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2 **Ice core records of levoglucosan, dehydroabietic and vanillic acids from Aurora**
3 **Peak in Alaska since the 1660s: A proxy signal of biomass burning activities in**
4 **the North Pacific Rim**

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15 **Abstract**

16 A 180 m-long (343 years) ice core was drilled in the saddle of Aurora Peak in
17 Alaska (63.52°N; 146.54°W, elevation: 2,825 m) and studied for biomass burning
18 tracers. Concentrations of levoglucosan and dehydroabietic and vanillic acids exhibit
19 multi-decadal variability with higher spikes in the 1678, 1692, 1695, 1716, 1750,
20 1764, 1756, 1834, 1898, 1913, 1966 and 2005 A.D. Historical trends of these
21 compounds showed enhanced biomass burning activities in the deciduous broad leaf
22 forests, boreal conifer forests and/or tundra woodland and mountain ecosystems
23 before the 1830s and after the Great Pacific Climate Shift (GPCS). The gradually
24 elevated level of dehydroabietic acid after the GPCS is similar to p-hydroxybenzoic
25 acid (p-HBA) from Svalbard ice core, suggesting common climate variability in the
26 Northern Hemisphere. The periodic cycle of levoglucosan, which seemed to be
27 associated with the Pacific Decadal Oscillation (PDO), may be more involved with
28 the long-range atmospheric transport than other species. These compounds showed
29 significant correlations with global lower tropospheric temperature anomalies
30 (GLTTA). The relations of the biomass burning tracers with PDO and GLTTA in this
31 study suggest that their emission, frequency, and deposition are controlled by the
32 climate driven forces. In addition, historical trends of dehydroabietic and vanillic
33 acids (burning products of resin and lignin, respectively) from our ice core
34 demonstrate the northern hemispheric connections to the common source regions as
35 suggested from other ice core studies from Svalbard, Akademii Nauk and Tunu
36 Greenland in the Northern Hemisphere.

37 (Words: 240)

38 1. Introduction

39 Biomass burning tracers (e.g., levoglucosan, dehydroabietic, vanillic, p-
40 droxybenzoic, and syringic acids) are ubiquitous in the atmosphere and well deposited
41 on ice sheets as snow particles (i.e., precipitation) (Muller-Tautges et al., 2016;
42 Grieman et al., 2018a,b; Shi et al., 2019). Previously, ammonium (NH_4^+), nitrite
43 (NO_2^-), nitrate (NO_3^-) and sulfate (SO_4^{2-}) were used to understand the atmospheric
44 signals of biomass burning and/or the Pioneer Agriculture Revolution (PIA-GREV) in
45 the Northern Hemisphere (Holdsworth et al., 1996; Legrand and Mayewski, 1997;
46 Legrand et al., 2016). For instance, a signal of biomass burning is ammonium (e.g.,
47 $[\text{NH}_4]_2\text{SO}_4$) in snow particles, which is a constituent of forest fire smoke (Holdsworth
48 et al., 1996; Tsai et al., 2013). Biomass burning activities such as forest fires and
49 residential heating may affect climate change (Legrand and De Angelis, 1996;
50 Savarino and Legrand 1998; Gambaro et al., 2008; Keywood et al., 2011).

51 Ice core records archive the long-term changes in deposition and concentration
52 of organic (e.g., biomass burning tracers, ethane, formate, acetate, dicarboxylic acids,
53 pyruvic acid and α -dicarbonyls) and inorganic species (e.g., NH_3^+ , SO_4^{2-} , NO_3^- , K^+
54 and NO_2^-) (Yang et al., 1995; Legrand and Mayewski, 1997; Andreae and Merlet,
55 2001; Kaufmann et al., 2010; Lamarque et al., 2010; Wolff et al., 2012; Kawamura et
56 al., 2012; Kehrwald et al., 2012; Legrand et al., 2016; Shi et al., 2019). Many studies
57 have shown that there are some discrepancies of temporal and spatial biomass burning
58 activities in ice core proximity records (Legrand et al., 1992,1996; Kaplan et al.,
59 2010; Kawamura et al., 2012; Grieman et al., 2015; Rubino et al., 2016; Legrand et al.,
60 2016; Grieman et al., 2017; Zennaro et al., 2018; Li et al., 2018; Grieman et al.,
61 2018a,b; You et al., 2019) in both Northern and Southern Hemisphere (NH/SH).

62 Previous proxy records of biomass burning activities from Lomonosovfona,
63 Svalbard (Grieman et al., 2018a) showed different trend between vanillic acid and p-
64 hydroxybenzoic acid (p-HBA) within the same ice core sample. Interestingly, ice core
65 records of NEEM (Zennarao et al., 2014; 2018) demonstrated a human impact on the
66 climate system since four thousand years ago. A different circumpolar region in the
67 NH has a different atmospheric air mass circulation with different results of biomass
68 burning tracers such as levoglucosan, vanillic, dehydroabietic and syringic acids,
69 ethane, ammonium and other carboxylic acids, suggesting potential discrepancies of
70 origin, transport, and deposition of these compounds on the ice crystals.

