1 **Ice core records of biomass burning tracers (levoglucosan, dehydroabietic and**

2 **vanillic acids) from Aurora Peak in Alaska since 1660s: A new dimension of**

3 **forest fire activities in the Northern Hemisphere**

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15   **Abstract**

16   A 180 m long (ca. 274 years) ice core was drilled in the saddle of the Aurora

17   Peak of Alaska (63.52°N; 146.54°W, elevation: 2,825 m). The ice core samples were

18   melt, concentrated and then derivatized with N,O-bis-(trimethylsilyl)

19   trifluoroacetamide with 1% trimethylsilyl chloride and pyridine followed by gas

20   chromatography/mass spectrometry analyses. Levoglucosan, dehydroabietic acid, and

21   vanillic acid are reported for the first time from the alpine glacier to better understand

22   historical biomass burning activities in the source region of southern Alaska. These

23   organic compounds showed higher concentrations with many sporadic peaks in the

24   1660s-1830s, 1913, and 2005. Moreover, there are few discrepancies of higher spikes

25   among them after the 1970s with sporadic peaks in 1994-2007 for dehydroabietic acid.

26   Historical trends of levoglucosan, dehydroabietic and vanillic acid showed that

27   biomass burning activities from resin and lignin in boreal conifer trees, other higher

28   plants and grasses were significant before the 1840s and after the 1970s in the source

29   regions of southern Alaska, being different from previous ice core studies. Long-

30   range atmospheric transport could be important for levoglucosan compared to

31   dehydroabietic acid in the North Pacific Rim (NPR). We found weak or no

32   correlations of levoglucosan with NO_2^- (r=0.06), NO_3^- (0.04), nss-SO_4^{2-} (0.08), nss-K^+

33   (0.11), and NH_4^+ (0.11) from the same ice core, suggesting that these anions and

34   cations do not represent a gleaming signal of biomass burning activities in the source

35   regions for southern Alaska. Hence, this study revels a new dimension of biomass

36   burning periodic cycles in the NPR.

37

1. Introduction

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39 Ice core records provide the long-term changes in deposition and

40 concentration of biomass burning organic (e.g., formate, acetate, dicarboxylic acid,

41 pyruvic acid and α-dicarbonyls) and inorganic (e.g., NH_3^+, SO_4^{2-}, NO_3^- and NO_2^-)

42 atmospheric chemical species, which are reported elsewhere (Giorio et al., 2018;

43 Wolff et al., 2012; Kawamura et al., 2012; Lamarque et al., 2010; Kaufmann et al.,

44 2010; Andreae and Merlet, 2001; Legrand and Mayewski, 1997; Yang et al., 1995).

45 Biomass burning activities such as forest fires and residential heating have some

46 extent on climate change effect (Keywood et al., 2011; Whitlow et al., 1994). Many

47 studies have shown that there is some discrepancy of temporal and spatial biomass

48 burning activities (Kawamura et al., 2012; Whitlow et al., 1994; Kaplan et al., 2010

49 and references therein) in the Northern and Southern Hemisphere (NH/SH). These

50 studies found different atmospheric transport patterns from source region to sampling

51 site for different ice core records (Whitlow et al., 1994), which can alter the glacio-

52 chemical cycle in the NH and SH.

53 There are a few studies of specific organic tracers of biomass burning for an

54 ice core, such as levoglucosan (1,6-anhydro-β-D-glucopyranose), which is pyrolysis

55 product of cellulose and hemicellulose); dehydroabietic acid (1-

56 phenanthrenecarboxylic acid) and vanillic acid (4-hydroxy-3-methoxybenzoic acid);

57 and other compounds (e.g. mannosan and galactosan) in the NH (Kawamura et al.,

58 2012). Kawamura et al. (2012) first reported these specific biomass burning tracers

59 (levoglucosan, dehydroabietic and vanillic acid) for an ice core (AD 1693-1997),

60 collected from the Kamchatka Peninsula near the eastern coast of Russia (56º04'N,

61 160º28'E, Elevation: 3,903 m).

62   This paper reports three compounds in an ice core, which was collected from

63   the Aurora Peak of southern Alaska (APA), inland of the northeast Pacific Ocean. The

64   study covers 1665-2008 to better understand the historical atmospheric transport

65   variability between the western North Pacific region (Kawamura et al., 2012) and

66   eastern North Pacific region (this study) from source regions. Particularly, 10 day

67   backward trajectory from 1992-2002 showed that southern Alaska can receive air

68   masses from the North Pacific Regions, East Asia, Eastern Russia-Siberia, higher

69   latitudes of Alaskan regions, Japan, and Canadian regions in the troposphere (>300

70   hPa) (Yasunari and Yamazaki, 2009). Similarly, the Kamchatka Peninsula also can

71   receive air masses from Siberia, Far East, North China and Eastern Europe[2]

72   (Kawamura et al., 2012).

