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

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16 Abstract

17 An ice core drilled at Aurora Peak in southeast Alaska was analysed for homologous
18 series of straight chain fatty acids ($C_{12:0}$ - $C_{30:0}$) including unsaturated fatty acid (oleic acid)
19 using gas chromatography (GC/FID) and GC/mass spectrometry (GC/MS). Molecular
20 distributions of fatty acids are characterized by even carbon number predominance with a peak
21 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
22 ng/g-ice) and myristic acid ($C_{14:0}$, 15.3 ±21.9 ng/g-ice). The historical trends of short-chain
23 fatty acids, together with correlation analysis with inorganic ions and organic tracers suggest
24 that short-chain fatty acids (except for $C_{12:0}$ and $C_{15:0}$) were mainly derived from sea surface
25 micro layers through bubble bursting mechanism and transported over the glacier through the
26 atmosphere. This atmospheric transport process is suggested to be linked with Kamchatka ice
27 core δD record from Northeast Asia and Greenland Temperature Anomaly (GTA). In contrast,
28 long-chain fatty acids ($C_{20:0}$ - $C_{30:0}$) are originated from terrestrial higher plants, soil organic
29 matter and dusts, which are also linked with GTA. Hence, this study suggests that Alaskan
30 fatty acids are strongly influenced by Pacific Decadal Oscillation/North Pacific Gyre
31 Oscillation and/or extra tropical North Pacific surface climate and Arctic oscillation. We also
32 found that decadal scale varaibility of $C_{18:1}/C_{18:0}$ ratios in the Aurora Peak ice core correlate
33 with the Kamchatka ice core δD, which reflects climate oscillations in the North Pacific. This
34 study suggests that photochemical aging of organic aerosols could be controlled by climate
35 periodicity.

36 (246)

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 (BF_3)/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 wieght 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 Artic 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 histrical 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 excellet 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 gradaully 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 assoaciated with an enhanced phytoplankton productivity in the open ocean due to the retreat of sea ice and an enhanaced 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 $C_{14:0}$, $C_{16:4\omega1}$ and $C_{20:5\omega3}$ have been reported during the phytoplankton bloom whereas $C_{18:0}$, $C_{18:1\omega9}$, $C_{18:2\omega2}$ and $C_{18:4\omega3}$ 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 mircrobial lipids by soil remobilazation (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

190 soil dust particles in few ice core sections in this study. Cahill (2003) reported, based on the
191 chemical composition study of Alaskan aerosols, that Europe, Russia, Asia and other upwind
192 areas are significant source regions for the aerosol loading over and/or around the North Pacific
193 regions. In addition, higher plant-derived pollens, fungi, bacteria, spores and soil organic
194 matter can easily supply HFAs in the atmosphere with high speed winds (Lechevalier, 1977).
195 Updraft of wind from earth surface to cloud level and/or any type of atmospheric instability
196 could act as a driving force for the significant transport of HFAs over the ice sheet at high
197 mountains.

198 The concentration ratios of atmospheric compounds can be used to determine the origin
199 of these atmospheric tracers and sometimes source, sinks and other important hidden
200 characteristics. Alkanoic acids $<C_{20}$ can be derived from marine phytoplankton, bacteria,
201 spores, and organic detritus as mentioned above. Thus, ratio of $\geq C_{22}/<C_{20}$ under 1 and C_{max} at
202 C_{16} and C_{18} can reflect microbial activities for aerosols with less contribution from terrestrial
203 higher plants (Fang et al., 1999; Oliveira et al., 2007). Interestingly, the ratio obtained in this
204 study is 0.13, which is significantly lower than 1.0 with C_{max} at C_{16}. This again suggests that
205 fatty acids in the ice core are mainly derived from marine biota via sea-to-air emission and
206 subsequent atmospheric transport over the Alaskan mountain area.

