



Title	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
Author(s)	Pokhrel, Ambarish; Kawamura, Kimitaka; Seki, Osamu; Matoba, Sumito; Shiraiwa, Takayuki
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1 Ice core profiles of saturated fatty acids (C<sub>12:0</sub> - C<sub>30:0</sub>) and oleic acid (C<sub>18:1</sub>) from southern  
2 Alaska since 1734 AD: A link to climate change in the Northern Hemisphere

3

4 Ambarish Pokhrel<sup>1,2</sup>, Kimitaka Kawamura<sup>1,\*</sup>, Osamu Seki<sup>1</sup>, Sumio Matoba<sup>1</sup> and Takayuki  
5 Shiraiwa<sup>1</sup>

6

7 <sup>1</sup>Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan

8 <sup>2</sup>Graduate School of Environmental Science, Hokkaido University, Sapporo, Japan

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

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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.  $20.3 \pm SD. 29.8$  ng/g-ice) followed by oleic acid ( $C_{18:1}$ ,  $19.6 \pm 38.6$   
22 ng/g-ice) and myristic acid ( $C_{14:0}$ ,  $15.3 \pm 21.9$  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  $\delta D$  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 variability of  $C_{18:1}/C_{18:0}$  ratios in the Aurora Peak ice core correlate  
33 with the Kamchatka ice core  $\delta D$ , 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)

## 37 1. Introduction

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

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

56 Fatty acids in ice core are closely related to past climatic changes (Kawamura et al.,  
57 1995, 1996; Nishikiori et al., 1997). Their ice core profiles can be employed as a proxy to  
58 assess the past changes in marine and terrestrial emissions on multidecadal-to-centennial time  
59 scales. Here, we investigated homologous series of straight chain fatty acids (C<sub>12</sub> - C<sub>30</sub>) from  
60 Aurora Peak of Alaska to better understand the past atmospheric transport of fatty acids and to  
61 reconstruct the paleoclimate conditions and sources of fatty acids since 1734 – 2008. The

62 historical trends of fatty acids are discussed in terms of past changes in atmospheric circulation  
63 in the northern North Pacific and its surroundings.

64

## 65 2. Ice Core Samples and Analytical Procedures

66 Aurora Peak of Alaska (APA) is located in the southeast of Fairbanks (63.521°N,  
67 146.542°W) with an elevation of 2,825 meter above sea level (Figure 1). About 180 m long ice  
68 core was drilled on the saddle of APA (Fukuda et al, 2011). The ice core ages were determined  
69 by annual counting of the peaks in hydrogen isotope ( $\delta D$ ) and  $Na^+$  seasonal cycles, in which an  
70 age control was provided by reference horizons of tritium peaks in 1963 and 1964. By this  
71 methods, bottom of ice core sample was estimated to be 274 years old ( $\pm 3$  years); i.e., 1734  
72 AD (Tsushima et al., 2014).

73 The ice core was cut into ~50 cm sections and transported to the laboratory of Institute  
74 of Low Temperature Science, Hokkaido University, Japan and stored in a cold room at -20°C  
75 until analysis. To avoid the possible contaminations during sample collection and transport, ca.  
76 5 - 10 mm surfaces of the ice sections were shaved off using a ceramic knife inside a clean  
77 bench in the cold (-15°C) room (Kawamura and Yasui, 1991; Savarino and Legrand, 1998).  
78 Fatty acids were determined using butyl ester derivatization method (Mochida et al., 2003).  
79 Numbers of total ice core sections are 122, which is equivalent to ~35% of the 180 m long ice  
80 core recovered from the APS site.

81 100 mL of melt water from ice core section were placed into a pear shape flask (300  
82 mL) and the pH of the sample was adjusted to 8.5-9.0 using a 0.05 M KOH solution. The  
83 sample were concentrated down to near 5 mL using a rotary evaporator under vacuum. The  
84 concentrates were transferred to a pear shape flask (50 mL), concentrated until dryness using a  
85 rotary evaporator under vacuum, and then reacted with ~0.25 mL of 14% boron trifluoride  
86 ( $BF_3$ )/n-butanol to derive carboxyl groups to butyl esters at 100°C for 1 hour. The butyl ester

