Ice core profiles of saturated fatty acids (C\textsubscript{12:0} - C\textsubscript{30:0}) and oleic acid (C\textsubscript{18:1}) from southern Alaska since 1734 AD: A link to climate change in the Northern Hemisphere

Ambarish Pokhrel\textsuperscript{1,2}, Kimitaka Kawamura\textsuperscript{1,*}, Osamu Seki\textsuperscript{1}, Sumio Matoba\textsuperscript{1} and Takayuki Shiraiwa\textsuperscript{1}

\textsuperscript{1}Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan
\textsuperscript{2}Graduate School of Environmental Science, Hokkaido University, Sapporo, Japan

*Corresponding author (email: kawamura@lowtem.hokudai.ac.jp)

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Abstract

An ice core drilled at Aurora Peak in southeast Alaska was analysed for homologous series of straight chain fatty acids (C_{12:0} - C_{30:0}) including unsaturated fatty acid (oleic acid) using gas chromatography (GC/FID) and GC/mass spectrometry (GC/MS). Molecular distributions of fatty acids are characterized by even carbon number predominance with a peak at palmitic acid (C_{16:0}, av. 20.3 ± SD. 29.8 ng/g-ice) followed by oleic acid (C_{18:1}, 19.6 ±38.6 ng/g-ice) and myristic acid (C_{14:0}, 15.3 ±21.9 ng/g-ice). The historical trends of short-chain fatty acids, together with correlation analysis with inorganic ions and organic tracers suggest that short-chain fatty acids (except for C_{12:0} and C_{15:0}) were mainly derived from sea surface micro layers through bubble bursting mechanism and transported over the glacier through the atmosphere. This atmospheric transport process is suggested to be linked with Kamchatka ice core δD record from Northeast Asia and Greenland Temperature Anomaly (GTA). In contrast, long-chain fatty acids (C_{20:0} - C_{30:0}) are originated from terrestrial higher plants, soil organic matter and dusts, which are also linked with GTA. Hence, this study suggests that Alaskan fatty acids are strongly influenced by Pacific Decadal Oscillation/North Pacific Gyre Oscillation and/or extra tropical North Pacific surface climate and Arctic oscillation. We also found that decadal scale variability of C_{18:1}/C_{18:0} ratios in the Aurora Peak ice core correlate with the Kamchatka ice core δD, which reflects climate oscillations in the North Pacific. This study suggests that photochemical aging of organic aerosols could be controlled by climate periodicity.
1. Introduction

Alkyl lipids such as \( n \)-fatty acids as well as \( n \)-alkanes and \( n \)-alkanols that are ubiquitous in continental (Simoneit et al., 1991; Simoneit and Mazurek, 1982; Ho et al., 2011) and remote marine aerosols (Conte and Weber, 2002; Kawamura et al., 2003; Bendle et al., 2007; Mochida et al., 2007). They are emitted from biogenic sources including terrestrial higher plants, soil organic matter, microbial activities and marine phytoplankton (Kawamura et al., 1996; Rogge et al., 1993, 2006; Seki et al., 2010). Hence, alkyl lipids can be used as organic tracers to investigate the sources of organic aerosols and long-range atmospheric transport (Kawamura et al., 1995; Fang et al., 2002).

Fatty acids can be deposited over ice sheet and be stored in ice for several hundred years or more (Kawamura et al., 1995, 1996; Nishikiori et al., 1997). Fatty acids are produced by biological activities of many biota (Fang et al., 2002). For example, oleic acid (\( C_{18:1} \)) is the major constituent of cell membranes in marine phytoplankton and terrestrial higher plants and can be emitted to the atmosphere directly from the leaf surface and wood combustion as well as bubble bursting in the surface ocean (Kawamura and Gagosian, 1987; Marty et al., 1979; Fine et al., 2001). However, there are very few studies on the homologous series of fatty acids (\( C_{12:0} - C_{30:0} \)) in ice core samples from Greenland and Antarctica ice sheets (Kawamura et al., 1996; Nishikiori et al., 1997). In particular, ice core collected from mountain glacier has not been explored for fatty acids yet.

