Concentrations, deposition rates and source variations of \( n \)-alkanes in Sofiyskiy Glacier, Russian Altai Mountains

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(Received October 4, 2004; Revised manuscript received December 2, 2004)

Abstract

Snow and ice samples collected from a snow pit and underlying ice layers in Sofiyskiy Glacier, Russian Altai Mountains, were analyzed for \( n \)-alkanes by gas chromatography. The total concentrations of \( n \)-alkanes (T-HCs) widely ranged from 0.67 to 9.86 ng g\(^{-1}\) in the samples. Annual deposition fluxes of \( n \)-alkanes showed a seasonal variation with higher levels during spring than autumn. The values of carbon preference index (CPI) of \( n \)-alkanes ranged from 0.95 to 3.35, which were similar to those reported for snow samples in Himalaya and urban aerosols. The higher values among them were close to those reported of \( n \)-alkanes in loess particles, which were of plant wax origin. Both the 3.00-7.67 m and the 12.14-16.80 m layers had higher concentrations and annual deposition fluxes of non-WaxC\(_n\), suggesting that the relative contribution of anthropogenic \( n \)-alkanes, for example, fossil-fuel combustion products, to Sofiyskiy Glacier would increase in recent years. The WaxC\(_n\) representing a portion of \( n \)-alkanes derived from plant waxes in T-HCs widely ranged from 7.3 to 65.5% in these samples. It is evident that \( n \)-alkanes of plant waxes could contribute less than 50% to T-HCs in most samples at this glacier.

1. Introduction

It is well known that various organic and inorganic compounds exist in glaciers and ice sheets on the continents, Greenland and Antarctica. These compounds are emitted from various natural and anthropogenic sources into the atmosphere, transported by wind and deposited through snowfall and/or dry fallout. Some compounds can be generated by atmospheric chemical reactions during the transport (Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 1998).

Thus, the chemical analysis of ice cores provides information on the global environmental change including concentration on source and transport process of chemical compounds as well as atmospheric condition (Delmas, 1992; GRIP members, 1993; Petit et al., 1999).

Some organic compounds can be good indicators for anthropogenic and/or natural sources. For example, polycyclic aromatic hydrocarbons (PAHs) are emitted together with soot (elemental carbon) chiefly from fossil fuel combustion and biomass burning, and some saturated straight-chain hydrocarbons (\( n \)-alkanes) are emitted from anthropogenic (fossil fuel combustion) and natural (plants and soil) sources (Seinfeld and Pandis, 1998; Simoneit, 2002). Some organic acids are known to be tracers of atmospheric reactions (Seinfeld and Pandis, 1998). However, the results for organic analysis of the ice core have been reported much less than those for the inorganic one (Legrand and Mayewski, 1997; Kawamura, 2002).

In this study, the analysis for \( n \)-alkanes was car-
Our samples were collected from an ice core and a pit as well as snowfall at Sofyskiy Glacier. The ice core and snow samples were then thawed with the same sampling procedure of Fujii et al. (2002). Since only a small amount of sample (20 mL portion of each 20- or 10-cm section of ice core and snow samples) could be used for organic analyses of ice core due to a limited sample amount, the water samples taken from 25 sections were combined without filtration. Thus, five samples, each of which covered ca. 5 m depth in the ice core, were obtained in series. In a similar manner, five samples (1 m or 0.5 m depth/each sample) were obtained from a pit. All these samples were refrigerated in situ to prevent the biodegradation. The fresh snowfall samples (seven samples) were taken from the glacier surface after snowfall. After these procedures in situ, all frozen samples for organic analyses were sent to Japan and kept in a freezer until analysis.

After the samples were melted at room temperature in the laboratory, they were filtered through the glass fiber filter (Whatman GF/F, diameter: 25 mm) which was combusted before use at 450 °C for 4 hours to remove organic matters. The particle matters on the filter were extracted three times with 5 mL of organic solvent in an ultrasonic cleaner for 5 min each time; first time with methanol/dichloromethane (2: 1), and second and third times with dichloromethane. The extracts were combined, filtered and concentrated. The condensate was fractionated by a column chromatograph using 1 g of silica gel (Merck, Silica gel 60) which was sufficiently pre-cleaned with hexane to remove organic contaminants. The \( n \)-alkanes were eluted with 4 mL of hexane. The \( n \)-alkanes fraction was spiked with an internal standard (Merck, \( C_{29}D_{58} \)) and dried by using a rotary evaporator and nitrogen stream.