87 derivatives were determined using a capillary gas chromatography (GC; HP 6890). The GC  
88 peak identification was performed using a GC/MS (Agilent). The laboratory blanks of C<sub>14:0</sub>,  
89 C<sub>16:0</sub>, C<sub>17:0</sub>, C<sub>18:0</sub>, C<sub>18:1</sub>, C<sub>20:0</sub>, C<sub>22:0</sub> and C<sub>24:0</sub> relative to real samples were 3.9, 3.7, 1.8, 4.1, 3.8,  
90 2.6, 1.7 and 2.4 %, respectively. The analytical errors for C<sub>14:0</sub>, C<sub>16:0</sub>, C<sub>17:0</sub>, C<sub>18:1</sub>, C<sub>20:0</sub>, C<sub>24:0</sub>  
91 and C<sub>28:0</sub> fatty acids in the replicate analyses were 4.9, 3.1, 9.3, 3.5, 1.6, 2.6 and 2.5%,  
92 respectively. Here, we present concentrations of lower molecular weight fatty acids (C<sub>12:0</sub> -  
93 C<sub>19:0</sub>: LFAs) and higher molecular weight fatty acids (C<sub>20:0</sub> - C<sub>30:0</sub>: HFAs), which are all  
94 corrected for procedural blanks.

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

102

### 103 3. Results

104 Figure 2 shows the average molecular distribution of homologous series of straight  
105 chain fatty acids (C<sub>12:0</sub> - C<sub>30:0</sub>) including unsaturated fatty acid (oleic acid, C<sub>18:1</sub>) for 1734 -  
106 2008. Their molecular distributions are characterized by a strong even carbon number  
107 predominance with a peak at C<sub>16:0</sub>. C<sub>16:0</sub> comprised one third (av. 30.6%) of total fatty acids,  
108 followed by C<sub>14:0</sub> (19.3%) and C<sub>18:1</sub> (14.4%). The concentrations of C<sub>16:0</sub>, C<sub>18:1</sub> and C<sub>14:0</sub> range  
109 from below detection limit (BDL: 0.001ng/g-ice) to 95.1 ng/g (av. 20.3 ±SD 29.8 ng/g-ice),  
110 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.  
111 We also detected significant amounts of C<sub>18:0</sub> and C<sub>12:0</sub> (Table 1). HFAs (C<sub>20:0</sub> - C<sub>30:0</sub>) are

112 dominated by lignoceric acid (C<sub>24:0</sub>), followed by arachidic (C<sub>20:0</sub>) and behenic (C<sub>22:0</sub>) acid  
113 (Figure 2 and Table 1).

114 Figure 3 shows historical changes of selected LFAs in the ice core collected from  
115 Aurora Peak in Alaska. Palmitic acid (C<sub>16:0</sub>), which is the most abundant FA species, showed  
116 several peaks around the years of 1780, 1800, 1850, 1990 and 2000. Interestingly, all the  
117 components of LFAs showed a large spike around 1840-1860 (Figure 3). The historical trend  
118 of C<sub>12:0</sub> is similar to that of C<sub>15:0</sub>, except for few points. The trends of C<sub>12:0</sub> and C<sub>15:0</sub> are  
119 different than those of other LFA components, except for some points. For instance, around  
120 1850s and after 1980s similar types of higher spikes were observed (Figure 3a-3g). Figure 4  
121 presents concentration changes of selected HFAs (C<sub>20:0</sub>-C<sub>26:0</sub>) in the ice core. Although HFAs  
122 showed large spikes around at 1740s and 1840s, their historical trends are not always similar to  
123 those of LFAs. Concentrations of HFAs are relatively low during the period from 1860s to  
124 1970s (Figures 3 and 4). Except for few points, HFA species showed similar historical trends  
125 each other with peaks at around 1750s, 1850s and 1980s (Figure 4a – 4f).

126

## 127 4. Discussion

### 128 4.1. Molecular compositions of fatty acids and their historical profile

129 The homologous series of fatty acids show a strong even carbon number predominance  
130 with a peak at C<sub>16:0</sub> followed by C<sub>18:1</sub> and C<sub>14:0</sub> as described above. The predominance of C<sub>16:0</sub>  
131 has also been reported in riverine and estuarine sediments (Naraoka and Ishiwatari, 2000),  
132 marine sediments (Ohkouchi et al., 1997), soil samples (Matsumoto et al., 2007) and remote  
133 marine aerosols (Conte and Weber, 2002; Bendle et al., 2007). LFAs are mainly originated  
134 from marine phytoplankton (Kawamura and Gagosian, 1987; Kawamura, 1995; Marty et al.,  
135 1979), while HFAs are originated from terrestrial higher plants and soil dust (Kawamura et  
136 al., 1996; Ohkouchi et al., 1997). The molecular distributions of fatty acids in this study are  
137 different than those from other studies on aerosols (Kawamura et al., 2010; Fang et al., 2002)

138 and ice cores from Antarctica (Nishikiori et al., 1997) and Greenland site-J (Kawamura et al.,  
139 1995, 1996). For example, fatty acids in Greenland site-J ice core are characterized by a strong  
140 even carbon number predominance with maximum at C<sub>16</sub> or C<sub>22</sub> followed by C<sub>24</sub> and lesser  
141 abundance of C<sub>18:1</sub> (Kawamura et al., 1995, 1996).

