a similarity in δD and δ13C trends can be qualitatively observed towards the end of the season.

Generally δD is not found to be diagnostic of the photosynthetic pathway, although in some cases C3 and C4 plants have displayed differing δD values at the same site (Chikarashi and Naraoka, 2003; Smith and Freeman, 2006). Bi et al. (2005) have reported a positive correlation between δD and δ13C in C3 trees, likely resulting from differences between plant species instead of the photosynthetic pathway. In our samples, the ACL values were typical for C3 trees, so perhaps the correlation between C27 δD and δ13C carries information about the vegetation type. However, a similar correlation between δD and δ13C was not found by e.g. Chikarashi and Naraoka (2007).

When constructing information about past vegetation from plant waxes preserved in natural archives, it is desirable to use both stable carbon and hydrogen isotopic compositions, where possible. To better utilize the isotopic data, it becomes necessary to know how and why δD and δ13C might co-vary. We note the correlation within our set of samples, but to explain it by referring to plant physiological mechanisms is not within the scope of this study.

Conclusions

Both the molecular distributions and the isotopic compositions of the n-alkanes in fresh snow were found to preserve information about the n-alkane sources. Although n-alkanes from both anthropogenic and natural sources were present, the distribution parameter Wax% indicated that in 13 out of 17 samples, the majority of the C23–C35 n-alkanes in the snow originated from terrestrial vegetation. C27 n-alkane, the target compound for the isotopic measurements, had plant wax input of more than 50% in 14 out of 17 samples.

The homologue distributions helped to assess the regionality of the n-alkane signal. In the Moshiri samples, a clear negative correlation was found between Wax% and ACL; with a purely local signal, a positive correlation would be more likely. For the Sapporo samples, no significant correlation was found between Wax% and ACL, likely due to less ideal sampling conditions. However, the plant wax percentages in the Sapporo samples were high enough to infer that input from the nearby Sapporo urban center did not dominate. We conclude that the n-alkane signal in the snow was regional rather than local.

δ13C values of the C27 indicated that the n-alkanes in our samples originated predominantly from C3 vegetation. We took a conservative approach to estimating C4 input, quantifying it only when the Wax% of the C27 n-alkane exceeded 90%. For these samples, the contribution from C4 vegetation was 11–24%, a plausible value in northern Asia. δ13C got lighter as the winter progressed, possibly because of the C4 contribution diminishing towards the spring. δD of the C27 n-alkane indicated that terrestrial plant waxes arrived at our sampling site from latitudes more northerly than Hokkaido; this is consistent with the weather patterns that typically bring snow to northern Japan. δD and δ13C values were seen to correlate to an extent, possibly due to source plant physiology.

Concerning the use of the terrestrial vegetation n-alkanes embedded within glacial ice as a climate proxy, we conclude that the extraction method used here is well suited for analyzing glacial samples. Laboratory contamination of the analyte peaks was insignificant, and the concentrations obtained for snow were sufficient for both δ13C and δD compound-specific measurements. Our results confirm that various kinds of information about the source vegetation are captured by the n-alkanes in the snow. ACL, δ13C, and δD combined can provide insights into the source plant photosynthetic pathway, growth location, and possibly even plant type. This information is regional in nature, and the prevailing atmospheric transport to the site must be considered in order to determine the relevant source region.

Both the concentrations and the distributions of n-alkanes in snow varied significantly from one snowfall event to another, and this variability persisted throughout the season. Even with the help of the relevant air mass back-trajectories, it was not possible to pinpoint the origin of the n-alkanes captured in individual snowfall events, and to explain the variability on a case-by-case basis. The airborne plant waxes mix during their residence time in the atmosphere, and when deposited into the ice archives, they will integrate a signal from a broad geographical area. Because the concentrations of n-alkanes in glacial ice are small, sampling an ice core will integrate the signal over time, smoothing out the variability between individual snowfall events, and permitting elucidation of broader trends in the source vegetation, both in terms of time and space.

If our method would be successfully extended to ice core studies, such an approach would yield novel insights into past regional changes in vegetation and hydrological conditions. Short cores dating back to industrial times would also provide a useful archive for studying anthropogenic pollution, whilst ice cores obtained from remote polar or mountainous locations, far away from the pollution sources, have the potential to record the background anthropogenic n-alkane input to the atmosphere.

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