207 Once unsaturated fatty acids (indicators of recent biogenesis) are emitted to the
208 atmosphere from the ocean surface, the double bond in their structures can be oxidized by OH
209 radicals, ozone and other oxidants, resulting in aldehydes and dicarboxylic acids (Kawamura
210 and Gagosian, 1987; Kawamura et al., 1995). Thus, the concentration ratios between saturated
211 alkanoic acid ($C_{18:0}$) and unsaturasted alkenoid acid ($C_{18:1}$) can be used as a proxy to estimate
212 the atmospheric aging of organic aerosols. For instance, Ho et al. (2010) used such ratios to
213 discuss the photochemical aging of organic aerosols. We found higher $C_{18:1}/C_{18:0}$ ratios around
214 at 1770s, 1850s, 1950s, 1980s and 2000s (Figure 5e), suggesting that marine-derived fresh
215 oragnic 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 $C_{18:1}/C_{18:0}$ 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 betwen photochemical tracer; azelaic acid (C_9) (Pokhrel et al., unpublished result) and $C_{18:1}$ (R=0.83), $C_{18:0}$ (0.75), and total LFAs ($C_{12:0}$ - $C_{19:0}$) (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 photochmemical degradation was not significant during the period. However, as seen in Figure 5e, a significant variation of $C_{18:1}/C_{18:0}$ ratios was detected in the ice core profile, a point to be discussed later. In contrast, levoglucosan, which is a unqiue 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 ($C_{16:0}$) (R = 0.10), $C_{18:0}$ (0.07), $C_{18:1}$ (0.11) and LFAs ($C_{12:0}$ - $C_{19:0}$) (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 arabitol, 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 ($C_{12:0}$ - $C_{19:0}$) 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 imporant 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 buring (Simoneit, 1989) whereas Ca^+ is abundant in continental dusts (Kawamrua 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 bilogical 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 oxidaiton 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 δD record from Kamchtaka (Figure 5f) (Sato et a., 2014), further supporting that these ions along with fatty acids are coupled with past climate change.

Historical trend of δD 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 δD data is also an indicator of changes

267 in atmospheric transport of moisture, rainfall, and snowfall seasonality and humidity source
268 (Dansgaard, 1964), which are essential factors for emission and deposition of fatty acids. For
269 example, water vapor transport analysis showed that almost 80% of winter and 50% of summer
270 precipitations over the Euraasian Continent originate from the North Pacific Ocean (Numaguti,
271 1999), which can support the southern Alaskan atmospheric circulation (Yasunari and
272 Yamazaki, 2009).

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

280 According to Sato et al. (2014), historical trend of δD in Kamchatska ice indicates the
281 variations of climate oscillation such as Pacific Decadal Oscillation (PDO) and North Pacific
282 Gyre Oscillation (NPGO). For instance, we found that correlation coefficient (R) of annual
283 mean of δD and NPGO (Di Lorenzo et al., 2008) is 0.70 ($p < 0.10$) after great climate shift
284 (1979-1997). Moreover, δD records seem to correlate with extended reconstructed sea surface
285 temperature of the mid to high latitude North Pacific (30-45° N, 165- E- 165° W), which can
286 represent the sea surface temperature anomaly and PDO (Sato et al., 2014, reference therein).
287 Relation between 15-point running mean (RM) of δD (15-RM δD) and 21-RM of $C_{18:1}/C_{18:0}$
288 showed a positive correlaltion (R = 0.80). It further suggests that photochemical aging is
289 associated with the climate periodicity cycle. Interestingly, 15-RM of LFAs and 15-RM of δD
290 showed a better correlation (R=0.79) as compared to 15-RM of HFAs (0.54), suggesting that
291 sea-to-air emissions of LFAs are associated with the climate periodicity. These results indicate

292 a significant atmospheric transport of air parcels from lower to higher latitudes in the North
293 Pacific rather than the continental source regions in Alaska. Hence, historical trend of fatty
294 acids in ice core is a good indicator for changes in atmospheric circulation over the North
295 Pacific, where PDO and NPGO seem to be important.