Fatty acids in ice core are closely related to past climatic changes (Kawamura et al., 1995, 1996; Nishikiori et al., 1997). Their ice core profiles can be employed as a proxy to assess the past changes in marine and terrestrial emissions on multidecadal-to-centennial time scales. Here, we investigated homologous series of straight chain fatty acids (\( C_{12} - C_{30} \)) from Aurora Peak of Alaska to better understand the past atmospheric transport of fatty acids and to reconstruct the paleoclimate conditions and sources of fatty acids since 1734 – 2008. The
historical trends of fatty acids are discussed in terms of past changes in atmospheric circulation in the northern North Pacific and its surroundings.

2. Ice Core Samples and Analytical Procedures

Aurora Peak of Alaska (APA) is located in the southeast of Fairbanks (63.521°N, 146.542°W) with an elevation of 2,825 meter above sea level (Figure 1). About 180 m long ice core was drilled on the saddle of APA (Fukuda et al, 2011). The ice core ages were determined by annual counting of the peaks in hydrogen isotope (δD) and Na⁺ seasonal cycles, in which an age control was provided by reference horizons of tritium peaks in 1963 and 1964. By this methods, bottom of ice core sample was estimated to be 274 years old (±3 years); i.e., 1734 AD (Tsushima et al., 2014).

The ice core was cut into ~50 cm sections and transported to the laboratory of Institute of Low Temperature Science, Hokkaido University, Japan and stored in a cold room at -20°C until analysis. To avoid the possible contaminations during sample collection and transport, ca. 5 - 10 mm surfaces of the ice sections were shaved off using a ceramic knife inside a clean bench in the cold (-15°C) room (Kawamura and Yasui, 1991; Savarino and Legrand, 1998).

Fatty acids were determined using butyl ester derivatization method (Mochida et al., 2003). Numbers of total ice core sections are 122, which is equivalent to ~35% of the 180 m long ice core recovered from the APS site.

100 mL of melt water from ice core section were placed into a pear shape flask (300 mL) and the pH of the sample was adjusted to 8.5-9.0 using a 0.05 M KOH solution. The sample were concentrated down to near 5 mL using a rotary evaporator under vaccum. The concentrates were transferred to a pear shape flask (50 mL), concentrated until dryness using a rotary evaporator under vaccum, and then reacted with ~0.25 mL of 14% boron trifluoride (BF₃)/n-butanol to derive carboxyl groups to butyl esters at 100°C for 1 hour. The butyl ester
derivatives were determined using a capillary gas chromatography (GC; HP 6890). The GC peak identification was performed using a GC/MS (Agilent). The laboratory blanks of C_{14:0}, C_{16:0}, C_{17:0}, C_{18:0}, C_{18:1}, C_{20:0}, C_{22:0} and C_{24:0} relative to real samples were 3.9, 3.7, 1.8, 4.1, 3.8, 2.6, 1.7 and 2.4 %, respectively. The analytical errors for C_{14:0}, C_{16:0}, C_{17:0}, C_{18:1}, C_{20:0}, C_{24:0} and C_{28:0} fatty acids in the replicate analyses were 4.9, 3.1, 9.3, 3.5, 1.6, 2.6 and 2.5%, respectively. Here, we present concentrations of lower molecular weight fatty acids (C_{12:0} - C_{19:0}: LFAs) and higher molecular weight fatty acids (C_{20:0} - C_{30:0}: HFAs), which are all corrected for procedural blanks.

Yasunari and Yamazaki, (2009) reported 10-day backward trajectory based on Lagrangian tracking method for 1992 - 2002 and suggested that southeast Alaskan regions can receive more air masses from the adjacent areas of the northern North Pacific regions, East Asia, Eastern Russia-Siberia, the Okhotsk-Bering Seas, higher latitudes of Alaskan regions, Japan, Canada and the Arctic Ocean in the troposphere (>300 hPa). Moreover, Cahill (2003) suggested that chemical compositions of Alaskan aerosols are dominated by oceanic components.

3. Results

Figure 2 shows the average molecular distribution of homologous series of straight chain fatty acids (C_{12:0} - C_{30:0}) including unsaturated fatty acid (oleic acid, C_{18:1}) for 1734 - 2008. Their molecular distributions are characterized by a strong even carbon number predominance with a peak at C_{16:0}. C_{16:0} comprised one third (av. 30.6%) of total fatty acids, followed by C_{14:0} (19.3%) and C_{18:1} (14.4%). The concentrations of C_{16:0}, C_{18:1} and C_{14:0} range from below detection limit (BDL: 0.001ng/g-ice) to 95.1 ng/g (av. 20.3 ±SD 29.8 ng/g-ice), BDL to 189 ng/g (19.6 ±38.6 ng/g-ice), BDL to 91.3 ng/g (15.3 ±21.9 ng/g-ice), respectively. We also detected significant amounts of C_{18:0} and C_{12:0} (Table 1). HFAs (C_{20:0} - C_{30:0}) are
dominated by lignoceric acid (C\(_{24:0}\)), followed by arachidic (C\(_{20:0}\)) and behenic (C\(_{22:0}\)) acid (Figure 2 and Table 1).