The dried \( n \)-alkanes fraction was dissolved in dichloromethane (20 \( \mu \)L), and then measured by a gas chromatograph with a flame ionization detector (GC-FID, Shimadzu, GC-14B) with a fused silica capillary column (GL Sciences, TC-1: 0.25 mm i.d. x 30 m length, 0.25 \( \mu \)m of film thickness). The GC conditions were as follows; injector temperature: 300 °C, detector temperature: 300 °C, column temperature program: from 80 to 300 °C at 3 °C min\(^{-1}\) and the hold time: 10 min at 300 °C. An integrator (Shimadzu, C-R6A) was used as a recorder of chromatogram. Detection limits for individual \( n \)-alkanes were ca. several to over ten pg g\(^{-1}\) for several-hundred mL samples. Analytical replicate precision (\( n=3 \)) of gas chromatograph for individual \( n \)-alkanes were below ca. 5%. The blank levels of organic solvents for \( n \)-alkanes were less than 10% of the peak levels of the samples.

The organic solvents (HPLC or pesticide analysis grade) were purchased from Wako Chemicals. The water used was prepared by Milli-Q Gradient (Millipore)
Table 1. Total concentrations (T-HCs), CPI (Carbon Preference Index) and percentages of WaxCn of n-alkanes in (a) ice core (OM-1-5), (b) snow from a pit (OM-6-10) and Snowfall (OM-11-17) at Sofiyskiy Glacier in 2001.

<table>
<thead>
<tr>
<th>Depth, m</th>
<th>(a) Ice core</th>
<th>(b) Snow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OM-1</td>
<td>OM-2</td>
</tr>
<tr>
<td>T-HCs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.53</td>
<td>2.54</td>
<td>1.86</td>
</tr>
<tr>
<td>CPI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.83</td>
<td>1.96</td>
<td>4.49</td>
</tr>
<tr>
<td>Wax Cn, %</td>
<td>39.6</td>
<td>38.7</td>
</tr>
</tbody>
</table>

Sampling time: 08:00/Jul./09 16:00/Jul./11 19:00/Jul./12 09:00/Jul./13 09:30/Jul./14 20:00/Jul./14 09:30/Jul./15

Sample ID | OM-11 | OM-12 | OM-13 | OM-14 | OM-15 | OM-16 | OM-17 |
| T-HCs     | 2.47  | NM³   | 9.86  | 0.67  | 2.83  | 3.01  |
| CPI       | 1.83  | NM³   | 1.96  | 0.95  | 2.30  | 1.81  | 3.35  |
| Wax Cn, % | 37.8  | NM³   | 44.9  | 7.3   | 51.6  | 42.5  | 65.5  |

Unit: ng g⁻¹ of T-HCs.
- a) Total concentration of n-alkanes from C₁₅ to C₃₅.
- b) CPI = (C₂₃: (100)/(C₂₃: n-alkanes).
- c) NM: n-alkanes could not be measured.

The n-alkanes in the ice core, snow pit and snowfall samples from Sofiyskiy Glacier consisted of the homologues with carbon numbers from 21 (C₂₁) to 32 (C₃₂). The total concentrations of n-alkanes (T-HCs) are listed with the CPI values and WaxCn percentages in Table 1. The T-HCs values in the ice core and snow samples were in the range of 1.08-3.53 and 1.70-3.58 ng g⁻¹, respectively. In the snow samples collected during snowfall, the T-HCs widely ranged from 0.67 to 9.86 ng g⁻¹. The T-HCs values were at the same order as the total concentrations of n-alkanes (C₁₅-C₃₂) in snow samples (0.86-1.57 ng g⁻¹) of Dasuopu Glacier in the central Himalayas (Xie et al., 2000) and a rain sample (1.2 ng g⁻¹) collected in Nagoya, Japan (Miyake, unpublished data). However, they were one order as high as those of n-alkanes (0.240-0.510 ng g⁻¹) in ice core samples from Site-J, Greenland (Kawamura and Suzuki, 1991). This suggests that the Asian continental glaciers suffer high loading of chemical materials from natural and anthropogenic sources through the atmospheric transport in comparison with Greenland and Antarctica as anthropogenic and biological activities are high in the Asian continent.