296 Similarly, Parkinson et al. (1999) reported the overall reduction of sea ice extent since
297 1978 to 1996, with somewhat extent for 1990-1996. Parkinson and Cavalieri, (2002) reported a
298 21-year microwave data set of Arctic regions and demonstrated that there is a reduction of sea
299 ice extent at a rate of –2.7±0.5 % per decade, in which summer rate is greater (-4.9±1.5 %)
300 compared to winter (-1.8 ±0.6 %). In addition, National Snow and Ice Data Center (nsidc.org)
301 and/or Alaska Ocean Observing System (www.aoos.org) also reported that sea ice extent is
302 declined from 1978 to 2010 for the Northern Hemisphere. Following the declined sea ice
303 extent in the Arctic region, we observed a distinct increase of LFAs in ice core during 1980-
304 2000 (Figure 5c). Hence, fatty acids in ice core are likely linked to the atmospheric transport of
305 plankton-derived organic matter emitted from the ocean.

306 Historical trends of LFAs and HFAs are somewhat similar to solar irradiance (e.g.,
307 Lean, 2000, 2010) and reconstructed Greenland temperarure anomaly (GTA) (e.g., Kobashi et
308 al., 2013), the latter primarily reflects Arctic Oscillations (AO) except for few points around
309 AD 1870s (Figure 5c, d). Strong correlations between 30-RM of LFAs and 30-RM of GTA
310 (0.86), and 21-RM of HFAs and 21-RM of GTA (0.86) suggest that long-range transport and
311 deposition of LFAs and HFAs are linked to AO. This agreement further suggests that
312 varaibility of LFAs and HFAs in the Alaskan ice core could be significantly controlled by
313 large-scale atmospheric circulation in the Northern Hemisphere on a multi-decadal scale
314 (Figures 3, 4 and 5a-d). Concentrations of LFAs and HFAs increase when AO shows an
315 increased negative phase. It is likely that when the sinusoidal jet streams travel (ridge) over the
316 Alaskan regions, they rapidly deliver the air parcels from southern part of Alaska (the Bering

317 Sea, western North Pacific, and/or East Asian regions) during negative AO phase, and
318 gradually travell over the southwestern to southeastern part of North America (trough) due to
319 the weakening of Icelandic low and Azores high pressure center (http://www.nc-
320 climate.ncsu.edu/climate/). This result also reveals that the sea-to-air emission of fatty acids
321 followed by subsequent transport to the APA site sensitively responds to the multidecadal
322 climatic periodicity cycle (e.g., PDO, NPGO and AO).
323
324 5. Conclusions
325 This study demonstrates that fatty acids are abundant in the Aurora Peak ice core (180
326 m long, 1734 - 2008) from southern Alaska. The molecular distributions of fatty acids were
327 characterized by the predominance of $C_{16:0}$, followed by $C_{18:1}$ and $C_{14:0}$. This distribution
328 pattern is different from that of other ice core from Greenland Site-J where longer-chain fatty
329 acids of terrestrial higher plant origin are often more abundant. Correlation analyses of LMW
330 fatty acids with azelaic acid, major ions, levoglucosan and sugar compounds suggest that fatty
331 acids are mainly derived by sea-to-air emissions of phytoplankton-derived organic matter in the
332 northern North Pacific including the Gulf of Alaska. This study further demonstrates that fatty
333 acids are strongly associated with climate periodicity cycle, which could be transported via
334 atmospheric circulation in the circumpolar regions. Comparisons of fatty acid profiles in the ice
335 core with paleoclimate proxy records such as Arctic Oscillation (AO) index and δD records in
336 the ice core from Northeast Asia showed a strong agreement, suggesting that fatty acids in ice
337 core can be used as useful indicators for the changes in marine biogenic inputs to Alaskan
338 region.
339
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504 (6239)
505