Figure 3 shows historical changes of selected LFAs in the ice core collected from Aurora Peak in Alaska. Palmitic acid (C\(_{16:0}\)), which is the most abundant FA species, showed several peaks around the years of 1780, 1800, 1850, 1990 and 2000. Interestingly, all the components of LFAs showed a large spike around 1840-1860 (Figure 3). The historical trend of C\(_{12:0}\) is similar to that of C\(_{15:0}\), except for few points. The trends of C\(_{12:0}\) and C\(_{15:0}\) are different than those of other LFA components, except for some points. For instance, around 1850s and after 1980s similar types of higher spikes were observed (Figure 3a-3g). Figure 4 presents concentration changes of selected HFAs (C\(_{20:0}-\)C\(_{26:0}\)) in the ice core. Although HFAs showed large spikes around at 1740s and 1840s, their historical trends are not always similar to those of LFAs. Concentrations of HFAs are relatively low during the period from 1860s to 1970s (Figures 3 and 4). Except for few points, HFA species showed similar historical trends each other with peaks at around 1750s, 1850s and 1980s (Figure 4a – 4f).

4. Discussion

4.1. Molecular compositions of fatty acids and their historical profile

The homologous series of fatty acids show a strong even carbon number predominance with a peak at C\(_{16:0}\) followed by C\(_{18:1}\) and C\(_{14:0}\) as described above. The predominance of C\(_{16:0}\) has also been reported in riverine and estuarine sediments (Naraoka and Ishiwatari, 2000), marine sediments (Ohkouchi et al., 1997), soil samples (Matsumoto et al., 2007) and remote marine aerosols (Conte and Weber, 2002; Bendle et al., 2007). LFAs are mainly originated from marine phytoplankton (Kawamura and Gagosian, 1987; Kawamura, 1995; Marty et al., 1979), while HFAs are originated from terrestrial higher plants and soil dust (Kawamura et al., 1996; Ohkouchi et al., 1997). The molecular distributions of fatty acids in this study are different than those from other studies on aerosols (Kawamura et al., 2010; Fang et al., 2002).
and ice cores from Antarctica (Nishikiori et al., 1997) and Greenland site-J (Kawamura et al., 1995, 1996). For example, fatty acids in Greenland site-J ice core are characterized by a strong even carbon number predominance with maximum at C$_{16}$ or C$_{22}$ followed by C$_{24}$ and lesser abundance of C$_{18:1}$ (Kawamura et al., 1995, 1996).

Unsaturated LFAs such as C$_{18:1}$ are abundant in marine phytoplankton (especially diatom) (Napolitano et al., 1997) and are dominant in the sea surface micro layer (Marty et al., 1979; Garrett, 1967). Hence, the higher abundance of C$_{18:1}$ than C$_{18:0}$ in our ice core suggests an enhanced emission of C$_{18:1}$ from the surrounding oceans via long-range atmospheric transport to Alaskan ice core site. This is consistent with the fact that diatom is dominant species in high latitudinal oceans (Napolitano et al., 1997) and C$_{18:1}$ is one of a dominant marine fatty acid in the sea surface microlayer (Kawamura and Gagosian, 1987; Marty et al., 1979). In general, unsaturated FAs are labile compounds compared to saturated ones and can be easily decomposed during long-range transport (Kawamura and Gagosian, 1987). However, C$_{18:1}$ was abundantly detected in almost all ice core sections, suggesting that the deposition and subsequent incorporation of fresh marine aerosol components in the glacier occurred without severe photochemical degradation during atmospheric transport. This suggests that APA is an excellent site to record the historical changes in emission and transport of fresh marine organic matter from the surrounding oceans.