142 Unsaturated LFAs such as C<sub>18:1</sub> are abundant in marine phytoplankton (especially  
143 diatom) (Napolitano et al., 1997) and are dominant in the sea surface micro layer (Marty et al.,  
144 1979; Garrett, 1967). Hence, the higher abundance of C<sub>18:1</sub> than C<sub>18:0</sub> in our ice core suggests  
145 an enhanced emission of C<sub>18:1</sub> from the surrounding oceans via long-range atmospheric  
146 transport to Alaskan ice core site. This is consistent with the fact that diatom is dominant  
147 species in high latitudinal oceans (Napolitano et al., 1997) and C<sub>18:1</sub> is one of a dominant  
148 marine fatty acid in the sea surface microlayer (Kawamura and Gagosian, 1987; Marty et al.,  
149 1979). In general, unsaturated FAs are labile compounds compared to saturated ones and can  
150 be easily decomposed during long-range transport (Kawamura and Gagosian, 1987). However,  
151 C<sub>18:1</sub> was abundantly detected in almost all ice core sections, suggesting that the deposition and  
152 subsequent incorporation of fresh marine aerosol components in the glacier occurred without  
153 severe photochemical degradation during atmospheric transport. This suggests that APA is an  
154 excellent site to record the historical changes in emission and transport of fresh marine organic  
155 matter from the surrounding oceans.

156 LFAs (except for C<sub>12:0</sub> and C<sub>15:0</sub>) showed similar historical profiles each other (Figure  
157 3a – 3g) with lower concentration after 1860s to 1980s, suggesting a marked decrease in the  
158 sea-to-air emission and subsequent transport of FAs during the period. In contrast, total FA  
159 concentrations gradually increased after 1960s, except for few points around 1875, 1920, 1975  
160 and 2005 (Figure 5a). The lower concentrations of LFAs during 1860-1980 AD (Figure 5c)  
161 may be in part attributed to depressed emission of marine derived fatty acids probably due to  
162 the extension of sea ice coverage around the Alaskan regions. In fact, sea ice reconstruction in  
163 Arctic region including the Chukchi Sea shows a significant expansion of sea ice area during



164 the period (de Vernal et al., 2008; Kinnard et al., 2011; Cavalieri et al., 1997). Another reason  
165 for the decreased concentrations of LFAs may be the shifting of atmospheric transport over  
166 Aurora Peak in Alaska, which could be associated with multidecadal climatic cycle in the  
167 Pacific regions (Figure 5d and 5f), a point to be discussed later. We have presented a vertical  
168 depth profile of ice core as a function of the proposed chronology by Tsushima et al. (2014)  
169 (Figure 5g).

170 In contrast, the high concentrations of LFAs before 1860s may be in part associated  
171 with an enhanced phytoplankton productivity in the open ocean due to the retreat of sea ice and  
172 an enhanced emission of fatty acids via bubble bursting processes from sea surface  
173 microlayers (de Vernal et al., 2008; Kinnard et al., 2011; Kawamura and Gagosian, 1987;  
174 Garrett, 1976). In fact, high concentrations of fatty acids like  $C_{14:0}$ ,  $C_{16:4\omega1}$  and  $C_{20:5\omega3}$  have  
175 been reported during the phytoplankton bloom whereas  $C_{18:0}$ ,  $C_{18:1\omega9}$ ,  $C_{18:2\omega2}$  and  $C_{18:4\omega3}$  were  
176 abundantly detected during the post bloom of phytoplankton in the east coast of Canada  
177 (Napolitano et al., 1997). Moreover, there could be some other contributors, for instance, from  
178 bacteria, spores, pollen, plant organelles, leaf cells, chloroplast and microbial lipids by soil  
179 remobilization (Rogge et al., 1993; Simoneit, 1989; Kawamura et al., 2003; 2010) as well as  
180 biomass burning (Oros and Simoneit, 1999). Interestingly, Nishikiori et al. (1997) reported  
181 higher concentrations of fatty acids in the Site H15 of Antarctica after 1850s and considered  
182 the results due to the enhanced sea-to-air emission of marine-derived fatty acids. Higher spikes  
183 of fatty acids could be caused by the retreat of sea ice and subsequent expansion of open ocean  
184 associated with global warming (de Vernal et al., 2008; Kinnard et al., 2011; Kawamura et al.,  
185 1995, 1996; Nishikiori et al., 1997).