71 These discrepancies of biomass burning tracers in different ice core records
72 may suggest the different glacio-chemical cycles in the NH and SH throughout
73 decadal to centennial and even millennia. For example, centennial and/or shorter time
74 scale of trends exhibited different elevated/suppressed concentration trends of p-
75 HBA/vanillic acid during 1600 A.D. and vanillic/p-HBA during 2000-2008 A.D.
76 (Grieman et al., 2018a). Similarly, Svalbard ice core record (Grieman et al., 2018a)
77 showed different elevated/suppressed historical trends/peaks from NEEM- ice core of
78 Greenland (Zennaro et al., 2018). These results most likely suggest the occurrence of
79 changing/shifting contributions of source regions with the different ecosystem of trees,
80 shrubs, and grasses to the sampling sites.

81 There are a few ice core studies of biomass burning-derived specific organic
82 tracers, including levoglucosan that is a pyrolysis product of cellulose and
83 hemicellulose and other sugar compounds such as mannosan and galactosan, as well
84 as dehydroabietic and vanillic acids which are biomass burning products of resin and
85 lignin, respectively (Kawamura et al., 2012; Legrand et al., 2016; Grieman et al.,
86 2017; Zennaro et al., 2018; Li et al., 2018; Grieman et al., 2018a,b; You et al., 2019).

87 Kawamura et al. (2012) reported specific biomass burning tracers (levoglucosan,
88 dehydroabietic and vanillic acid) for an ice core (1693-1997 A.D.), collected from the
89 Kamchatka Peninsula (56°04'N, 160°28'E, Elevation: 3,903 m) in the western North
90 Pacific Rim.

91 In this paper, we report levoglucosan, dehydroabietic acid and vanillic acid in
92 an ice core collected from Aurora Peak of southern Alaska, an inland site facing to the
93 northeast of Pacific Ocean. This ice core covers 1665-2008 A.D., which can help to
94 better understand the historical variability in the atmospheric transport of biomass
95 burning tracers between the western North Pacific (Kawamura et al., 2012) and
96 eastern North Pacific (this study). We also compare the present results with other ice
97 core studies from Greenland, Svalbard and Akademii Nauk in the NH. The results of
98 this study can further disclose the database of levoglucosan, dehydroabietic and
99 vanillic acids from the alpine glacier in the North Pacific Rim to explore their possible
100 sources, origin, long- and short-range atmospheric transport, ecological changes and
101 climate variability in the NH.

102 2. Materials and Methods

103 An ice core (180.17 m deep, 343 years old) was drilled in the saddle of the
104 Aurora Peak of southern Alaska (location: 63.52°N, 146.54°W, elevation: 2,825 m,
105 see Fig. 1 for sampling site). The annual mean temperature at the site was minus
106 2.2°C, which matched to the temperature of 10 m depth in the borehole-ice. The
107 annual accumulation rate of snow is 8 mm yr⁻¹ since 19 century and 23 mm yr⁻¹ after
108 the Great Pacific Climate Shift (GPCS, cold water masses were replaced by warm
109 water since 1977, e.g., Meehl et al, 2009). The 180 m long core was divided into ~50
110 cm pieces and directly transported to the laboratory of the Institute of Low

111 Temperature Science, Hokkaido University, Japan and stored in a dark, cold room at -
112 20°C until analysis.

113 The ice core ages were determined by using annual counting of hydrogen
114 isotopes (δD) and Na^+ seasonal cycles (Tshushima, 2015; Tsushima et al., 2015) with
115 tritium-peak reference horizons of 1963 and 1964 and volcanic eruptions of Mt. Spurr
116 and Mt. Katmai in 1992 and 1912 with dating error was ± 3 years of 0.02 m resolution.
117 These ice core samples (50 cm long, one-quarter cut by circumference) were
118 mechanically shaved off ($\sim 5 - 10$ mm thickness of the out core surface) on a clean
119 bench at $-15^\circ C$ in a cold room. A ceramic knife was used to avoid a possible
120 contamination during sample collection. We cleaned ceramic knife (total 12 times)
121 three times by using organic free pure water (MiliQ water), methanol (MeOH),
122 dichloromethane (DCM) and a mixture of 2:1 of DCM and MeOH. These scraped ice
123 samples were placed in a clean glass jar (Iwaki Glass, 1000 mL) for 24 hours with
124 aluminum foil as a cap cover in a level-2 clean room, After 24 hours, these shaving
125 ice core samples were kept at room temperature (ca. $25^\circ C$) to which small amount (ca.
126 10 mg) of $HgCl_2$ was added (Pokhrel, 2015). Finally, the thawed sample was
127 transferred into a 800 ml pre-cleaned brown glass bottle and stored at $4^\circ C$. The clean
128 glass jars and bottles were pre-heated at $450^\circ C$ for 12 hours. The total number of ice
129 core sections was 147 with sampling frequency of $\sim 40\%$ of ice core.