The annual deposition fluxes of n-alkanes to Sofiyskiy Glacier were estimated from the T-HCs, ice density and annual layer depth determined by pollen analysis (Nakazawa et al., 2004). We calculated the annual deposition fluxes of n-alkanes from surface (0 m) to 16.80 m-depth in the snow (0-3.00 m, n = 3) and ice core (3.00-16.80 m, n = 3) samples at Sofiyskiy Glacier, because pollen analyses were made from surface to 18.60 m-depth. Kameda et al. (2003) reported that ice layers at relatively regular intervals of about 2 m were observed in the ice core taken in Sofiyskiy Glacier in 2000. Furthermore, according to the stratigraphy of Kameda et al. (2004) and Nakazawa et al. (2004), thin
infiltration ice layers and thick firn layers except at 7–8 m and 15–16 m in depth with thick ice layers were alternately observed until 18 m depth in the ice core. Thus, the seasonal fluctuation patterns seemed to be observed obviously in n-alkanes more than in ionic compositions and isotopes of water in the ice core as most n-alkanes, especially homologues of those more than C_{35}, exist as particulate phase in the atmosphere (Kadowaki, 1994), although perhaps the ice layers are formed at the previous spring-summer surface by percolation of melt water in the next summer (Kameda et al., 2003). Furthermore, n-alkanes may be relatively stable in ice layer since these in the atmosphere are more stable than other organic compounds (alkenes and aromatics) (Finlayson-Pitts and Pitts, 1986) in spite of no sufficient data on preservation in ice layer. Therefore, it seems that the annual deposition fluxes of n-alkanes are relatively reasonable because sample intervals (ca. 5 m) are more than annual accumulation in snow depth (1.78 m; Nakazawa et al., 2004), although vertical transport and preservation of n-alkanes in snow and ice layers are not solved until future studies.

Figure 2 shows the profiles of T-HCs from 0 to 24.29 m in depth, annual deposition flux of n-alkanes and average water accumulation rates from 0 to 16.80 m with time scale of summer layer determined by pollen analysis (Nakazawa et al., 2004), in the snow and ice core samples. The concentration and deposition flux values of n-alkanes in the 3.00–7.57 m layer are calculated from OM-1 (1.91–7.57 m layer) in Table 1. These two profiles were similar to each other, although the water accumulation rates estimated from the ice density and annual layer depth largely fluctuated from year to year. We speculate that the deposition fluxes of n-alkanes in Sofiyskiy Glacier would mainly depend on atmospheric n-alkanes concentra-
Fig. 3. The homologue distributions of \( n \)-alkanes in ice core ((a)-(e)), snow ((f)-(i)) and snowfall ((j)-(o)) samples at Sofisky Glacier, and rain sample collected in Nagoya, Japan in December 2001 (p). Envelopes upper or under the dashed line indicate the estimated concentrations of \( n \)-alkanes from plant waxes (WaxC\(_n\)) and petroleum (non-WaxC\(_n\)) sources, respectively.

Section, although the fluxes of \( n \)-alkanes are calculated from \( n \)-alkanes concentrations and average water accumulation rates. Actually, vertical variation of T-HCs of \( n \)-alkanes is more than that of average water accumulation rate in Fig. 2. However, more meteorological data in situ are necessary to solve in the problem. The snow samples were better in time resolution than underlying ice-core samples. The top (0-1.00 m) and third (2.00-3.00 m) layers in the pit were shown by the pollen analysis to deposit during spring seasons in 2001 and 2000, respectively, and the second one (1.00-2.00 m) was during autumn season in 2000. Greater deposition fluxes of \( n \)-alkanes in the top and third layers than the second one (Fig. 2) showed that \( n \)-alkanes were at higher levels in atmospheric concentration during spring than autumn.

3.2. Sources of \( n \)-alkanes

The CPI values of \( n \)-alkanes derived from plant waxes range 5.9-9.2 with strong odd-carbon-number
predominance, whereas \( n \)-alkanes originating from petroleum and its combustion products show the CPI values near 1 (Gagosian et al., 1981; Simonite and Mazurek, 1982; Kawamura and Kaplan, 1986). Thus, the CPI has been used to evaluate the relative contribution of biogenic to anthropogenic sources. Among 15 samples of Sofiyskiy Glacier samples, 13 samples gave the CPI values ranging 0.95–2.30 (Table 1), which were similar to the values (1.05–1.88) of snow samples from Dasuopo glacier, central Himalaya (Xie et al., 2000). All these values are close to those of urban aerosols (1.8–2.8; Simonite and Mazurek, 1982) and urban rain in Nagoya (0.97; Miyake, unpublished data), but are far from those (3.87–13.0) of rain and snow in semi-rural to rural areas receiving biogenic contributions (Kawamura and Kaplan, 1986). This suggests that the glaciers in the Asian Continent are under the considerable influence of anthropogenic sources in spite of their long distances from urbanized areas. Two samples of the Sofiyskiy Glacier gave the CPI values of 3.07 (OM-8) and 3.35 (OM-17). These values are close to the CPI of about 3 reported for \( n \)-alkanes in loess (Simonite et al., 1991), which were derived from plant waxes. But, more studies are necessary to estimate the contribution of loess from the arid and semi-arid areas in China to \( n \)-alkanes in Sofiyskiy Glacier.