186 Detection of HFAs are characterized in the ice core suggests that the deposition of  
187 terrestrial plant-derived HFAs occurred over the saddle of APA. HFAs are originated from  
188 epicuticular waxes of terrestrial higher plants and soil dust (Simoneit and Mazurek, 1982; Ho  
189 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 alkanolic acid ( $C_{18:0}$ ) and unsaturated 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 organic aerosols were more frequently transported and stored in the ice core without severe

216 photochemical processing in the air and on the glacier. On the other hand, lower  $C_{18:1}/C_{18:0}$   
217 ratios were recorded during 1730s-1750s, 1870s and 1920s (Figure 5e), suggesting that oleic  
218 acid was more oxidized during the long distance transport before the wet scavenging over the  
219 saddle of APA.

220

#### 221 *4.2. Multiple responses of Alaskan ice core to climate change*

222 We found a strong correlation between photochemical tracer; azelaic acid ( $C_9$ ) (Pokhrel  
223 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).  
224 Because azelaic acid is a photo-oxidation product of unsaturated fatty acids (Kawamura and  
225 Gagosian, 1987), the positive correlations suggest that the sea-to-air emission is the major  
226 source of LFAs in ice core and variations of photochemical degradation was not significant  
227 during the period. However, as seen in Figure 5e, a significant variation of  $C_{18:1}/C_{18:0}$  ratios  
228 was detected in the ice core profile, a point to be discussed later. In contrast, levoglucosan,  
229 which is a unique biomass-burning tracer (Simoneit, 2002) did not show the spikes in 1850s  
230 when LFAs are abundant in the ice core (Figure 5c). However, almost all compounds (diacids  
231 and fatty acids) showed higher spikes in 1850s (Figures 3, 4 and 5). No correlation of  
232 levoglucosan with palmitic acid ( $C_{16:0}$ ) ( $R = 0.10$ ),  $C_{18:0}$  (0.07),  $C_{18:1}$  (0.11) and LFAs ( $C_{12:0} -$   
233  $C_{19:0}$ ) (0.33) suggest that biomass burning is not a major source of fatty acids in ice core.

234 We detected significant amounts of sugar compounds including arabitol, mannitol,  
235 inositol (sources: virus, bacteria, algae and fungal spores),  $\alpha$ -glucose,  $\beta$ -glucose,  $\alpha$ -fructose,  $\beta$ -  
236 fructose (pollen, fruits and yeast fragments), trehalose (fungi, bacteria, soil surface and  
237 unpaved dust) and sucrose (buds and roots) (Fu et al., 2012, and references therein) in the ice  
238 core for the years of 1734 – 2008 (Pokhrel et al., unpublished results). However, we found very  
239 weak or no correlations ( $R < 0.14$ ) between LFAs ( $C_{12:0} - C_{19:0}$ ) and the above mentioned sugar  
240 compounds, indicating that the terrestrial sources are not main contributors of ice core LFAs.  
241 This again suggests that marine sources are important sources of LFAs in ice core.

242 LFAs showed weak or no correlation with some inorganic ions (unpublished results).  
243 For example, correlation coefficients (R) of  $C_{18:1}$  with  $nss-K^+$ ,  $nss-Ca^+$  and  $NH_4^+$  are 0.11, 0.23  
244 and 0.02, respectively.  $nss-K^+$  is a good tracer of biomass burning (Simoneit, 1989) whereas  $Ca^+$   
245 is abundant in continental dusts (Kawamura et al., 2004; Mkombe and Kawamura, 2014;  
246 Kunwar and Kawamura, 2014). Similarly, very weak correlations ( $<0.19$ ) were found for fatty  
247 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  
248 polluted aerosols (Legrand and Mayewski, 1997, references therein). These results suggest that  
249 LFAs are not derived from continental sources.

250 In contrast, we found a positive correlation between  $Na^+$  and  $C_{18:1}$  ( $R = 0.67$ ), and  $Na^+$   
251 and LFAs ( $R=0.50$ ). The slightly weaker correlation may be due to the possible fractionation  
252 between  $Na^+$  and LFAs during the bubble bursting process in the ocean surface. We also found  
253 a positive correlation between methanesulfonate ( $MSA^-$ ) (a good tracer of marine biological  
254 activity: oxidation product of dimethyl sulfide (DMS) emitted from the ocean by microbial  
255 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  
256 low value for  $C_{18:1}$  may be caused by its photochemical oxidation during atmospheric transport.  
257 On the other hand, correlation coefficients for  $C_{16:0}$ ,  $C_{18:0}$  and  $C_{18:1}$  with  $nss-SO_4^{2-}$  (oxidation  
258 product of DMS and  $MSA^-$ ) are 0.79, 0.77 and 0.88, respectively. These results strongly support  
259 that LFAs are derived from marine source rather than continental source. It is clear that  
260 historical trends of  $MSA^-$  and  $nss-SO_4^{2-}$  are similar (except for 1930s) ( $R=0.85$ ). Interestingly,  
261 both  $nss-SO_4^{2-}$  and  $MSA^-$  somewhat follow the  $\delta D$  record from Kamchatka (Figure 5f) (Sato et  
262 al., 2014), further supporting that these ions along with fatty acids are coupled with past climate  
263 change.