130 These melted ice core samples (150 mL) were concentrated to almost dryness
131 using a rotary evaporator under a vacuum in a pear shaped flask (300 ml) and
132 extracted by a mixture of DCM/MeOH (2:1) using an ultrasonic bath. The extracts
133 were transferred to 1.5 mL glass vial and dried under a nitrogen stream. Extracts were
134 derivatized with 99% N, O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) + 1%

135 trimethylchlorosilane (TMCS) and 10 μl of pyridine at 70°C for three hours (Fu et al.,
136 2011; Kawamura et al., 2012). Before injection to gas chromatography (GC)/mass
137 spectrometry (MS), known volume of internal standard (n-C₁₃ alkane) was added. GC
138 peaks were analyzed by GC/MS: a Hewlett–Packard Model 5973 MSD coupled to a
139 HP 6890 GC using a capillary column (HP-5MS, 30 m \times 0.32 mm I.D., 0.25 μm film
140 thickness) installed with a split/splitless injector. The GC oven temperature was
141 programmed from 50°C (2 min) to 120°C at 30°C/min, and then to 300°C at 6°C/min
142 and maintained at 300°C for 20 min. Helium was used as a carrier gas. The GC/MS
143 was operated on a scan mode (m/z=50-650) with an electron impact mode at 70 eV
144 (Pokhrel et al., 2016).

145 Fragment ions at m/z = 217, 204 and 333 for levoglucosan, m/z = 239 for
146 dehydroabietic acid and m/z = 297/312/267 for vanillic acid were processed on the
147 Chemstation software and used for quantification. Peaks were further confirmed by
148 comparing the mass spectra with those of authentic standards and the mass spectral
149 data in the NIST/Willey library. An aliquot of authentic standard solution (10 μL)
150 containing levoglucosan, dehydroabietic acid, vanillic acid and syringic acid (5.5, 4.7
151 and 4.2 ng/ μL , respectively) was spiked to organic free Milli-Q water (200 ml) placed
152 in the pear-shaped flask. The water sample was concentrated and dried by the
153 procedure described above. The concentrates were derivatized with BSTFA and peaks
154 were analyzed by GC/MS. The recoveries of the spiked samples of levoglucosan,
155 dehydroabietic acid, and vanillic acid were more than 83%. Duplicate analyses were
156 conducted to check analytical error of target compounds, which were less than 9%.
157 Laboratory blanks was measured using Milli-Q water (200 ml). The procedural blanks
158 showed no detectable peaks of these compounds. Detection limits of these species
159 were 0.002-0.005 ng/kg-ice.

160 We performed cluster analysis for 10 days backward trajectories at 500 hPa
161 for 2002 to 2007 (Fig. 7a-f) computed for every 6 hours, which disclose that long-
162 range atmospheric circulation was significant in the study site of Aurora Peak. To
163 identify the possible source regions of biomass burning events, we prepared annual
164 composite maps (2002 to 2008 AD) of the Moderate Resolution Imaging
165 Spectroradiometer (i.e. MODIS) effective hot spot (Fig. 7a-f) from the Earth
166 Observing System Data and Information System (EOSDIS) using the Terra and Aqua
167 satellites of NASA ([https://earthdata.nasa.gov/data/near-real-time-data/firms/active-
168 fire-data](https://earthdata.nasa.gov/data/near-real-time-data/firms/active-fire-data)). The 10 days backward trajectory analysis from 2002 to 2007 showed that
169 Aurora Peak received air masses from the North Pacific Ocean, East Asia, Siberia,
170 Europe, Canada, and higher latitude of Alaska (Fig. 7a-f). Similar sources were
171 reported using 10-days backward trajectory from 1992-2002 (>300 hPa) (Yasunari
172 and Yamazaki, 2009). The Kamchatka Peninsula also receives air masses from China,
173 Mongolia, Siberia, Eastern Russia, and Europe (Kawamura et al., 2012).

174 3. Results and Discussion

175 Anhydrosugars such as levoglucosan are ubiquitous in the atmosphere, which
176 are emitted significantly from biomass burning activities and deposited on the ice
177 crystals, and contribute to water-soluble organic carbon (WSOC) (Gennaro et al.,
178 2015; Verma et al., 2015; Gao et al., 2015; Legrand et al., 2016; Grieman et al., 2017;
179 Li et al., 2018; Grieman et al., 2018a,b; You et al., 2019). These are produced from
180 the pyrolysis and combustion of cellulose and/or hemicellulose from wildfires and
181 domestic wood fires at temperatures above 300 °C (Shafizadeh, 1984; Fraser and
182 Lakshmanan, 2000; Simoneit et al., 2002) during the smoldering stage of a fire.
183 Recently, Kuo et al. (2011) reported that levoglucosan and its isomers are produced at
184 temperature up to 350°C. Many studies have shown that levoglucosan is the most

185 abundant anhydrous monosaccharide (Engling et al., 2006; Hoffmann et al., 2010;
186 Kuo et al., 2011), which is tracked by other species of anhydromonosaccharides; e.g.
187 mannosan, galactosan and/or dehydroabietic acid. Such specific characters and the
188 sources can make levoglucosan a unique tracer (Simoneit et al., 1999; Jordan et al.,
189 2006) in the southern Alaska as shown in Fig. 1.