LFAs (except for C$_{12:0}$ and C$_{15:0}$) showed similar historical profiles each other (Figure 3a – 3g) with lower concentration after 1860s to 1980s, suggesting a marked decrease in the sea-to-air emission and subsequent transport of FAs during the period. In contrast, total FA concentrations gradually increased after 1960s, except for few points around 1875, 1920, 1975 and 2005 (Figure 5a). The lower concentrations of LFAs during 1860-1980 AD (Figure 5c) may be in part attributed to depressed emission of marine derived fatty acids probably due to the extension of sea ice coverage around the Alaskan regions. In fact, sea ice reconstruction in Arctic region including the Chukchi Sea shows a significant expansion of sea ice area during
the period (de Vernal et al., 2008; Kinnard et al., 2011; Cavalieri et al., 1997). Another reason for the decreased concentrations of LFAs may be the shifting of atmospheric transport over Aurora Peak in Alaska, which could be associated with multidecadal climatic cycle in the Pacific regions (Figure 5d and 5f), a point to be discussed later. We have presented a vertical depth profile of ice core as a function of the proposed chronology by Tsushima et al. (2014) (Figure 5g).

In contrast, the high concentrations of LFAs before 1860s may be in part associated with an enhanced phytoplankton productivity in the open ocean due to the retreat of sea ice and an enhanced emission of fatty acids via bubble bursting processes from sea surface microlayers (de Vernal et al., 2008; Kinnard et al., 2011; Kawamura and Gagosian, 1987; Garrett, 1976). In fact, high concentrations of fatty acids like C14:0, C16:4ω1 and C20:5ω3 have been reported during the phytoplankton bloom whereas C18:0, C18:1ω9, C18:2ω2 and C18:4ω3 were abundantly detected during the post bloom of phytoplankton in the east coast of Canada (Napolitano et al., 1997). Moreover, there could be some other contributors, for instance, from bacteria, spores, pollen, plant organelles, leaf cells, chloroplast and microbial lipids by soil remobilization (Rogge et al., 1993; Simoneit, 1989; Kawamura et al., 2003; 2010) as well as biomass burning (Oros and Simoneit, 1999). Interestingly, Nishikiori et al. (1997) reported higher concentrations of fatty acids in the Site H15 of Antarctica after 1850s and considered the results due to the enhanced sea-to-air emission of marine-derived fatty acids. Higher spikes of fatty acids could be caused by the retreat of sea ice and subsequent expansion of open ocean associated with global warming (de Vernal et al., 2008; Kinnard et al., 2011; Kawamura et al., 1995, 1996; Nishikiori et al., 1997).

Detection of HFAs are characterized in the ice core suggests that the deposition of terrestrial plant-derived HFAs occurred over the saddle of APA. HFAs are originated from epicuticular waxes of terrestrial higher plants and soil dust (Simoneit and Mazurek, 1982; Ho et al., 2010, 2011). It should be noted that we confirmed by visible observation the presence of
soil dust particles in few ice core sections in this study. Cahill (2003) reported, based on the
crystallographic data, that Europe, Russia, Asia and other upwind
areas are significant source regions for the aerosol loading over and/or around the North Pacific
regions. In addition, higher plant-derived pollens, fungi, bacteria, spores and soil organic
matter can easily supply HFAs in the atmosphere with high speed winds (Lechevalier, 1977).
Updraft of wind from earth surface to cloud level and/or any type of atmospheric instability
could act as a driving force for the significant transport of HFAs over the ice sheet at high
mountains.

The concentration ratios of atmospheric compounds can be used to determine the origin
of these atmospheric tracers and sometimes source, sinks and other important hidden
characteristics. Alkanoic acids <C20 can be derived from marine phytoplankton, bacteria,
spores, and organic detritus as mentioned above. Thus, ratio of ≥C22/<C20 under 1 and Cmax at
C16 and C18 can reflect microbial activities for aerosols with less contribution from terrestrial
higher plants (Fang et al., 1999; Oliveira et al., 2007). Interestingly, the ratio obtained in this
study is 0.13, which is significantly lower than 1.0 with Cmax at C16. This again suggests that
fatty acids in the ice core are mainly derived from marine biota via sea-to-air emission and
subsequent atmospheric transport over the Alaskan mountain area.