264 Historical trend of  $\delta D$  records in the Kamchatska ice core represents surface  
265 temperature for 1958-1996 and extended the reconstructed sea surface temperature from 1854  
266 to 1995 (Sato et al., 2014; Smith et al., 2008). Historical  $\delta D$  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 Eurasian 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  $\delta D$  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  $\delta D$  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  $\delta D$  and NPGO (Di Lorenzo et al., 2008) is 0.70 ( $p < 0.10$ ) after great climate shift  
284 (1979-1997). Moreover,  $\delta D$  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  $\delta D$  (15-RM  $\delta D$ ) and 21-RM of  $C_{18:1}/C_{18:0}$   
288 showed a positive correlation ( $R = 0.80$ ). It further suggests that photochemical aging is  
289 associated with the climate periodicity cycle. Interestingly, 15-RM of LFAs and 15-RM of  $\delta D$   
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  $-2.7 \pm 0.5$  % per decade, in which summer rate is greater ( $-4.9 \pm 1.5$  %)  
300 compared to winter ( $-1.8 \pm 0.6$  %). In addition, National Snow and Ice Data Center (nsidc.org)  
301 and/or Alaska Ocean Observing System (www.aos.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 temperature 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 variability 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 travel 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-  
321 climate.ncsu.edu/climate/](http://www.nc-<br/>320 climate.ncsu.edu/climate/)). This result also reveals that the sea-to-air emission of fatty acids  
322 followed by subsequent transport to the APA site sensitively responds to the multidecadal  
323 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<sub>16:0</sub>, followed by C<sub>18:1</sub> and C<sub>14:0</sub>. 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<sub>12:0</sub>-C<sub>30:0</sub>) in the ice  
 507 core from Aurora Peak, Alaska since 1734-2008.

Common Name	Formula	Abbr.	Concentrations (ng/g-ice)			
			Ave.	Min.	Max.	SD
Lauric acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> COOH	C <sub>12:0</sub>	4.82	BDL	21.6	4.65
Myristic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> COOH	C <sub>14:0</sub>	15.3	BDL	91.3	21.9
Pentadecylic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>13</sub> COOH	C <sub>15:0</sub>	3.56	BDL	17.9	4.69
Palmitic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH	C <sub>16:0</sub>	20.3	BDL	95.1	29.8
Margaric acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> COOH	C <sub>17:0</sub>	5.29	BDL	59.2	10.7
Stearic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	C <sub>18:0</sub>	10.7	BDL	84.3	17.8
Oleic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH=CH (CH <sub>2</sub> ) <sub>7</sub> COOH	C <sub>18:1</sub>	19.6	BDL	188.9	38.6
Arachidic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>18</sub> COOH	C <sub>20:0</sub>	2.03	BDL	26.3	4.48
Behenic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>20</sub> COOH	C <sub>22:0</sub>	1.72	BDL	21.8	3.66
Tricosylic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>21</sub> COOH	C <sub>23:0</sub>	0.83	BDL	10.2	1.81
Lignoceric acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>22</sub> COOH	C <sub>24:0</sub>	3.32	BDL	47.7	7.74
Pentacosylic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>23</sub> COOH	C <sub>25:0</sub>	1.02	BDL	12.4	2.27
Cerotic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>24</sub> COOH	C <sub>26:0</sub>	1.57	BDL	19.5	3.44
Heptacosylic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>25</sub> COOH	C <sub>27:0</sub>	0.36	BDL	1.48	0.41
Montanic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>26</sub> COOH	C <sub>28:0</sub>	1.09	BDL	9.41	2.16
Nonacosylic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>27</sub> COOH	C <sub>29:0</sub>	0.09	BDL	0.19	na
Melissic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>28</sub> COOH	C <sub>30:0</sub>	0.15	BDL	0.23	0.07