73   **2.   Materials and Methods**

74   An ice core (180 m deep, 274 years old) was drilled in the saddle of the

75   Aurora Peak of southern Alaska, which is located at 63.52°N, 146.54°W, elevation:

76   2,825 m (Figure 1). This 180 m long core was divided into ~50 cm pieces and directly

77   transported to the laboratory of the Institute of Low Temperature Science (ILTS),

78   Hokkaido University, Japan and stored in a dark cold room at - 20ºC until analysis.

79   The ice core ages were determined by using annual counting of hydrogen isotopes

80   (δD) and Na^+ seasonal cycles (Tsushima, 2015; Tsushima et al., 2015). These ice core

81   samples were shaved off (~5 – 10 mm) on a clean bench at -15°C in a cold room. A

82   ceramic knife was used to avoid a possible adsorbed contamination during sample

83   collection using the method previously reported (Kawamura et al., 2012; Pokhrel et

84   al., 2015). These scraped samples were kept for 24 hours in a container in a standard

85   clean room and were transferred into 800 ml glass bottles. All steps are followed as

86   reported previously prior to analyses (Pokhrel et al., 2015; Pokhrel, 2016; Kawamura

87   et al., 2001). Total number of ice core sections was 147 (50 cm long, one quarter cut);

88   i.e., sampling frequency was ~40% of 180 m deep ice core.

89   These melt ice core samples (150 mL) were concentrated to almost dryness

90   using a rotary evaporator under a vacuum in a pear shape flask (300 ml) and extracted

91   by a mixture of CH_2Cl_2/CH_3OH (2:1) using an ultrasonic bath (Kawamura et al.,

92   2012). The total dissolved and particulate organic matter was further eluted with

93   CH_2Cl_2 and methanol to extract the organic compounds adsorbed on the particles as

94   reported previously (Fu et al., 2008; Simoneit et al., 2004). The extract and eluents

95   were transferred to 1.5 mL glass vials and again dried under a nitrogen stream.

96   Extracts were derivatized with 99% N, O-bis-(trimethylsilyl) trifluoroacetamide

97   (BSTFA) +1%trimethylchlorosilane (TMCS) at 70°C for two hours (Kawamura et al.,

98   2012). The derivatized fractions were further dissolved in n-hexane and determined

99   by gas chromatography/mass spectrometry (GC/MS) using a capillary column (HP-

100   5MS, 30 m × 0.32 mm I.D. × 0.25 μm film thickness) installed with a split/splitless

101   injector (Kawamura et al., 2012). Levoglucosan, dehydroabietic acid and vanillic acid

102   were determined using GC/MS by comparing the authentic standards and mass

103   spectral data of NIST/Willey library as external standards. More details are reported

104   elsewere (Fu et al., 2008; Simoneit et al., 2004).

105   We conducted triplicate analyses for three real ice core samples to check the

106   uncertainty in the determinations of concentrations. The uncertainty (standard

107   deviation) of levoglucosan, dehydroabietic and vanillic acid were 6.72, 0.74 and

108   2.40 %, respectively. Moreover, recovery of traject compounds were better than 85%.

109   To identify the physical functioning fire smoldering spot as possible source

110   regions of biomass burning events, we prepared annual composite maps (2001 to

111   2008 AD) of the Moderate Resolution Imaging Spectroradiometer (i.e. MODIS)

112 effective hot spot from the Earth Observing System Data and Information System

113 (EOSDIS) using the Terra and Aqua satelllites of NASA

114 (https://earthdata.nasa.gov/data/near-real-time-data/forms/).

115 **3.   Results and Discussion**

116   Anhydromonosaccharides can lead an important fraction of water-soluble

117 organic carbon (Gao et al., 2015; Verma et al., 2015). It is produced from the

118 pyrolysis and/or combustion of cellulose and/or hemi-cellulose from wildfires and

119 domestic wood fires (Simoneit, 2002) at temperatures above 300 °C (Simoneit et al.,

120 2002; Fraser and Lakshmanan, 2000; Shafizadeh, 1984). Many studies have shown

121 that levoglucosan ($C_6H_{10}O_5$) is the most abundant anhydrous monosaccharide

122 (Simoneit, 2002; Kuo et al., 2011; Hoffmann et al., 2010; Engling et al., 2006;),

123 which is tracked by other species of anhydromonosaccharides; e.g. mannosan (1,6-

124 anhydro-β-D-mannopyranose; $C_6H_{10}O_5$), galactosan (1,6-anhydro-β-D-

125 galactopyranose; $C_6H_{12}O_6$) and/or dehydroabietic acid ($C_{20}H_{28}O_2$). Such specific

126 factors and the sources (i.e., distribution) can make levoglucosan a unique tracer

127 (Jordan et al., 2006; Simoneit et al., 1999) in the source regions of southern Alaska

128 because the saddle of the Aurora Peak is far from the biomass burning source regions,

129 as shown in Figure 1.

130 **3.1 Levoglucosan**

131   This study showed that concentrations of levoglucosan are 8.6 times higher

132 (range: BDL-20800, average: 543±2340ng/L) than those of dehydroabietic acid

133 (range: BDL-556, ave. 62.0±97.2 ng/L) and four hundred times higher than those of

134 vanillic ($C_8H_8O_4$) acid (range: BDL-18.6, ave. 1.51±2.96ng/L) for 1665-2008. It

135 should be noted that combustion of lignite (lignite includes fossilized cellulose) or

136 hemicellulose emits levoglucosan and its isomers; e.g., mannosan and glactosan (Kuo

137   et al., 2011; Hoffmann et al., 2010). However, we did not detect these isomer

138   compounds at a significant concentration (ranges: BDL-0.0) in this study. Thus,

139   levoglucosan/mannosan mass ratios (L/M) could be relatively high. In contrast many

140   aerosol samples showed significant concentrations of these isomers and levoglucosan

141   are reported in many aerosol samples collected from the oceans via "round-the-world

142   cruise" (Fu et al., 2011), Mt. Tai in the North China Plain (Fu et al., 2008), and urban

143   tropical India (Fu et al., 2010).