Once unsaturated fatty acids (indicators of recent biogenesis) are emitted to the
atmosphere from the ocean surface, the double bond in their structures can be oxidized by OH
radicals, ozone and other oxidants, resulting in aldehydes and dicarboxylic acids (Kawamura
and Gagosian, 1987; Kawamura et al., 1995). Thus, the concentration ratios between saturated
alkanoic acid (C18:0) and unsaturated alkenoid acid (C18:1) can be used as a proxy to estimate
the atmospheric aging of organic aerosols. For instance, Ho et al. (2010) used such ratios to
discuss the photochemical aging of organic aerosols. We found higher C18:1/C18:0 ratios around
at 1770s, 1850s, 1950s, 1980s and 2000s (Figure 5e), suggesting that marine-derived fresh
organic aerosols were more frequently transported and stored in the ice core without severe
photochemical processing in the air and on the glacier. On the other hand, lower C\textsubscript{18:1}/C\textsubscript{18:0} ratios were recorded during 1730s-1750s, 1870s and 1920s (Figure 5e), suggesting that oleic acid was more oxidized during the long distance transport before the wet scavenging over the saddle of APA.

4.2. Multiple responses of Alaskan ice core to climate change

We found a strong correlation between photochemical tracer; azelaic acid (C\textsubscript{9}) (Pokhrel et al., unpublished result) and C\textsubscript{18:1} (R=0.83), C\textsubscript{18:0} (0.75), and total LFAs (C\textsubscript{12:0} - C\textsubscript{19:0}) (0.83). Because azelaic acid is a photo-oxidation product of unsaturated fatty acids (Kawamura and Gagosian, 1987), the positive correlations suggest that the sea-to-air emission is the major source of LFAs in ice core and variations of photochemical degradation was not significant during the period. However, as seen in Figure 5e, a significant variation of C\textsubscript{18:1}/C\textsubscript{18:0} ratios was detected in the ice core profile, a point to be discussed later. In contrast, levoglucosan, which is a unique biomass-burning tracer (Simoneit, 2002) did not show the spikes in 1850s when LFAs are abundant in the ice core (Figure 5c). However, almost all compounds (diacids and fatty acids) showed higher spikes in 1850s (Figures 3, 4 and 5). No correlation of levoglucosan with palmitic acid (C\textsubscript{16:0}) (R = 0.10), C\textsubscript{18:0} (0.07), C\textsubscript{18:1} (0.11) and LFAs (C\textsubscript{12:0} - C\textsubscript{19:0}) (0.33) suggest that biomass burning is not a major source of fatty acids in ice core.

We detected significant amounts of sugar compounds including arabinol, mannitol, inositol (sources: virus, bacteria, algae and fungal spores), α-glucose, β-glucose, α-fructose, β-fructose (pollen, fruits and yeast fragments), trehalose (fungi, bacteria, soil surface and unpaved dust) and sucrose (buds and roots) (Fu et al., 2012, and references therein) in the ice core for the years of 1734 – 2008 (Pokhrel et al., unpublished results). However, we found very weak or no correlations (R < 0.14) between LFAs (C\textsubscript{12:0} - C\textsubscript{19:0}) and the above mentioned sugar compounds, indicating that the terrestrial sources are not main contributors of ice core LFAs. This again suggests that marine sources are important sources of LFAs in ice core.
LFAs showed weak or no correlation with some inorganic ions (unpublished results). For example, correlation coefficients (R) of C$_{18:1}$ with nss-K$^+$, nss-Ca$^+$ and NH$_4^+$ are 0.11, 0.23 and 0.02, respectively. nss-K$^+$ is a good tracer of biomass burning (Simoneit, 1989) whereas Ca$^+$ is abundant in continental dusts (Kawamrue et al., 2004; Mkoma and Kawamura, 2014; Kunwar and Kawamura, 2014). Similarly, very weak correlations (<0.19) were found for fatty acids (C$_{14:0}$, C$_{16:0}$, C$_{17:0}$, and C$_{18:0}$) with NO$_2^-$ or NO$_3^-$, which are abundant in continental polluted aerosols (Legrand and Mayewski, 1997, references therein). These results suggest that LFAs are not derived from continental sources.