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

509

510 **Figure Captions**

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

513

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

516

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

519

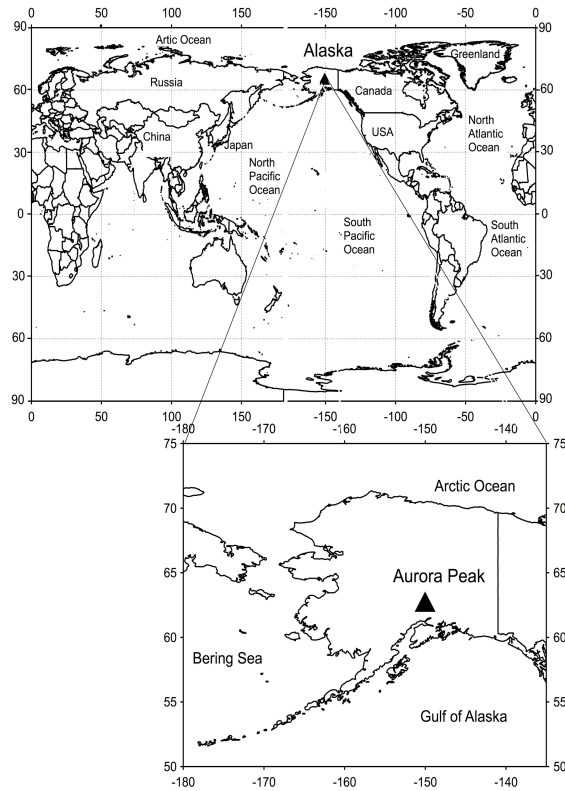
520 Figure 4. Concentration changes of selected higher molecular weight fatty acids in the  
521 ice core from Aurora Peak in Alaska for 1734-2008.

522

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

531

532



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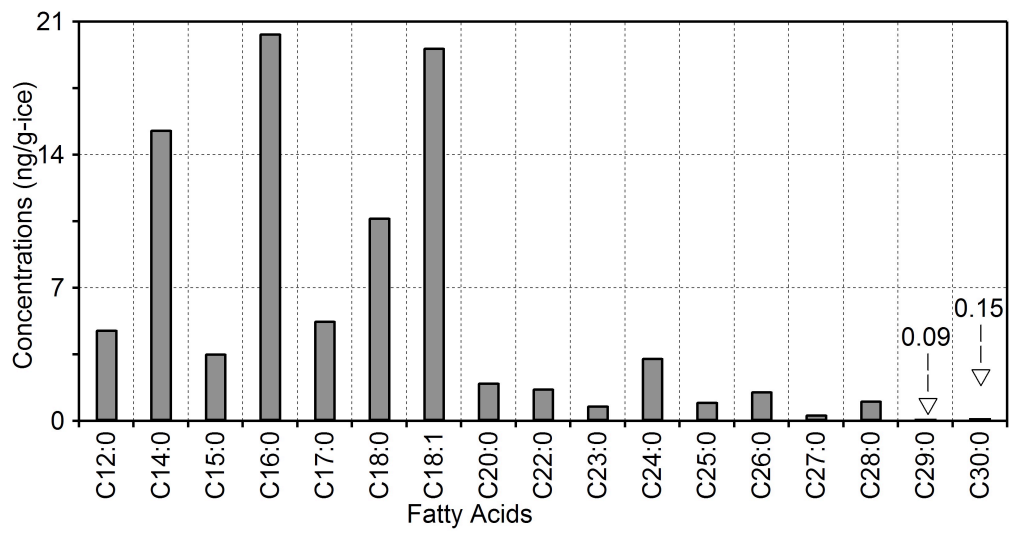
534

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.