190 In addition, historical trends of biomass burning tracers may represent the bulk
191 effects of emissions, transport, transformations, and depositional and post-
192 depositional process on the ice crystals (Grieman et al., 2017). Comparison of this
193 study (e.g., concentration trends) with other ice core studies suggested that these
194 compounds are well captured in the atmosphere and deposited to the ice sheets.
195 Backward trajectories of this study and other ice core studies suggested common
196 source regions (e.g., Russia, Siberia, and East Asia), from which it takes several days
197 to reach the sampling sites (e.g., Greenland-Tunu, Svalbard, Akademii Nauk, and
198 Aurora Peak of Alaska).

199 3.1 Levoglucosan

200 This study showed that average concentration of levoglucosan (range: BDL-
201 20800, average: 543 ± 2340 ng/kg-ice) is 8.6 times higher than that of dehydroabietic
202 acid (range: BDL-556, ave. 62 ± 97 ng/kg-ice) and 400 times higher than that of
203 vanillic acid (range: BDL-18.6, ave. 1.5 ± 2.9 ng/kg-ice) for 1665-2008 A.D. It should
204 be noted that combustion of lignite (lignite includes fossilized cellulose) or
205 hemicellulose emits levoglucosan and its isomers; e.g., mannosan and galactosan
206 (Hoffmann et al., 2010; Kuo et al., 2011). However, we did not detect these isomer
207 compounds (less than DL). In contrast, higher concentrations of these isomers and
208 levoglucosan were reported in aerosol samples collected from the oceans via “round-

209 the-world cruise” (Fu et al., 2011), Mt. Tai in the North China Plain (Fu et al., 2008),
210 and urban tropical India (Fu et al., 2010) using the same method.

211 Levoglucosan may not be as stable as previously thought in the atmosphere
212 (Fraser and Lakshmanan, 2000; Hoffmann et al., 2010), however, its concentrations
213 are not seriously influenced during transport for several days (Fraser and Lakshmanan,
214 2000; Lai et al., 2014). Hence, we may speculate that levoglucosan could be stable
215 enough in the ice core studies. However, degradation of levoglucosan depends upon
216 the OH radical (Hennigan et al., 2010), which are automatically affected by relative
217 humidity of the atmosphere and air mass aging during long range atmospheric
218 transport from Japan, China, Mongolia, Siberia, and Russia to Aurora Peak.

219 Levoglucosan showed higher concentrations in around 1660s-1830s (Figure
220 2a) with sporadic peaks in 1678 (ice core depth: 174.6 m; concentration: 593 ng/kg-
221 ice), 1692 (172.2 m; 704), 1695 (170.3 m; 1250), 1716 (165.6 m; 990), 1750 (156.7
222 m; 913), 1764 (151.5 m; 1433), 1786 (147.3 m; 7057), 1794 (146.1 m; 3302) and
223 1834 (138.4m; 944) above its average concentration (542 ng/kg-ice). Source regions
224 of these higher spikes could be East Asia, Eastern Russia, Siberia, higher latitudes of
225 Alaskan regions, and Canadian regions. For instance, Ivanova et al. (2010) reported
226 the frequently occurred heavy forest fires (e.g., boreal forest) in spring, summer and
227 autumn in eastern Siberia in the past, which is a potential source region to Alaska.
228 This study showed higher concentrations of levoglucosan before the 1840s (Figure
229 2a). Marlon et al. (2008) further confirmed that there was intensive biomass burning
230 between the 1750s -1840s on a global scale, which is linked to increasing
231 anthropogenic activities (e.g., population growth and land-use change).

232 Similarly, we detected higher spikes of levoglucosan in 1898 (120.7 m; 577
233 ng/kg-ice), 1913 (114.8 m; 20800), 1966 (77.7 m; 692) and 2005 (13.7 m; 598) above
234 the average concentration (542). Figure 2a clearly shows its lower levels than the
235 average after the 1830s (except for 1898, 1913, 1966 and 2005 A.D.) compared to
236 before 1830s. This decline could be attributed to less forest fire activity due to
237 intensive grazing, agriculture, and forest fire management system (Marlon et al., 2008;
238 Eichler et al., 2011). It should be noted that charcoal signals are scarce for Siberian
239 regions compared to North American and European ice core records (Eichler et al.,
240 2011). Moreover, two-third of Earth's boreal forest (17 million km²) lies in Russia,
241 which is a potential source of forest fires with a significant effect on a global air
242 quality (Isaev et al., 2002; Eichler et al., 2011).