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

			Concentrations (ng/g-ice)			
Common Name	Formula	Abbr.	Ave.	Min.	Max.	SD
Lauric acid	$CH_3(CH_2)_{10}COOH$	$C_{12:0}$	4.82	BDL	21.6	4.65
Myristic acid	$CH_3(CH_2)_{12}COOH$	$C_{14:0}$	15.3	BDL	91.3	21.9
Pentadecylic acid	$CH_3(CH_2)_{13}COOH$	$C_{15:0}$	3.56	BDL	17.9	4.69
Palmitic acid	$CH_3(CH_2)_{14}COOH$	$C_{16:0}$	20.3	BDL	95.1	29.8
Margaric acid	$CH_3(CH_2)_{15}COOH$	$C_{17:0}$	5.29	BDL	59.2	10.7
Stearic acid	$CH_3(CH_2)_{16}COOH$	$C_{18:0}$	10.7	BDL	84.3	17.8
Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	$C_{18:1}$	19.6	BDL	188.9	38.6
Arachidic acid	$CH_3(CH_2)_{18}COOH$	$C_{20:0}$	2.03	BDL	26.3	4.48
Behenic acid	$CH_3(CH_2)_{20}COOH$	$C_{22:0}$	1.72	BDL	21.8	3.66
Tricosylic acid	$CH_3(CH_2)_{21}COOH$	$C_{23:0}$	0.83	BDL	10.2	1.81
Lignoceric acid	$CH_3(CH_2)_{22}COOH$	$C_{24:0}$	3.32	BDL	47.7	7.74
Pentacosylic acid	$CH_3(CH_2)_{23}COOH$	$C_{25:0}$	1.02	BDL	12.4	2.27
Cerotic acid	$CH_3(CH_2)_{24}COOH$	$C_{26:0}$	1.57	BDL	19.5	3.44
Heptacosylic acid	$CH_3(CH_2)_{25}COOH$	$C_{27:0}$	0.36	BDL	1.48	0.41
Montanic acid	$CH_3(CH_2)_{26}COOH$	$C_{28:0}$	1.09	BDL	9.41	2.16
Nonacosylic acid	$CH_3(CH_2)_{27}COOH$	$C_{29:0}$	0.09	BDL	0.19	na
Melissic acid	$CH_3(CH_2)_{28}COOH$	$C_{30:0}$	0.15	BDL	0.23	0.07

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

509

Figure Captions

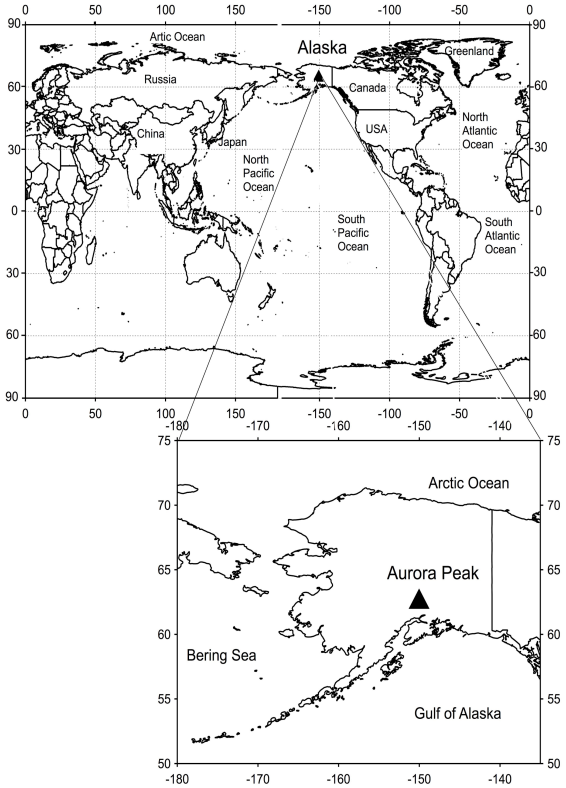
Figure 1. Geographical location of Aurora Peak in Alaska, where 180-meter long ice core was drilled on the saddle of this peak in 2008.

Figure 2. Average molecular distributions of fatty acids ($C_{12:0}$-$C_{30:0}$) 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 ($C_{12:0}$ - $C_{30:0}$), (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 $C_{18:1}$ and $C_{18:0}$ 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 (Tsushiman et al., 2014).