537

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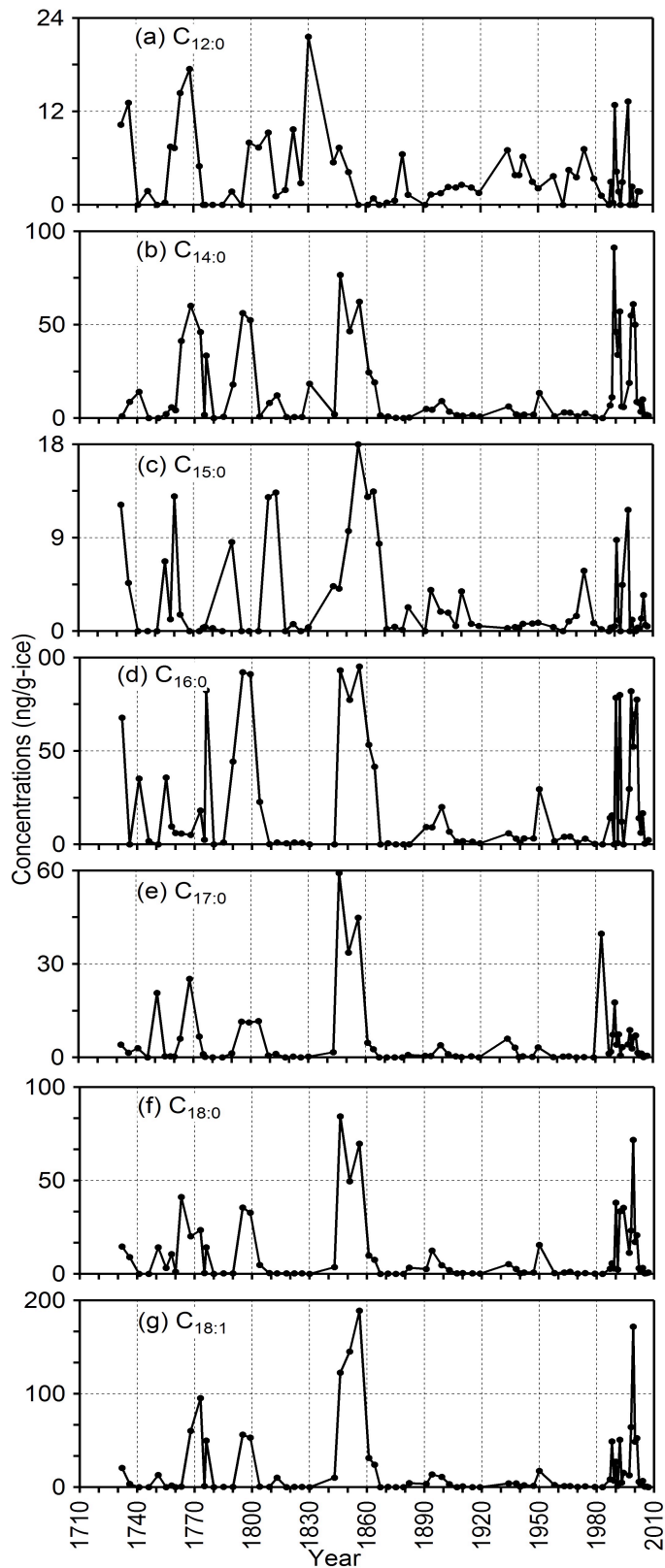
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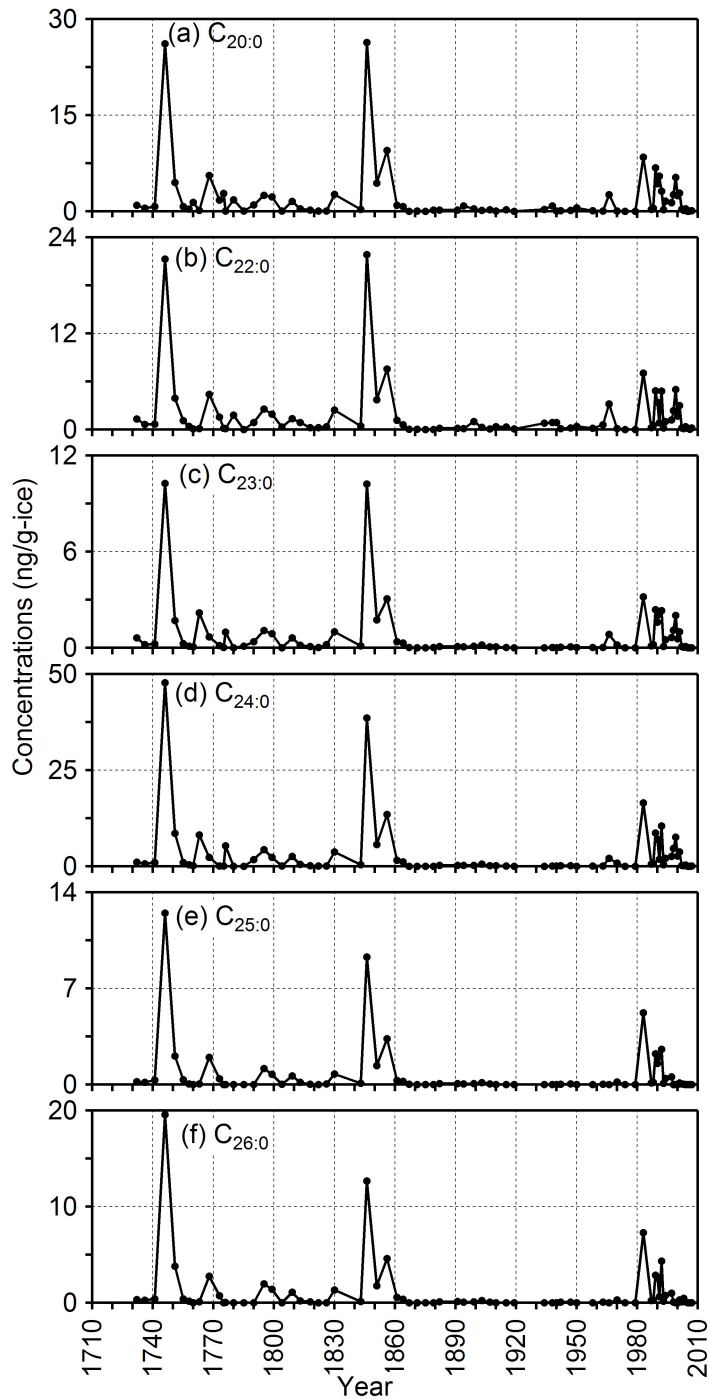
541 Figure 2. Average molecular distributions of fatty acids (C<sub>12:0</sub>-C<sub>30:0</sub>) in the ice core samples  
542 (age: 1734 – 2008) collected from Aurora Peak of Alaska.