243 Ice core records of Mt. Logan from Canada, GISP2 and 20D (older than the
244 1850s) from Greenland are characterized by higher spikes of NH₄⁺ superimposed with
245 relatively uniform summertime and wintertime minimum (Whitlow et al., 1994). We
246 obtained higher spikes of levoglucosan before the 1840s (Fig. 2a), which is consistent
247 with higher spikes of NH₄⁺ in 1770-1790 and 1810-1830 in the Mt. Logan data (e.g.,
248 Whitlow et al., 1994). This comparison suggests similar source regions of NH₄⁺ for
249 different sampling sites before the 1830s. In contrast, Mt. Logan data showed higher
250 spikes of NH₄⁺ in the intervals of 1850-1870 and 1930-1980, which is dissimilar
251 (except for two points) to our results from Aurora Peak (Fig. 2a). It should be noted
252 that Greenland ice core records (GISP2 and 20D) showed lower spikes of NH₄⁺
253 compared to Mt. Logan (Whitlow et al., 1994) during these intervals (1850-1870 and
254 1930-1980). This is consistent with the results of Aurora Peak (except for 1966),
255 again suggesting similar source regions (Holdsworth et al., 1992; Davidson et al.,
256 1993; Whitlow et al., 1994). The potential source regions for Greenland ice cores

257 include northern North America, Europe, and Siberia, which are also likely source
258 regions for Mt. Logan (Holdsworth et al., 1992; Davidson et al., 1993; Whitlow et al.,
259 1994; Legrand et al., 2016). These regions may be associated with higher spikes in ice
260 cores from Mt. Logan, Greenland and Aurora Peak of Alaska.

261 Except for a few points, e.g., 1999 (436 ng/kg-ice) and 2005 (598),
262 concentrations of levoglucosan drastically decreased in 1980-2008. This decrease
263 infers that forest fire activities could be depressed by many factors. For instance,
264 Central and East Siberian forest fire activities were controlled by strong climate
265 periodicity, e.g., Arctic Oscillation (AO), El Nino, intensification of the hydrological
266 cycle in central Asia, and other human activities in the NH (Robock, 1991; Wallenius
267 et al., 2005; Balzter et al., 2007; Achard et al., 2008; Eichler et al., 2011). Eichler et al.
268 (2009) further confirmed that from 1816 to 2001 higher amounts of NH_4^+ and formate
269 (HCOO^-) were directly emitted from biogenic sources rather than biomass burning
270 (Olivier et al., 2006) in the Belukha glacier in the Siberian Altai Mountains. Moreover,
271 lower concentrations of charcoal between 1700 and 2000 in this Altai Mountain
272 further suggest that forest fire activities were weaker than anthropogenic activities in
273 the source regions (Eichler et al., 2011).

274 Similarly, the sparsity of levoglucosan after the 1840s compared to the period
275 of 1660s to 1840s means low intensity of biomass burning and/or significant
276 deposition before reaching to the saddle of Aurora Peak, except for 1898, 1913, 1947
277 and 1966 A.D., which could be due to a point source around Alaskan region for
278 levoglucosan rather than long-range atmospheric transport. For example, higher
279 spikes of NH_4^+ at Mt. Logan during 1900-1990 A.D. are likely originated from central
280 and eastern Siberia (Robock, 1991), which is dissimilar to the source regions in this
281 study. The only exception is 1966 (2000 ng/kg-ice), suggesting that local biomass

282 burning and/or different source regions could be activated for levoglucosan is
283 important in southern Alaska during this period. Moreover, vanillic acid (VA) and p-
284 hydroxybenzoic acid (p-HBA) of Svalbard and Akademii Nauk (Eurasian Arctic) did
285 not show similar trends (Grieman et al., 2017, 2018a). It further suggests that central
286 and eastern Siberian regions did not contribute this compound significantly during
287 this period (1900-1990 A.D.) compared to other ice core studies (e.g., Fig. 6a-e)
288 and/or atmospheric circulations could be shifted.

289 The above results suggest the subsequent evidences: (a) heavy biomass
290 burning could be activated in the source regions, (b) short-range air mass circulation
291 could quickly reach southern Alaska, causing higher levels of levoglucosan; (c)
292 dilution and/or scavenging of biomass plume enroute could be maximized after 1830s,
293 whose mechanisms could be associated with dry and wet deposition, diffusion, and
294 degradation by hydroxyl radicals in the atmosphere during long range atmospheric
295 transport, (d) a common NH summertime biomass burning plume could be
296 significantly deposited during short-range atmospheric circulation on the exposed
297 surface area of the glaciers. Particular, Mt. Logan, Svalbard, Tunu of Greenland and
298 Aurora have common source regions, e.g., Russia and/or Siberian forest as well North
299 America/Canadian forest (Figure 6a-e). These considerations support that Alaskan
300 glaciers can preserve most biomass burning events in the circumpolar regions, which
301 occurred in the source regions of Siberia, East Asia, Canada and Alaska.

302 Hence, these historical records of levoglucosan before the 1830s suggest that
303 long-range atmospheric transport was significant rather than short-range transport
304 from intense and widespread forest fires. For instance, forest fire intensity in 1660s-
305 1830s A.D. could be induced by lightning during drought seasons in the Siberian

306 regions as well as extensive burning to clear land for agriculture purposes in the NH
307 (Whitlow et al., 1994; Legrand et al., 2016; Grieman et al., 2017; 2018a, b).