144   It should be noted that higher ratios of levoglucosan (L) to mannosan (M)

145   indicated a sifnificant contributions of deciduous forest fire activities (Kawamura et

146   al., 2012). For example, Kawamura et al. (2012) reported very low ratios of L/M

147   (range: 3.3 – 5.0) for an ice core of the Kamchatka Peninsula in Northeast Asia

148   compared to lignite burning (30-90) at 200° C (Kuo et al., 2011), and aerosols samples

149   of Gosan site in south Korea (15-40, ave. 21) (Simoneit et al., 2004), suggesting

150   gymnosperm sources for anhydrosugars (Kawamura et al., 2012). Hence, we cannot

151   discuss more about the contributions of deciduous forest fire activities for our ice core

152   from the source regions of southern Alaska.

153   Insignificant concentrations of mannosan and galactosan in our ice core

154   indicate that combustion of lignite in the source regions of southern Alaska was minor.

155   These results suggest that contribution of lignite burning from East Asia, Eastern

156   Russia, Siberia, higher latitudes of Alaskan regions, Japan, and Canadian regions to

157   the ice core site was not significant. In contrast, western North Pacific ice core records

158   from the Kamchatka Peninsula (Kawamura et al., 2012) showed these anhydrosugars.

159   This suggests that western and eastern North Pacific regions could be influenced by

160   different air mass chemistry (e.g. lignite burning plume did not influence the southern

161   Alaskan glaciers) corresponding to other BB tracers. It should be noted that the

162 Kamchatka Peninsula's L/M ratios (range, 3.3-5.0) are close to those of gymnosperm

163 (conifer) burning. This is an evidence to suggest that lignite burning didn't alter the

164 Alaskan glacier's chemistry for 1665-2008.

165   It should be noted that degradation fluxes of levoglucosan in cloud droplets

166 and aqueous particles (deliquescent particles) by OH radicals have been reported

167 recently. For example, mean degradation fluxes were around 7.2 ng m^{-3} h^{-1} in

168 summer and 4.7 ng m^{-3} h^{-1} in winter (Hoffmann et al., 2010). Hence, we can

169 speculate that levoglucosan could be more stable compared to isomer compounds ,

170 whose degradation fluxes are lower than 7.2 and/or 4.7 ng m^{-3} h^{-1}(e.g., Fraser and

171 Lakshmanan, 2000; Hoffmann et al., 2010) during long-range atmospheric transport

172 from source points to southern Alaska. Stability of levoglucosan is further confirmed

173 in an aerosol chamber study with atmospheric lifetime of 0.7-2.2 days in summer

174 (Hennigan et al., 2010). These results demonstrate the biomass burning emissions in

175 source apportionment for the saddle of the APA.

176   Levoglucosan showed higher concentrations in around 1660s-1830s (Figure

177 2a) with sporadic peaks in 1678 (ice core depth in meter: 174.6 and concentration 593

178 ng/L), 1692 (172.2 m; 704), 1695 (170.3 m; 1250), 1716 (165.6 m; 990), 1750 (156.7

179 m; 913), 1764 (151.5 m; 1433), 1786 (147.3m; 7057), 1794 (146.1 m; 3302) and

180 1834 (138.4m; 944) above its average concentration (542 ng/L). These higher spikes

181 could be related to forest fire activities in the source regions of southern Alaska.

182 Source regions could be East Asia, Eastern Russia, Siberia, higher latitudes of

183 Alaskan regions, Japan, and Canadian regions (Yasunari and Yamazaki, 2009). For

184 instance, Ivanova et al. (2010) reported the frequency of heavy forest fires (e.g., borel

185 forest) in spring, summer and autumn in eastern Siberia, which is a potential source to

186 Alaska (Yasunari and Yamazaki, 2009). This study showed higher concentrations of

187 levoglucosan before 1840s (Figure 2a). Marlon et al. (2008) further confirmed that

188 there was heavy biomass burning between 1750s -1840s on a global scale, which is

189 linked to increasing anthropogenic activities (e.g., population growth and land-use

190 change).

191   Similalry, we detected high spikes in 1898 (120.7m; 577 ng/L), 1913 (114.8m;

192 20800), 1966 (77.7m; 692) and 2005 (13.7m; 598) above the average concentration

193 (542 ng/L). Figure 2a clearly shows lower concentrations level of Levoglucosan (less

194 than 542 ng/L) after 1830s (except for 1898, 1913, 1966 and 2005) compared to

195 before 1830s. This could be attributed to intensive grazing, agriculture and forest fire

196 management (Marlon et al., 2008; Eichler et al., 2011). It should be noted that

197 charcoal signals are scarce for Siberian regions compared to Northern American and

198 European ice core records (Eichler et al., 2011). We did not detect significant

199 conentrations of any isomers as we have discussed above. Moreover, two thirds of

200 Earth's borel forest (17 million km^2) lies in Russia, which is a potential source of

201 forest fires that could have significance on a global scale (Eichler et al., 2011; Isaev et

202 al., 2002).