In contrast, we found a positive correlation between Na$^+$ and C$_{18:1}$ (R = 0.67), and Na$^+$ and LFAs (R=0.50). The slightly weaker correlation may be due to the possible fractionation between Na$^+$ and LFAs during the bubble bursting process in the ocean surface. We also found a positive correlation between methanesulfonate (MSA$^-$) (a good tracer of marine biological activity: oxidation product of dimethyl sulfide (DMS) emitted from the ocean by microbial activity, e.g., Miyazaki et al., 2010), and C$_{16:0}$ (R=0.81), C$_{18:0}$ (0.77) and C$_{18:1}$ (0.49). Relatively low value for C$_{18:1}$ may be caused by its photochemical oxidation during atmospheric transport. On the other hand, correlation coefficients for C$_{16:0}$, C$_{18:0}$ and C$_{18:1}$ with nss-SO$_4^{2-}$ (oxidation product of DMS and MSA) are 0.79, 0.77 and 0.88, respectively. These results strongly support that LFAs are derived from marine source rather than continental source. It is clear that historical trends of MSA$^-$ and nss-SO$_4^{2-}$ are similar (except for 1930s) (R=0.85). Interestingly, both nss-SO$_4^{2-}$ and MSA$^-$ somewhat follow the $\delta$D record from Kamchatka (Figure 5f) (Sato et a., 2014), further supporting that these ions along with fatty acids are coupled with past climate change.

Historical trend of $\delta$D records in the Kamchatska ice core represents surface temperature for 1958-1996 and extended the reconstructed sea surface temperature from 1854 to 1995 (Sato et al., 2014; Smith et al., 2008). Historical $\delta$D data is also an indicator of changes
in atmospheric transport of moisture, rainfall, and snowfall seasonality and humidity source (Dansgaard, 1964), which are essential factors for emission and deposition of fatty acids. For example, water vapor transport analysis showed that almost 80% of winter and 50% of summer precipitations over the Euraaian Continent originate from the North Pacific Ocean (Numaguti, 1999), which can support the southern Alaskan atmospheric circulation (Yasunari and Yamazaki, 2009).

It should be noted that this δD record of ice core signal has a positive relation with mid-latitude North Pacific (20-30° N) surface temperature and negative correlation with sub polar North Pacific (40-50° N, 180-150° W) surface temperature. On the other hand, snow accumulation rate of Kamchatka has significant negative correlation with the sub polar North Pacific (40-60° N, 180-150° W) and significant positive correlation with the western coast of North America (40° N, 125° W and 60° N, 145° W). These two results indicate the extra tropical North Pacific surface climate conditions (Sato et al., 2014; Smith et al., 2008).

According to Sato et al. (2014), historical trend of δD in Kamchatka ice indicates the variations of climate oscillation such as Pacific Decadal Oscillation (PDO) and North Pacific Gyre Oscillation (NPGO). For instance, we found that correlation coefficient (R) of annual mean of δD and NPGO (Di Lorenzo et al., 2008) is 0.70 (p < 0.10) after great climate shift (1979-1997). Moreover, δD records seem to correlate with extended reconstructed sea surface temperature of the mid to high latitude North Pacific (30-45° N, 165- E- 165° W), which can represent the sea surface temperature anomaly and PDO (Sato et al., 2014, reference therein).

Relation between 15-point running mean (RM) of δD (15-RM δD) and 21-RM of C_{18:1}/C_{18:0} showed a positive correlation (R = 0.80). It further suggests that photochemical aging is associated with the climate periodicity cycle. Interestingly, 15-RM of LFAs and 15-RM of δD showed a better correlation (R=0.79) as compared to 15-RM of HFAs (0.54), suggesting that sea-to-air emissions of LFAs are associated with the climate periodicity. These results indicate
a significant atmospheric transport of air parcels from lower to higher latitudes in the North Pacific rather than the continental source regions in Alaska. Hence, historical trend of fatty acids in ice core is a good indicator for changes in atmospheric circulation over the North Pacific, where PDO and NPGO seem to be important.

Similarly, Parkinson et al. (1999) reported the overall reduction of sea ice extent since 1978 to 1996, with somewhat extent for 1990-1996. Parkinson and Cavalieri, (2002) reported a 21-year microwave data set of Arctic regions and demonstrated that there is a reduction of sea ice extent at a rate of \(-2.7\pm0.5\%\) per decade, in which summer rate is greater \((-4.9\pm1.5\%)\) compared to winter \((-1.8\pm0.6\%)\). In addition, National Snow and Ice Data Center (nsidc.org) and/or Alaska Ocean Observing System (www.aoos.org) also reported that sea ice extent is declined from 1978 to 2010 for the Northern Hemisphere. Following the declined sea ice extent in the Arctic region, we observed a distinct increase of LFAs in ice core during 1980-2000 (Figure 5c). Hence, fatty acids in ice core are likely linked to the atmospheric transport of plankton-derived organic matter emitted from the ocean.