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

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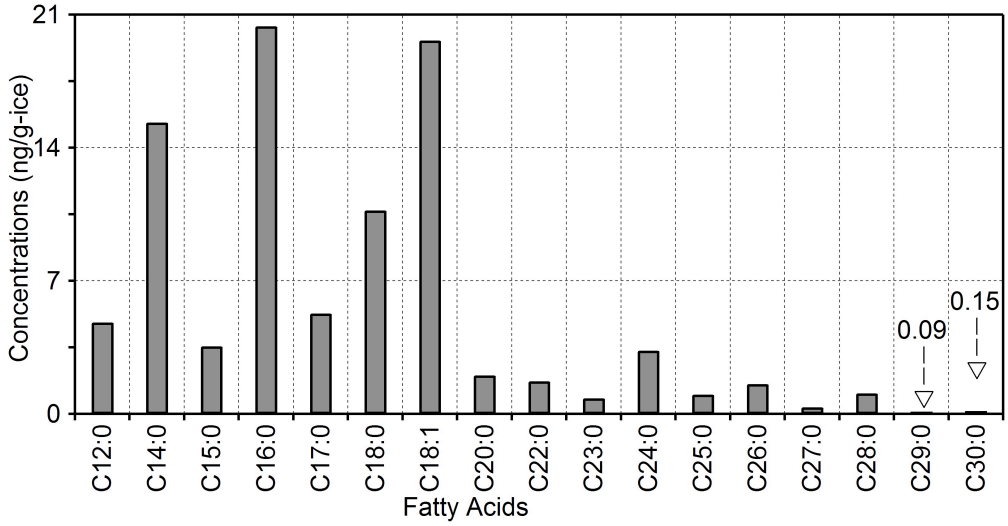