203   Mt. Logan Canada, GISP2, and 20D (older than 1850s) ice core records of

204 Greenland are characterized by higher spikes of NH_4^+ superimposed with a relatively

205 uniform summertime and wintertime minimum (Whitlow et al., 1994). These suggest

206 that ice core NH_4^+ has common sources in the circumpolar regions. We got higher

207 spikes of levoglucosan before 1840s (Figure 2a), which is consistent with higher

208 spikes of NH_4^+ in 1770-1790 and 1810-1830 in the Mt. Logan data (e.g., Whitlow et

209 al., 1994). This comparison suggests similar source regions of NH_4^+ for different

210 sampling sites. In contrast, Mt. Logan data showed higher spikes of NH_4^+ in the

211 intervals of 1850-1870 and 1930-1980, which is dissimilar (except for two points) to

212   our results from Aurora Peak (Figure 2a). It should be noted that Greenland records

213   (GISP2 and 20D) showed lower spikes of NH_4^+ compared to Mt. Logan (Whitlow et

214   al., 1994) during these intervals (1850-1870 and 1930-1980), which is consistent to

215   the results of Aurora Peak (except for 1966), again suggesting similar source regions

216   (Whitlow et al., 1994; Davidson et al., 1993; Holdsworth et al., 1992). The potential

217   source regions for Greenland ice cores include northern North America, Europe and

218   Siberia. Simialry, Siberia, Alaska and British Columbia are likely source regions for

219   Mt. Logan (Whitlow et al., 1994; Davidson et al., 1993; Holdsworth et al., 1992).

220   Except for a few points, e.g., 1999 (436 ng/L) and 2005 (598 ng/L)),

221   concentrations of levoglucosan drastically decreased in 1980-2008. This infers that

222   forest fire activities could be controlled by many factors. For instance, Central and

223   East Siberian forest fire activities were controlled by strong climate periodicity, e.g.,

224   Arctic Oscillation (AO), El Nino, intensification of the hydrological cycle in central

225   Asia, and other human activities in the NH (Eichler et al., 2011; Robock, 1991;

226   Achard et al., 2008; Balzter et al., 2007; Wallenius et al., 2005). Eichler et al. (2009)

227   further confirmed that from 1816 to 2001 higher amounts of NH_4^+ and formate

228   ($HCOO^-$) were directly emitted from biogenic sources rather than biomass burning

229   (Olivier et al., 2006) in the Belukha glacier in the Siberian Altai mountains. Similarly,

230   lower concentrations of charcoal between 1700 and 2000 in this Altai mountain

231   further suggest that forest fire activities were stronger than anthropogenic activities in

232   the source regions (Eichler et al., 2011).

233   Similarly, the sparsity of NH_4^+ spikes after 1920 in Greenland (GISP2 and

234   20D) suggest low intensity of biomass burning and/or significant deposition before

235   reaching Greenland from North America (Whitlow et al., 1994). This is similar to the

236   saddle of Aurora Peak, except for 1910 (20800 ng/L), which may be due to a point

237   source around Alaskan region. Higher spikes of NH_4^+ at Mt. Logan during 1900-1990

238   are likely originated from central and eastern Siberia (Robock, 1991), which is

239   dissimilar to the source regions in this study. Only the exception is 1966 (2000 ng/L),

240   suggesting that local biomass burning is also important in southern Alaska.

241   Above results and discussions suggest the subsequent evidences: (a) heavy

242   biomass burning could be activated in the source regions; (b) short range air mass

243   circulation could quickly reach souhtern Alaska, causing higher concentration of

244   levoglucosan; (c) dilution and/or scavenging of biomass plume enroute could be

245   maximized after 1830s; (d) a common NH summertime biomass burning plume (e.g.,

246   same ice core records of SO_4^{2-}, NO_3^-, NH_4^+ showed significant concentrations during

247   same periods) could be significantly deposited by short range atmospheric circulation

248   on the exposed surface area of the glaciers. These special events further suggest that

249   Alaskan glaciers can not preserve most biomass burning events in the circumpolar

250   regions, which occured in the source regions of Siberian and North America.

251   Hence, these historical records of levoglucosan before the 1830s suggest long

252   range atmospheric transport rather than short range transport from heavy forest fires.

253   For instance, forest fire intensity in 1660s-1830s could be induced by lightning during

254   drought seasons in the Siberian regions as well as extensive burning to clear land for

255   agriculture purposes in the NH (Whitlow et al., 1994 and reference therein). Declined

256   concentrations of levoglucosan trend after the 1830s (except for few points), showing

257   that sources could be changed significantly and/or forest fire activities could be

258   suppressed and/or controlled in 1830s-1980s (Whitlow et al., 1994). It should be

259   noted that mid to late 1800s are considered as the Little Ice Age (Mayewski et al.,

260   1993). Moreover, recent changes of the concentration trends in the Alaskan source

261   regions is thought to be climate driven (Whitlow et al., 1994 and reference therein).

262 **3.2 Dehydroabietic acid**

263   Dehydroabietic acid is produced by pyrolytic dehydration of abietic acid from

264 conifer resin. In other words, dehydroabietic acid is produced during the burning process

265 of conifer resins (Kawamura et al., 2012; Simoneit et al., 1993). It can be used as a

266 specific biomass-burning tracer for conifer trees and/or soft wood burning in an ice

267 core study. Dehydroabietic acid was detected as the second dominant species (range:

268 BDL-556, ave. 62.4±97.2 ng/L), whose concentrations are 9 times lower than

269 levoglucosan but more than 46 times higher than vanillic acid (range: BDL-18.6, ave.

270 1.51±2.96 ng/L). Dehydroabietic acid showed higher spikes in 1678 (ice core depth in

271 meter, 173.9m; 200 ng/L), 1716 (165.3 m; 67.5), 1728 (161.5 m; 139), 1732 (159.6

272 m; 233), 1738 (158.3 m; 113), 1750 (156.7 m; 66.9), 1764 (151.5 m; 331), 1786

273 (147.3 m; 386), 1794 (146.1 m; 78.6), 1913 (114.8 m; 101), and 1994-2007 (depth is

274 44.8-0.88 m), respectively having 92.8, 199, 141, 203, 136, 109, 98.4, 124, 174, 121,

275 298, and 555 ng/L.