Figure 2 also shows the vertical distributions of WaxC\(_n\) and non-WaxC\(_n\) (total – WaxC\(_n\); petroleum-derived \( n \)-alkane concentrations) portions of T-HCs and annual deposition fluxes of \( n \)-alkanes in snow and ice layer with the estimated annual fluxes of corresponding to waters. In the ice core, the portions of both WaxC\(_n\) and non-WaxC\(_n\) of \( n \)-alkanes have recently increased on both the T-HCs and annual fluxes. Especially, a peak appeared in the 3.00–7.57 m layer which both WaxC\(_n\) and non-WaxC\(_n\) portions of T-HCs and annual fluxes of \( n \)-alkanes in this layer were largest in the ice core, suggesting that the intensity of natural and anthropogenic sources of \( n \)-alkanes was larger than the previous period. Thus, it seems reasonable that the relative contribution of anthropogenic \( n \)-alkanes, for example, fossil-fuel (mainly petroleum) combustion products transported from remote urban areas, to Sofiyskiy Glacier would increase in recent year.

Figure 3 shows the homologue distributions of \( n \)-alkanes in ice core, snow and snowfall samples at Sofiyskiy Glacier with rain sample collected at Nagoya, Japan in December 2001. The homologue distribution pattern, which had C\(_{29}\) and C\(_{31}\) as the most dominant \( n \)-alkanes in the glacier samples, indicated that \( n \)-alkanes were of plant wax origin (Simonite and Mazurek, 1982), although the distribution pattern should be considerably modified through the biodegradation in soil and/or loess particles. Table 1 also shows the percentages of WaxC\(_n\) of \( n \)-alkanes in Sofiyskiy Glacier. The percentages of them widely range from 15.4 to 39.6% in ice core samples, from 15.3 to 49.6% in snow samples and from 7.3 to 65.5% in snowfall samples, respectively. It is evident that \( n \)-alkanes of plant waxes could contribute less than 50% to T-HCs in most samples at this glacier.

4. Conclusions

The present study showed that total \( n \)-alkane concentrations (T-HCs) widely range from 0.67 to 9.86 ng g\(^{-1}\) in ice core, snow and snowfall samples at Sofiyskiy Glacier. The compositional features of \( n \)-alkanes including CPI values, homologue distribution patterns and WaxC\(_n\) and non-WaxC\(_n\), indicated that \( n \)-alkanes in Sofiyskiy Glacier are derived from two major sources; soil (loess) particle constituents originating from plant waxes and fossil-fuel combustion products. Both the 3.00–7.57 m and the 12.14–16.80 m layers had higher non-WaxC\(_n\) concentrations and annual deposition fluxes of \( n \)-alkanes. Thus, it seems reasonable that the relative contribution of anthropogenic \( n \)-alkanes, for example, fossil-fuel (mainly petroleum) combustion products, to Sofiyskiy Glacier would increase in recent years. Although the WaxC\(_n\) representing a portion of \( n \)-alkanes derived from plant waxes in T-HCs widely ranged from 7.3 to 65.5% in these samples at the glacier, it is evident that those of plant waxes could contribute less than 50% to T-HCs in most samples.

Acknowledgments

We would like to express our gratitude to the Russian participants in the field work, namely Dr. Lev M. Savatyugin of Arctic and Antarctic Research Institute in St. Petersburg, Dr. Serguei M. Arkhipov of Institute of Geography in Moscow and Mr. Ivan A. Ponomarev of the Altai State University in Baumacl for their effort of Ice core drilling at Sofiyskiy Glacier, Russian Altai Mountains in 2000 and 2001. This study was supported by Grant-in-Aid for Scientific Research (No. 11208202 and No. 14208020) of the Ministry of Education, Culture, Sports, Science and Technology, Japan. This study was also supported by the Oasis Project (Historical evolution of adaptability in an oasis region to water resource change) proposed by Research Institute for Humanity and Nature, Japan and the research project ‘Aerolian Dust Experiment on Climate Impact (ADEC)’ funded by Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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