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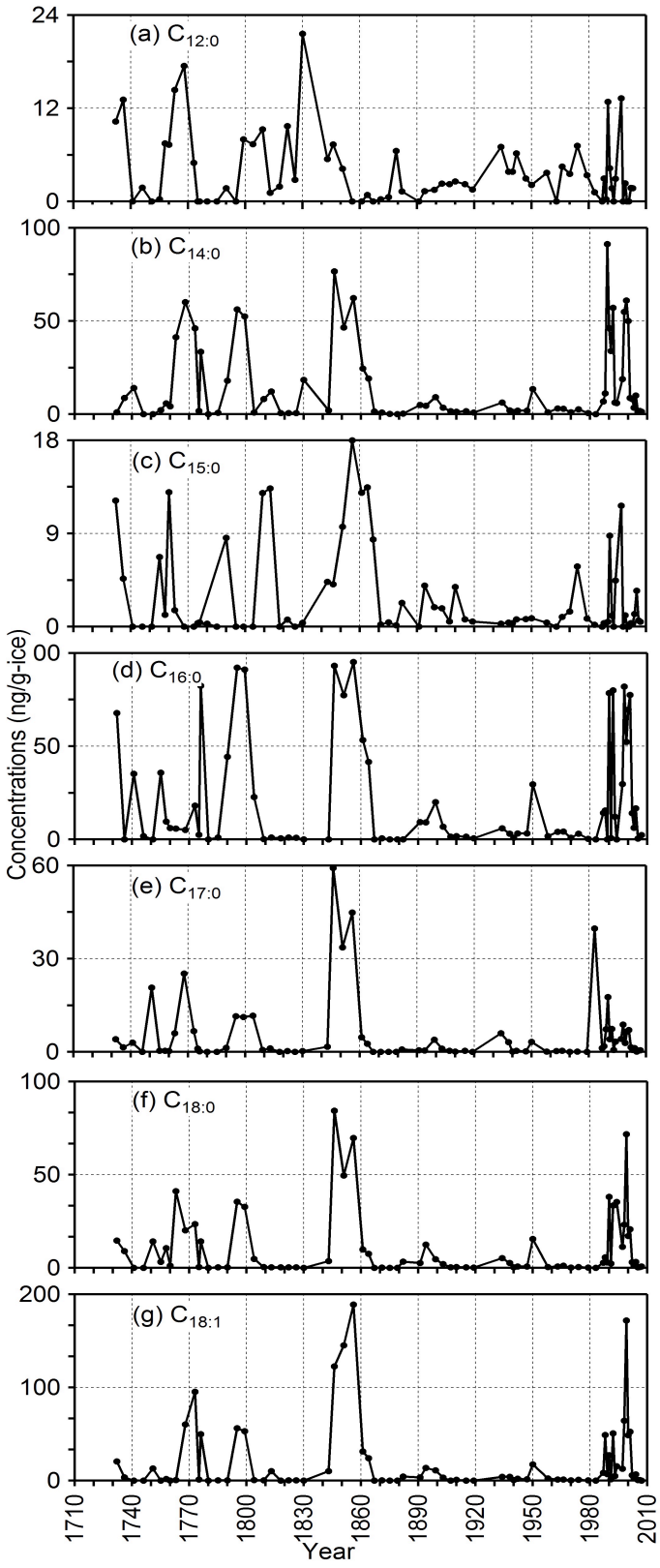
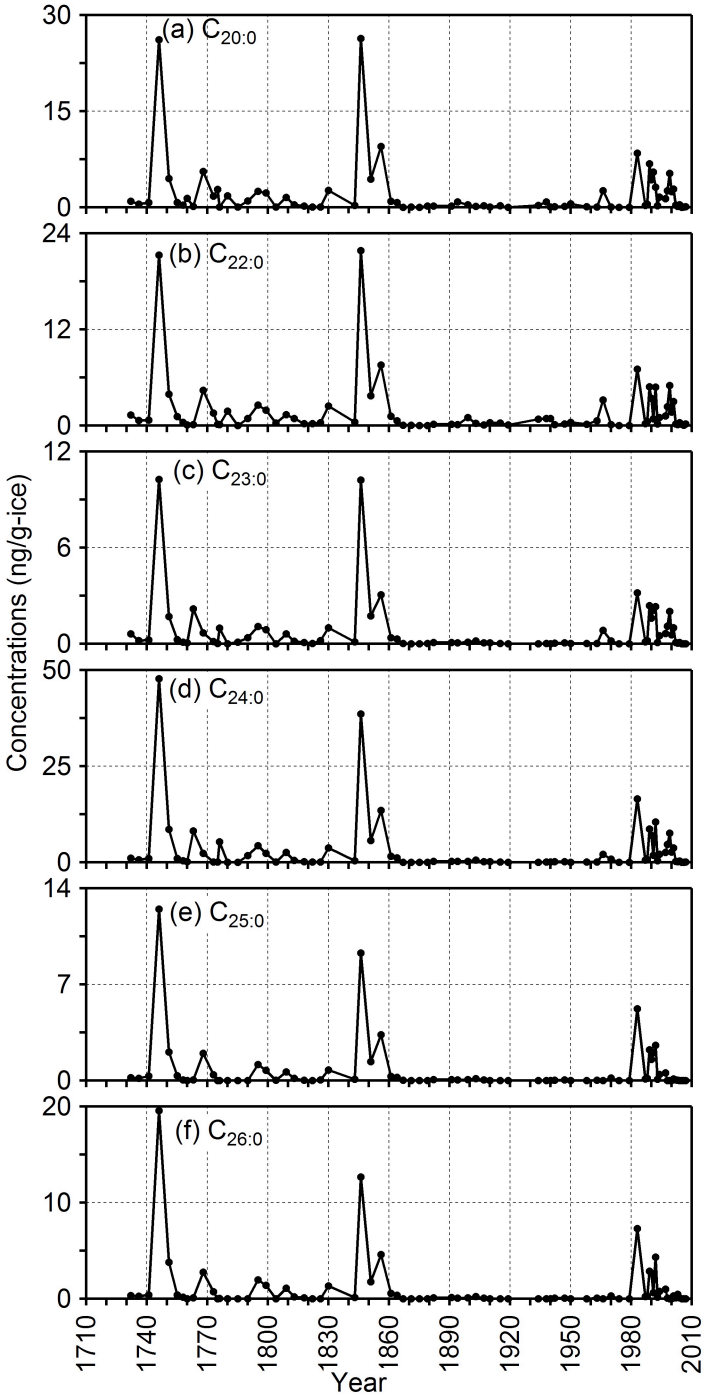
541 Figure 2. Average molecular distributions of fatty acids ($C_{12:0}$-$C_{30:0}$) in the ice core samples

542 (age: 1734 – 2008) collected from Aurora Peak of Alaska.