276   These periods are consistent with those of higher spikes of levoglucosan,

277 except for a few points (e.g., 1734-1738) before 1990 (Figure 2a, b). The historical

278 trend of dehydroabietic acid concentrations is also similar to that of levoglucosan

279 concentrations before 1980, which is similar to Kamchatka ice core records. In

280 contrast, Kamchatka showed gradual increase of dehydroabietic acid (Figure 2b) after

281 the 1950s (e.g., Kawamura et al., 2012). These results suggest that biomass burning

282 plumes of pine, larch, spruce and fir trees in Siberian regions (Kawamura et al., 2012;

283 Ivanova et al., 2010) could not reach southern Alaska significantly compared to

284 Kamchatka, south eastern Russia.

285   Dehydroabietic acid concentrations after the 1980s were higher than

286 levoglucosan, which is similar to Kamchatka records. This further suggests that

287 biomass burning plumes from Siberian borel conifer trees could be transported to the

288 North Pacific regions (Kawamura et al., 2012). It also suggests that East Asian

289 regions (broad-leaf trees are common) could be important for levoglucosan rather

290 than dehydroabietic acid (boreal forest fires in Siberia, i.e., pine trees). It should be

291 noted that Alaska can receive different air masses from East Asia, Eastern Russia,

292 Siberia, higher latitudes of Alaskan regions, Japan, and Canadian regions in the

293 troposphere (>300 hPa) (Yasunari and Yamazaki, 2009) and Kamchatka-Peninsula

294 also can receive air masses from Siberia, Far East, North China and Eastern Europe

295 (Kawamura et al., 2012).

296   These results showed some similarity between levoglucosan records of

297 Kamchatka and Alaska (except for few points) and some discrepancy between

298 dehydroabietic acid records between these sampling sites. Kamchatka showed gradual

299 increase after the 1950s. Alaska showed this after the 1980s, suggesting that conifer-

300 burning plumes could be transported significantly to Kamchatka, but not southern

301 Alaska, in the 1950s – 1980s. There is another possibility for this particular

302 discrepancy of Kamchatka and Alaska: dehydroabietic acids could be decomposed

303 during long-range transport (Kawamura et al., 2012; Simoneit and Elias, 2001) from

304 Siberia before reaching southern Alaska (i.e. eastern North Pacific ice core) but not

305 before reaching Kamchatka (i.e. western North Pacific). The Kamchatka ice core also

306 doesn't show high spikes (except 1970) in the 1950s-1970s compared to before and

307 after those decades. Moreover, a correlation of levoglucosan with dehydroabietic acid

308 from 1665-1918 (R = 0.74) is better than from 1918-1977 (0.13) and 1977-2007

309 (0.36). These relations are weaker (0.39, 0.04, and 0.22, respectively) for vanillic acid,

310 except for 1913 and 1966 at all cases. The representing figures are shown in Figure

311 3a-c. Such types of lower spikes and/or sporadic peaks of levoglucosan and

312   dehydroabietic acid after the 1920s (Figure 2a,b) and these correlations suggest that

313   source regions should be different (e.g. east Asian broad leaf trees and Siberian source,

314   e.g. boreal forest/pine trees), and long range atmospheric transport is insignificant for

315   these historical concentration trends of dehydroabietic acid rather than levoglucosan

316   over the saddle of Aurora Peak at least after the 1920s. Annual composite maps

317   (Figure 5a-f) since 2001 to 2008 of the Moderate Resolution Imaging

318   Spectroradiometer (MODIS) supported our above results and discussion. For example,

319   levoglucosan (in 2005, 2006 and 2004 AD with 598.0, 130.8, and 95.30ng/L,

320   respectively), dehydroabetic acid (in 2007, 2004, and 2006 AD with 555.9, 309.7, and

321   298.1ng/L, resppectively) and vanillic acid (in 2005, 2007 and 2006 with 18.57, 12.66,

322   and 7.27ng/L) showed descripency of higher spikes in the same years (Figure 5a-f)

323   suggested that they have different sources in the same years.

324   **3.3 Vanillic acid**

325   We detected vanillic acid (VA) in an ice core of the Aurora Peak (Figure 2c),

326   which is a biomass burning tracer of lignin (Simoneit et al., 1993). Particularly, VA

327   can be produced by incomplete combustion of conifer trees, i.e., conifer rich boreal

328   forest (Pokhrel, 2015; Simoneit et al., 1993). Figure 2c shows sporadic peaks of

329   lignin in 1672 (2.23 ng/L), 1678 (3.25), 1692 (3.23), 1695 (5.56), 1698 (1.50), 1732

330   (3.98), 1764 (1.56), 1786 (3.65), 1794 (1.35), 1814 (11.0), 1818 (5.50), 1913 (2.12),

331   1973 (5.52), 1989 (3.57), 1993 (2.66), 1996 (4.66), 1997 (3.57), 1999 (3.57), 2001

332   (3.26), and 2003-2007 (2.36, 2.07, 18.6, 7.27 and 12.6ng/L, respectively). We found

333   similar spikes of VA and levoglucosan during these periods (except for few points,

334   e.g., 2004, 2006 and 2007). The Kamchatka ice core showed similar types of high

335   spikes, except for a few points (e.g., 1972 and 1992).