Historical trends of LFAs and HFAs are somewhat similar to solar irradiance (e.g., Lean, 2000, 2010) and reconstructed Greenland temperature anomaly (GTA) (e.g., Kobashi et al., 2013), the latter primarily reflects Arctic Oscillations (AO) except for few points around AD 1870s (Figure 5c, d). Strong correlations between 30-RM of LFAs and 30-RM of GTA (0.86), and 21-RM of HFAs and 21-RM of GTA (0.86) suggest that long-range transport and deposition of LFAs and HFAs are linked to AO. This agreement further suggests that variability of LFAs and HFAs in the Alaskan ice core could be significantly controlled by large-scale atmospheric circulation in the Northern Hemisphere on a multi-decadal scale (Figures 3, 4 and 5a-d). Concentrations of LFAs and HFAs increase when AO shows an increased negative phase. It is likely that when the sinusoidal jet streams travel (ridge) over the Alaskan regions, they rapidly deliver the air parcels from southern part of Alaska (the Bering
Sea, western North Pacific, and/or East Asian regions) during negative AO phase, and gradually travel over the southwestern to southeastern part of North America (trough) due to the weakening of Icelandic low and Azores high pressure center (http://www.nc-climate.ncsu.edu/climate/). This result also reveals that the sea-to-air emission of fatty acids followed by subsequent transport to the APA site sensitively responds to the multidecadal climatic periodicity cycle (e.g., PDO, NPGO and AO).

5. Conclusions

This study demonstrates that fatty acids are abundant in the Aurora Peak ice core (180 m long, 1734 - 2008) from southern Alaska. The molecular distributions of fatty acids were characterized by the predominance of C$_{16:0}$, followed by C$_{18:1}$ and C$_{14:0}$. This distribution pattern is different from that of other ice core from Greenland Site-J where longer-chain fatty acids of terrestrial higher plant origin are often more abundant. Correlation analyses of LMW fatty acids with azelaic acid, major ions, levoglucosan and sugar compounds suggest that fatty acids are mainly derived by sea-to-air emissions of phytoplankton-derived organic matter in the northern North Pacific including the Gulf of Alaska. This study further demonstrates that fatty acids are strongly associated with climate periodicity cycle, which could be transported via atmospheric circulation in the circumpolar regions. Comparisons of fatty acid profiles in the ice core with paleoclimate proxy records such as Arctic Oscillation (AO) index and δD records in the ice core from Northeast Asia showed a strong agreement, suggesting that fatty acids in ice core can be used as useful indicators for the changes in marine biogenic inputs to Alaskan region.

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References:


Kawamura, K., 1995. Land-derived lipid class


Table 1. Concentrations of homologous series of fatty acids (C$_{12:0}$-C$_{30:0}$) in the ice core from Aurora Peak, Alaska since 1734-2008.