308 A declining trend in the concentrations of levoglucosan after the 1830s (except
309 for few points) showed that sources could be changed significantly and/or forest fire
310 activities could be suppressed and/or controlled in 1830s-1980s (Whitlow et al., 1994).
311 It should be noted that 1400 A.D. to the end of the 1700s A.D. is the Little Ice Age
312 (LIA) and after LIA to late 1800s is considered as the extended Little Ice Age (ELIA)
313 (Mann et al., 2009; Divine et al., 2011;). This study shows that intense biomass
314 burning activities (higher spikes) before the 1830s are somewhat similar to historical
315 records of p-HBA and vanillic acid of Lomonosovfonna (Svalbard) and Akademii-
316 Nauk ice core in the NH (Grieman et al., 2017, 2018a) except for some points (Fig.
317 6a,b,d). Hence, recent changes in the concentration trends in the Alaskan ice core are
318 thought to be climate-driven. These climate-driven effects are further discussed in
319 later section 3.4.

320 3.2 Dehydroabietic acid

321 Dehydroabietic acid is produced by pyrolytic dehydration of abietic acid from
322 conifer resin. In other words, dehydroabietic acid is produced during the burning
323 process of conifer resins (Simoneit et al., 1993; Kawamura et al., 2012;). It can be
324 used as a specific biomass-burning tracer for conifer trees and other resin-containing
325 softwoods in an ice core study. Dehydroabietic acid was detected as the second
326 dominant species (range: BDL-556, ave. 62.4 ± 97.2 ng/kg-ice), whose concentrations
327 are 9 times lower than levoglucosan but more than 46 times higher than vanillic acid
328 (range: BDL-18.6, ave. 1.62 ± 2.96 ng/kg-ice). Dehydroabietic acid showed higher
329 spikes in 1678 A.D. (ice core depth in meter, 173.9 m; 200 ng/kg-ice), 1716 (165.3 m;

330 67.5 ng/Kg-ice), 1728 (161.5 m; 139 ng/Kg-ice), 1732 (159.6 m; 233 ng/Kg-ice),
331 1738 (158.3 m; 113 ng/Kg-ice), 1750 (156.7 m; 66.9 ng/Kg-ice), 1764 (151.5 m; 331
332 ng/Kg-ice), 1786 (147.3 m; 386 ng/Kg-ice), 1794 (146.1 m; 78.6 ng/Kg-ice), 1913
333 (114.8 m; 101 ng/Kg-ice) than its average concentration (62.4 ng/kg-ice), and each
334 consecutive years from 1994 to 2007 A.D. (depth range: 44.8-0.88 m) have
335 concentrations of 92.8, 199, 141, 203, 136, 109, 98.5, 124, 124, 174, 309, 131, 298,
336 and 555 ng/kg-ice. Vanillic acid from Svalbard (Grieman et al., 2018a) showed
337 similar spikes with dehydroabiatic acid in this study during the 1660s to 1790s A.D.
338 In addition, Svalbard ice core showed relatively lower spikes from 1800s to 1980s as
339 compared to 1660s-1790s A.D. In contrast, p-HBA in this study did not show a
340 similar trend with Svalbard (Fig. 6a,b).

341 These periods are consistent with the higher spikes of levoglucosan, except for
342 a few points (e.g., 1734-1738 A.D.) before 1990 A.D. (Fig. 2a, b). The historical trend
343 of dehydroabiatic acid is also similar to that of levoglucosan before 1980, which is
344 consistent with Kamchatka ice core records (Kawamura et al., 2012). In contrast,
345 Kamchatka ice core showed a gradual increase of dehydroabiatic acid after the 1950s
346 However, we found an abrupt increase for dehydroabiatic and vanillic acids in the
347 Alaskan ice core after 1980 A.D. (Fig. 2b,c). These results suggest that biomass
348 burning plumes of pine, larch, spruce and fir trees in Siberian regions have a
349 substantial influence on Kamchatka, southeast Russia (facing to the western North
350 Pacific Rim) than southern Alaska (facing to the eastern North Pacific Rim).

351 We found that concentrations of dehydroabiatic acid in the Alaskan ice core
352 after the 1980s were higher than those of levoglucosan, which is consistent with
353 Kamchatka records (Kawamura et al., 2012). This further suggests that biomass
354 burning plumes from Siberian boreal conifer trees could be transported to the North

355 Pacific regions including the eastern North Pacific Rim. It also suggests that East
356 Asian regions (broad-leaf trees are common) could be important for levoglucosan
357 rather than dehydroabietic acid (boreal forest fires in Siberia, where pine trees are
358 dominant). For instance, correlation of levoglucosan versus dehydroabietic and
359 vanillic acid from 1660 to 1840 are weak but significant ($\tau=0.37$ and 0.33 , $p<0.05$,
360 respectively), suggesting the presence of common source region. Correlation of
361 levoglucosan with dehydroabietic and vanillic acids from 1920 to 1977 are not
362 significant (0.11 and 0.14 , respectively). On the other hand, vanillic vs.
363 dehydroabietic acid showed significant correlation (0.41 , $p<0.01$), suggesting a
364 different source region for levoglucosan. Backward trajectories analysis (500 hPa) of
365 air masses (2002-2007 A.D.) together with fire counts also showed that sources
366 regions also include Mongolia, China and Japan (Fig. 7a-f). Yasunari and Yamazaki
367 (2009) reported that Alaska can receive air masses from East Asia and Japan in the
368 troposphere (>300 hPa). The Kamchatka Peninsula also can receive air masses from
369 these regions (Kawamura et al., 2012).