336   Similarity of higher spikes suggests that biomass combustion sources (e.g.,

337   woody parts of trees) and source regions could be similar (Kawamura et al., 2012),

338   that is, lignin and cellulose source regions of southern Alaska were simultaneously

339   significant, before the 1920s. This result infers long-range atmospheric transport was

340   insignificant at least after the 1920s, which could be somewhat similar to the

341   dehydroabietic acid as we have discussed above sections. For example, the

342   correlations (Figure 3a-c) between dehydroabietic acid and vanillic acid (R$\geq$ 0.80) is

343   better than those of levoglucosan with dehydroabietic acid (0.36) and vanillic (except

344   for, 1999 and 2005) acid (0.22) after the Great Pacific Climate Shift (1977-2007). The

345   mean concentrations of dehydroabietic (127.9 ng/L-ice) and vanillic (2.29 ng/L-ice)

346   acids are secure with standard deviations ($\pm$126 and $\pm$3.04, respectively) compared to

347   levoglucosan (ave. 90.8$\pm$146 ng/g-ice) from 1977-2007. It suggests a short range

348   atmospheric transport, which could be from climate driven (Pokhrel et al., 2015b).

349   In other words, dehydroabietic acids and p-hydroxybenzoic acid (p-HBA)

350   could be more unstable compared to photo-degradation of levoglucosan during long

351   range transport. For instance, higher sensitivity of dehydroabietic acid was reported

352   compared to levoglucosan (Simoneit et al., 2002; Simoneit and Elias, 2001). It should

353   be noted that we did not detect p-HBA from the same ice-core sample, which can be

354   produced from incomplete combustion of grasses (Kawamura et al., 2012; Simoneit et

355   al., 2002). In constrast, we detected significant amounts of dehydroabietic acid from

356   1665-2007 (Figure 2b). Hence, we may speculate that p-HBA could be more unstable

357   compared to levoglucosan, dehydroabietic acid, and vanillic acid.

358   **3.4 Comparison with ammonium, nitrite, nitrate and SO$_4$$^{2-}$**

359   There are many studies of organic compounds and major inorganic ions of

360   biomass burning for aerosol samples in the NH, which are reported elsewhere

361   (Kunwar et al., 2016; Zhu et al., 2015; Cong et al., 2015; Kunwar and Kawamura,

362   2014; Lazaar et al., 2011; Kundu et al., 2010; Wang et al., 2009). In addition,

363   terephthalic acid could be a special tracer of plastic waste burning (Kawamura and

364   Pavuluri, 2010; Pavuluri et al., 2010; Kunwar and Kawamura, 2014b). Particularly,

365   ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) and sulfate (SO_4^{2-}) were used to

366   better understand the atmospheric signal of biomass burning and/or the Pioneer

367   Agriculture Revolution (PIA-GREV) in the NH. These results are reported elsewere

368   (Holdsworth et al., 1996, Legrand and Mayewski, 1997). For instance, a signal of

369   biomass burning is ammonium (e.g., ($[NH_4]_2SO_4$) in snow particles, which is a

370   constitute of forest fire smoke (Holdsworth et al., 1996; Tsai et al.,2013 and

371   references therein).

372   Similalry, levoglucosan is a unique biomass burning tracer (Simoneit, 2002).

373   We found weak correlations (R) of levoglucosan with NO_2^- (0.06), NO_3^- (0.04), nss-

374   SO_4^{2-} (0.08), nss-K^+ (0.11), nss-Ca^{2+} (0.072), and NH_4^+ (0.11) (Figure 4a-d), except

375   for a few points (e.g., 1998 and 1999). The correlations of MSA^- with NO_3^- (0.64),

376   unsaturated fatty acids, e.g., oleic ($C_{18:1}$) acid (0.70), and with other anions (nss-SO_4^{2-},

377   Cl^-, F^-, and Na^+) are strong (≥0.71), suggesting that major ions can not represent

378   pristine biomass-burning signals at least in the North Pacific rim (NPR) (Pokhrel,

379   2015; Pokhrel et al., 2016). The multi-decadal cycles of NO_2^-, SO_4^{2-} and $CH_3SO_3^-$

380   from the same ice core may be controlled by climate variability and/or climate driven

381   forces in the NPR (Pokhrel, 2015; Pokhrel et al., 2016; Whitlow et al., 1994;).

382   Moreover, the historical trend of vanillic acid from 1800-2000 for Greenland ice core

383   (McConnell et al., 2007) is completely different with this study. Hence, this study

384   revels a new dimension of biomass burning periodic cycles in the NPR, which can

385   alter the concept of other ice core studies in the NH.

386 **4. Summary and Conclusions**

387 Levoglucosan (ave. 543±2343 ng/L), dehydroabietic (62.4±97.2 ng/L) and

388 vanillic acid (1.36±3.03 ng/L) are present in the ice core from saddle of Aurora Peak

389 in Alaska. They have been reported to better understand temporal trends of biomass

390 burning activities in the source region of southern Alaska. Levoglucosan showed

391 sporadic peaks during the 1660s-1830s, 1898, 1913, 1966, and 2005. Dehydroabietic

392 and vanillic acid showed similar historical trends with levoglucosan at least before the

393 1970s. Historical trends of levoglucosan, dehydroabietic acid, and vanillic acid

394 showed that biomass burning activities from resin and lignin boreal conifer trees and

395 other higher plants/grasses were significant before the 1830s and after the 1970s in

396 the source regions of southern Alaska, which is different with earlier study from

397 Kamchatka ice core. Correlations of levoglucosan with NO_2^- (r=0.06), NO_3^- (0.04),

398 nss-SO_4^{2-} (0.08), nss-K^+ (0.11), nss-Ca^{2+} (0.072), and NH_4^+ (0.11) from the same ice

399 core suggest that these anions and cations can not represent the gleaming signal of

400 biomass burning activities in the source regions for southern Alaska. These results

401 further suggest that forest fire signals in the NH are dependent on the source regions

402 and ice core sampling sites. Hence, it inquires about the long-range and/or short-range

403 atmospheric transport, which will be important for biomass burning tracers (i.e.,

404 levoglucosan, dehydroabietic and vanillic acid), cations, and anions.