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Formula</th>
<th>Abbr.</th>
<th>Ave.</th>
<th>Min.</th>
<th>Max.</th>
<th>SD</th>
</tr>
</thead>
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<tr>
<td>Lauric acid</td>
<td>CH$_3$(CH$_2$)$_9$COOH</td>
<td>C$_{12:0}$</td>
<td>4.82</td>
<td>BDL</td>
<td>21.6</td>
<td>4.65</td>
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<td>Myristic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{11}$COOH</td>
<td>C$_{14:0}$</td>
<td>15.3</td>
<td>BDL</td>
<td>91.3</td>
<td>21.9</td>
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<td>Pentadecylic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{13}$COOH</td>
<td>C$_{15:0}$</td>
<td>3.56</td>
<td>BDL</td>
<td>17.9</td>
<td>4.69</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{15}$COOH</td>
<td>C$_{16:0}$</td>
<td>20.3</td>
<td>BDL</td>
<td>95.1</td>
<td>29.8</td>
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<td>Margaric acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{17}$COOH</td>
<td>C$_{17:0}$</td>
<td>5.29</td>
<td>BDL</td>
<td>59.2</td>
<td>10.7</td>
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<tr>
<td>Stearic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{17}$COOH</td>
<td>C$_{18:0}$</td>
<td>10.7</td>
<td>BDL</td>
<td>84.3</td>
<td>17.8</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{17}$CH=CH(CH$_2$)$_7$COOH</td>
<td>C$_{18:1}$</td>
<td>19.6</td>
<td>BDL</td>
<td>188.9</td>
<td>38.6</td>
</tr>
<tr>
<td>Arachidic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{21}$COOH</td>
<td>C$_{20:0}$</td>
<td>2.03</td>
<td>BDL</td>
<td>26.3</td>
<td>4.48</td>
</tr>
<tr>
<td>Behenic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{23}$COOH</td>
<td>C$_{22:0}$</td>
<td>1.72</td>
<td>BDL</td>
<td>21.8</td>
<td>3.66</td>
</tr>
<tr>
<td>Tricosyltic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{25}$COOH</td>
<td>C$_{23:0}$</td>
<td>0.83</td>
<td>BDL</td>
<td>10.2</td>
<td>1.81</td>
</tr>
<tr>
<td>Lignoceric acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{24}$COOH</td>
<td>C$_{24:0}$</td>
<td>3.32</td>
<td>BDL</td>
<td>47.7</td>
<td>7.74</td>
</tr>
<tr>
<td>Pentacosyl acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{25}$COOH</td>
<td>C$_{25:0}$</td>
<td>1.02</td>
<td>BDL</td>
<td>12.4</td>
<td>2.27</td>
</tr>
<tr>
<td>Cerotic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{26}$COOH</td>
<td>C$_{26:0}$</td>
<td>1.57</td>
<td>BDL</td>
<td>19.5</td>
<td>3.44</td>
</tr>
<tr>
<td>Heptacosyl acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{27}$COOH</td>
<td>C$_{27:0}$</td>
<td>0.36</td>
<td>BDL</td>
<td>1.48</td>
<td>0.41</td>
</tr>
<tr>
<td>Montanic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{28}$COOH</td>
<td>C$_{28:0}$</td>
<td>1.09</td>
<td>BDL</td>
<td>9.41</td>
<td>2.16</td>
</tr>
<tr>
<td>Nonacosyl acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{29}$COOH</td>
<td>C$_{29:0}$</td>
<td>0.09</td>
<td>BDL</td>
<td>0.19</td>
<td>na</td>
</tr>
<tr>
<td>Melissic acid</td>
<td>CH$_3$(CH$<em>2$)$</em>{30}$COOH</td>
<td>C$_{30:0}$</td>
<td>0.15</td>
<td>BDL</td>
<td>0.23</td>
<td>0.07</td>
</tr>
</tbody>
</table>

BDL = Below detection limit (0.001 ng/g-ice)
Figure Captions

Figure 1. Geographical location of Aurora Peak in Alaska, where 180-meter long ice core was drilled on the saddle of this peak in 2008.

Figure 2. Average molecular distributions of fatty acids (C\textsubscript{12:0}-C\textsubscript{30:0}) in the ice core samples (age: 1734 – 2008) collected from Aurora Peak of Alaska.

Figure 3. Historical changes of selected low molecular weight fatty acids in the ice core collected from Aurora Peak in Alaska for 1734-2008.

Figure 4. Concentration changes of selected higher molecular weight fatty acids in the ice core from Aurora Peak in Alaska for 1734-2008.

Figure 5. Concentration changes of (a) total fatty acids (C\textsubscript{12:0} - C\textsubscript{30:0}), (b) higher molecular weight fatty acids (HFAs) (c) lower molecular weight fatty acids (LFAs), (d) Greenland temperature anomalies (GTA) calculated from Greenland temperature and the NH temperature (Kobashi et al., 2013), (e) concentration ratios of C\textsubscript{18:1} and C\textsubscript{18:0} in the ice core since 1734-2008 collected from Aurora Peak in Alaska, (f) 20-year running mean of hydrogen isotope ratios (δD) in ice core from Kamchatka Peninsula, Russia (Sato et al., 2014), and (g) ice core depth v.s. estimated year (Tsushima et al., 2014).
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Highlights

1. Fatty acids in south Alaskan ice core are long-range atmospheric transported.
2. Shorter chain fatty acids are derived from phytoplankton in the North Pacific.
3. Fatty acid records are linked with climate periodic cycle of AO, PDO and NPGO.