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.



546

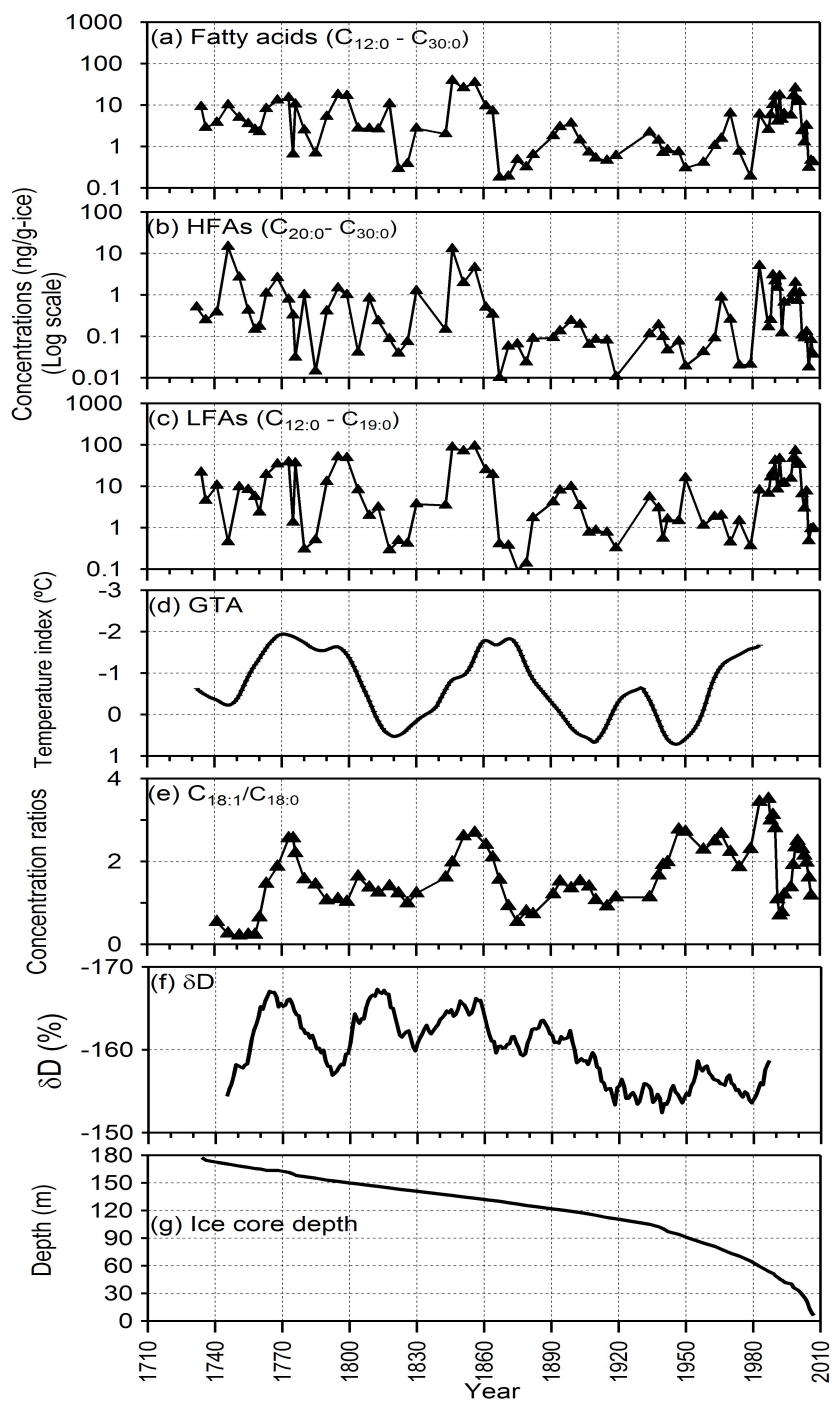
547 Figure 4. Concentration changes of selected higher molecular weight fatty acids in the ice  
 548 core from Aurora Peak in Alaska for 1734-2008.

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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 ( $\delta D$ ) in ice core from Kamchatka Peninsula, Russia (Sato et al., 2014), and (g)  
 560 ice core depth v.s. estimated year (Tsushima et al., 2014).

561 **Highlights**

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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)