405 Author contributions.

406 KK designed the research. TS and SM conducted ice core drilling. AT conducted ice

407 core dating. AP, KO and OS worked on ice core cutting for chemical analysis. AP

408 analyzed ice sections and BK supported data analysis. AP and KK wrote the

409 manuscript.

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415

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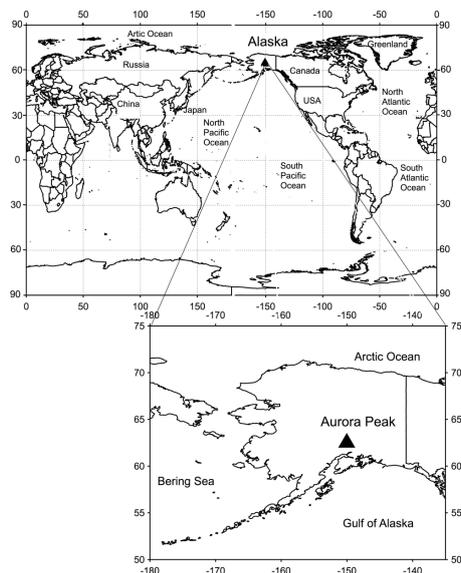
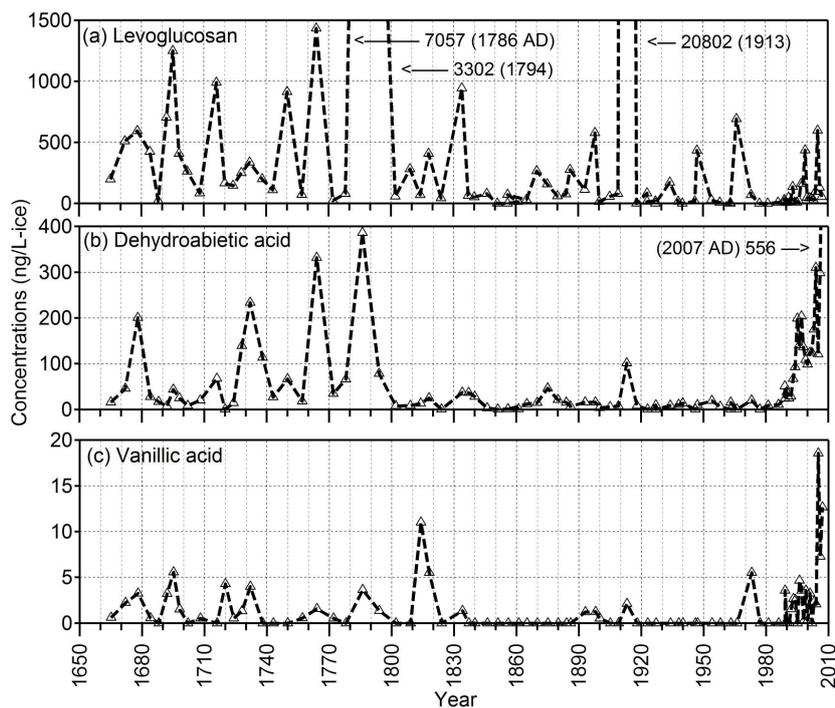


Figure 1. Geographical location of Aurora Peak in Alaska, where 180-meter long ice
core was drilled on the saddle of this peak in 2008[16] (*Pokhrel, 2015*).

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637   Figure 2. Concentration changes of (a) levoglucosan, (b) dehydroabietic, and (c)

638   vanillic acids in the ice core collected from Aurora Peak in Alaska for 1665-2008.

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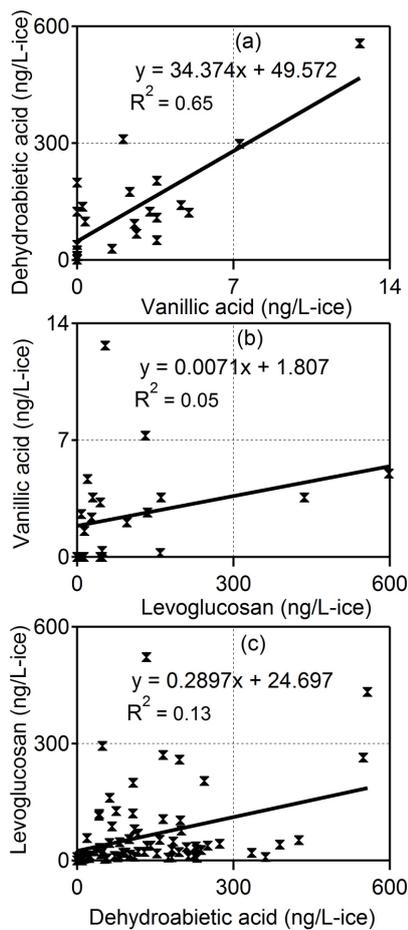
Figure 3. Correlations between the concentrations of (a) dehydroabietic and vanillic

(b) vanillic and levoglucosan, and (c) levoglucosan and dehydroabietic acid in the

Alaska ice core records collected from the saddle of Aurora Peak after the Great

Pacific Climate Shift (1977-2007).