543

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



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

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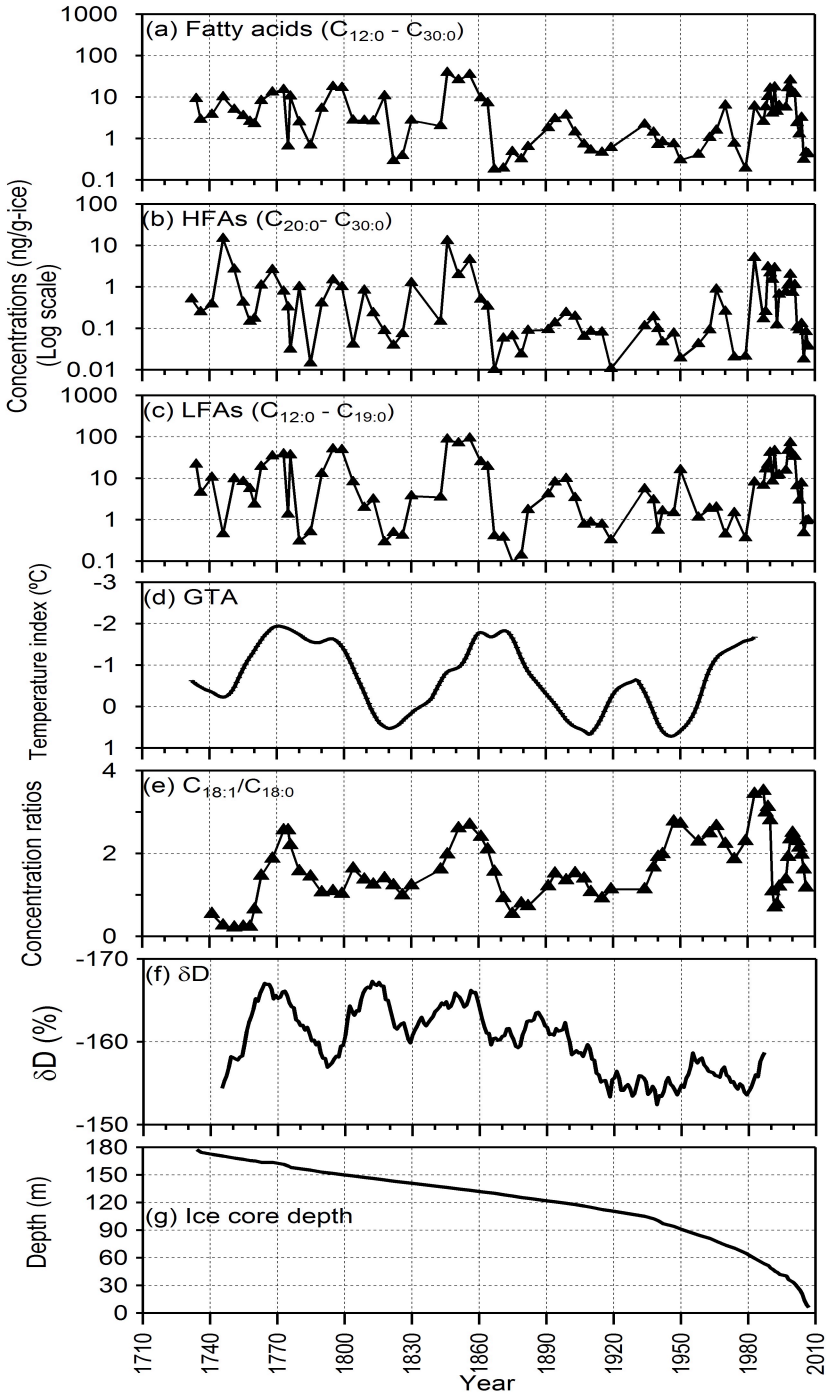

553

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

561 **Highlights**

562

563 **1.** Fatty acids in south Alaskan ice core are long-range atmospheric transported.

564 (77 with space)

565 **2.** Shorter chain fatty acids are derived from phytoplankton in the North Pacific.

566 (80 with space)

567 **3.** Fatty acid records are linked with climate periodic cycle of AO, PDO and NPGO.

568 (78 with space)