370 These results showed some similarity in the records of levoglucosan between
371 Kamchatka and Alaska ice cores (except for few points) and some discrepancies of
372 dehydroabietic acid between two sampling sites. Dehydroabietic acid concentrations
373 gradually increased in the Kamchatka ice core after the 1950s. Alaskan ice core
374 showed an increase after the 1970s (Fig. 6e), suggesting that conifer-burning plumes
375 could be transported significantly to Kamchatka as well, but not southern Alaska in
376 the 1950s-1980s. There is another possibility for this discrepancy between two sites,
377 i.e., dehydroabietic acid could be decomposed during long-range atmospheric
378 transport (Simoneit and Elias, 2001) from Siberia to southern Alaska although it could
379 easily reach to Kamchatka in the western North Pacific Rim. The Kamchatka ice core

380 also **did not** show high spikes (except 1970) in the 1950s-1970s. Such types of lower
381 spikes and/or sporadic peaks of levoglucosan and dehydroabietic acid after the 1910s
382 (Fig. 2a,b) and the correlations suggest that source regions should be different (e.g.
383 East Asian broad leaf trees and Siberian boreal forest/pine trees), or **regional transport**
384 **overwhelms the long range atmospheric transport of dehydroabietic acid rather than**
385 **levoglucosan over the saddle of Aurora Peak at least after the 1910s. Interestingly,**
386 **dehydroabietic acid showed an increasing trend from 1980s to onwards with higher**
387 **concentrations than levoglucosan, being consistent with Kamchatka ice core**
388 **(Kawamura et al., 2012).**

389 Annual composite maps (Fig. 7a-f) of the Moderate Resolution Imaging
390 Spectroradiometer (MODIS) from 2001 to 2007 show a continental outflow of air
391 masses from Eurasia to the Aurora site, generally supporting the above results and
392 implications for the Alaskan ice core. However, we detected higher spikes of
393 levoglucosan (in 2004, 2005 and 2006 A.D. with 95, 598 and 131 **ng/kg-ice**,
394 respectively), dehydroabietic acid (in 2004, 2006 and 2007 A.D. with 309, 298 and
395 556 **ng/kg-ice**, respectively) and vanillic acid (in 2005, 2006 and 2007 A.D. with 18.6,
396 7.30 and 12.7 **ng/kg-ice**, respectively) within these years, suggesting that they have
397 different sources. **It is well known that 2004 is the year of biomass burning in Alaska.**
398 **The concentration of dehydroabietic acid in 2004 (309 ng/kg-ice) is three times higher**
399 **than levoglucosan (95.3 ng/kg, see Fig. 2), suggesting that boreal forest fires**
400 **associated with conifer trees followed by short- and long-range atmospheric transport**
401 **are more important in recent decades in the Northern Hemisphere.**

402 **3.3 Vanillic acid**

403 We detected vanillic acid (VA) in the ice core from Aurora Peak (Fig. 2c),
404 which is a biomass-burning tracer of lignin (Simoneit et al., 1993). Particularly,
405 vanillic acid can be produced by incomplete combustion of conifer trees, i.e., **conifer-**
406 **rich** boreal forest (Simoneit et al., 1993; Pokhrel, 2015). We found that the levels of
407 vanillic acid are very low between 1830s and 1960s as shown in Figure 2c. Higher
408 spikes of a lignin tracer were detected in the following years: 1678 (3.25 ng/kg-ice),
409 1692 (3.23), 1695 (5.56), 1732 (3.98), 1786 (3.60), 1814 (11.0), 1818 (5.50), 1973
410 (5.52), 1989 (3.57), 1993 (2.66), 1996 (4.66), 1997 (3.5), 1999 (3.57), 2001 (3.26),
411 and 2007 (18.6). **We found that the spikes of vanillic acid are not consistent with**
412 **those of levoglucosan in the ice core during the periods (Fig. 2). In particular, in more**
413 **recent years after 1990, vanillic acid showed a clear abrupt increase in the ice core,**
414 **which is consistent with the increase of dehydroabietic acid but different from**
415 **levoglucosan (Fig. 2). The abrupt increase of vanillic acid in the Alaskan ice core is**
416 **consistent with that of the Kamchatka ice core (Kawamura et al. 2012).**