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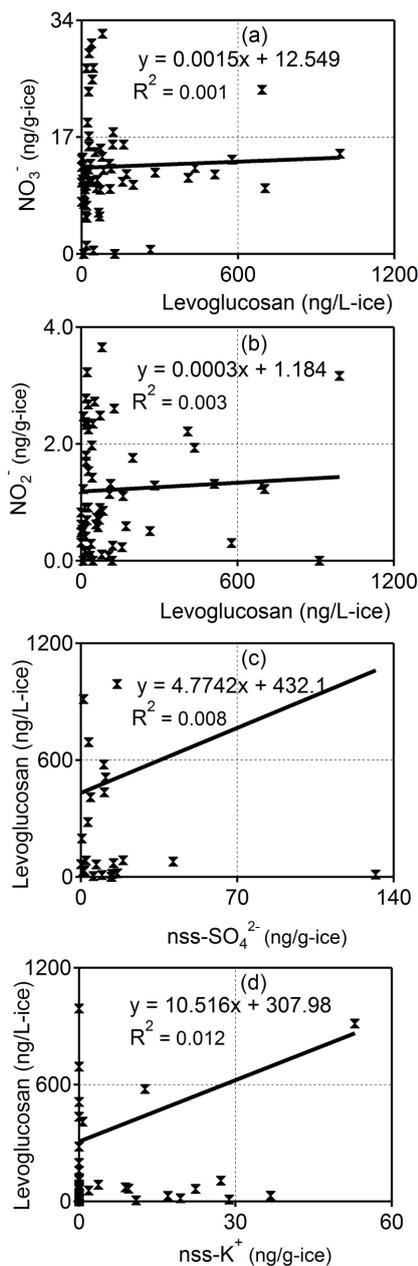
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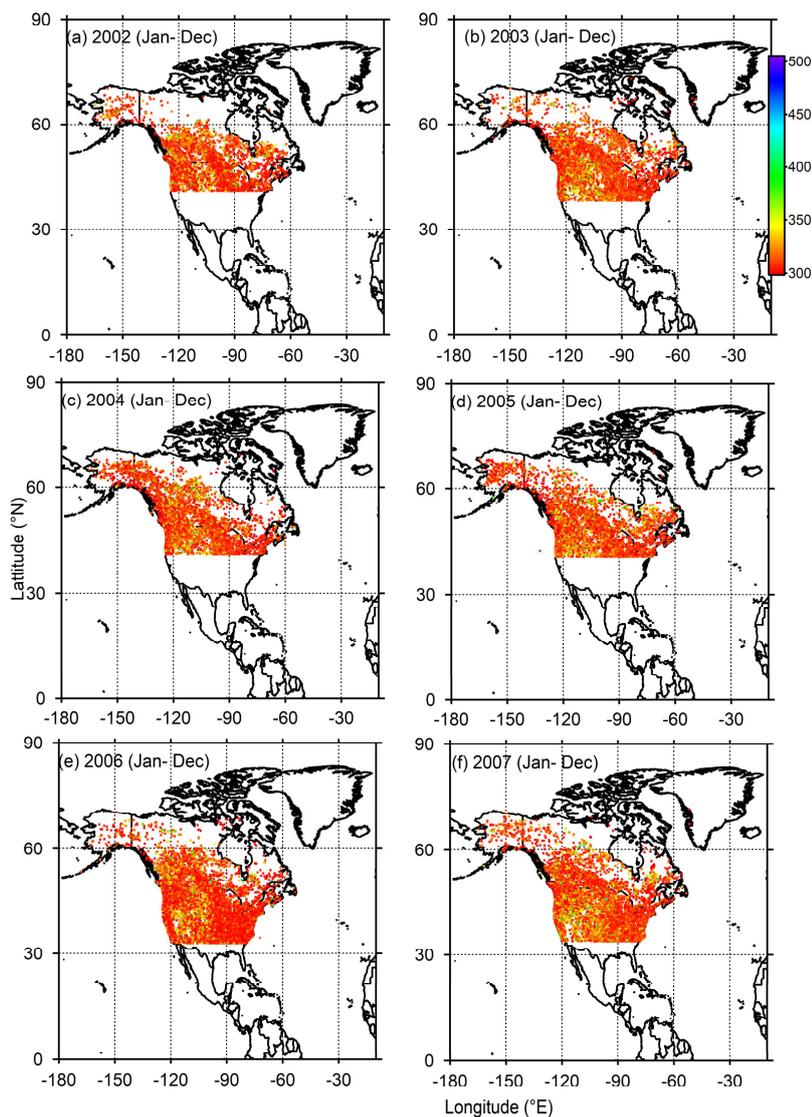
647   Figure 4. Correlations of the concentrations of (a) NO_3^-, (b) NO_2^-, (c) nss-SO_4^{2-}, and

648   (d) nss-K^+ with levoglucosan in the Alaskan ice core samples collected from saddle of

649   Aurora Peak (1665-2007).

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651 Figure 5. The MODIS fire spot (a-f) of Alaskan regions since 2001 to 2007, when

652 levoglucosan (2005, 2006, and 2004 AD), dehydroabetic (2007, 2004, and 2006) and

653 vanillic (2005, 2007 and 2006) acids showed higher spikes in order to first, second

654 and third positions, respectively.