417 The higher concentrations and similarity of vanillic and dehydroabietic acids
418 in the Alaskan ice core after the 1990 suggests an enhanced emission of biomass
419 burning products of conifer trees and lignin in the boreal forests in Alaska, which
420 could be imprinted in the southern Alaska ice core. **Interestingly, we found a**
421 **significant correlation (Fig. 3a) between dehydroabietic acid (except for 2005 A.D.)**
422 **and vanillic acid ($\tau=0.60$, $p<0.01$) after 1990s, whose period corresponds to the Great**
423 **Pacific Climate Shift (GPCS, 1977-2007 A.D.).** Being consistent with the warmer sea
424 surface temperature in the eastern North Pacific Rim during the GPCS periods (Meehl
425 et al., 2009), southern Alaska is influenced by the warmer temperature and dryness,
426 which triggered more chance of forest fires in the boreal forests, causing more
427 emissions of conifer and lignin tracers over the southern Alaskan atmosphere (Figs. 2

428 and 6). Interestingly, Kamchatka ice core also showed an increased concentration of
429 these tracers after 1970s (Kawamura et al., 2012).

430 Vanillic acid in the Alaskan ice core showed different trend from Svalbard ice
431 core (Fig. 6e) after the GPCS (1976-77), suggesting different source regions.
432 Dehydroabietic acid exhibits similar trend with p-hydroxybenzoic acid (p-HBA) of
433 Svalbard ice core (Grieman et al., 2018a). p-HBA is produced from tundra grasses
434 and peat species, suggesting a similar source of North Asia including Siberia. Its ice
435 core record may be climate-driven in the North Pacific Rim. In contrast, the historical
436 trend of vanillic acid from the 1770s to 1950s is similar to that (depressed trend) of
437 Tunu Greenland ice core, except for few years of 1851, 1870, 1880, 1934, and 1946
438 (Fig. 6c), which infers that long range atmospheric transport from Russia may be a
439 likely source. These two trends diverge markedly after the 1950s onwards. In addition,
440 vanillic acid in this study exhibits a similar trend with p-HBA and vanillic acid in the
441 ice core from Akademii Nauk (Grieman et al., 2017) in 1890s-1980s (Fig. 6d).

442 These results suggest that Alaskan glacier showed non-stationary multi-
443 decadal variability of biomass burning tracers from tundra grasses and peat species.
444 Notably, during the 1660s to 1820s, vanillic acid, dehydroabietic acid, and
445 levoglucosan have higher spikes (Fig. 6a,b,c) at 4 to 9 points, which are common in
446 other ice cores (Fig. 6a-d) in the NH. After these higher spikes, global (at least Tunu,
447 Akademii Nauk and Aurora) depression of vanillic acid and p-HBA (1830s-1950) can
448 be observed (e.g., Fig. 6a-d) in the NH, suggesting that similarity and variability of
449 these acids are temporally and spatially heterogeneous in the NH under the climate
450 driven forces. Historical trends of biomass burning tracers from this and other ice core
451 studies, together with backward trajectories (Fig. 7a-f), suggest a common potential

452 source region of North Asia and North America, which are characterized by fire
453 activities of boreal tundra woodlands, boreal conifer forests and peat.

454 Dehydroabietic acids and p-HBA may be unstable compared to photo-
455 degradation of levoglucosan during long-range transport. For instance, a higher
456 sensitivity of dehydroabietic acid was reported compared to levoglucosan (Simoneit
457 and Elias, 2001; Simoneit et al., 2002). It should be noted that we did not detect p-
458 HBA, which can be produced from incomplete combustion of grasses (Simoneit et al.,
459 2002; Kawamura et al., 2012;) although showed p-HBA was detected in Kamchatka
460 ice core (Kawamura et al., 2012). In contrast, we detected significant amounts of
461 dehydroabietic acid from 1665-2007 in this study (Figure 2b). Hence, we may
462 speculate that p-HBA could be unstable compared to levoglucosan, dehydroabietic
463 acid and vanillic acid during long-range atmospheric transport.

464 Moreover, the historical trend of vanillic acid from 1800-2000 in Greenland
465 ice core (McConnell et al., 2007) is entirely different from that of this study. Besides,
466 the historical trend of vanillic acid shows many higher sporadic peaks during the
467 Little Ice Age (LIA) and extended LIA (ELIA), which is somewhat similar to
468 concentration trends of 10-year bin averages of p-HBA and vanillic acid from
469 Svalbard ice core (Grieman et al., 2018a). These similarities could be due to a similar
470 source and source regions. In contrast, dissimilarity of historical records of these
471 compounds before and after ELIA suggests that shifting of atmospheric circulation or
472 different spatial pattern of biomass burning and/or that climate-driven effects are
473 deeply involved (Pokhrel et al., 2015). Hence these results further support a snap of
474 biomass burning periodic cycles of Alpine glacier in the North Pacific Rim

475 **3.4 Biomass burning tracers, temperature and climate: Atmospheric**
476 **consequences**

477 There is a direct relationship between the atmospheric temperature and
478 pressure in the NH; that is, one variable (temperature/pressure) follows the same
479 change when it comes to increasing and decreasing mode. This mechanism drives the
480 atmospheric air mass from one place to another in the NH. For example, the semi-
481 permanent Siberian High and Azores High drive the air mass from those regions to
482 Alaskan (e.g., Aleutian Low) and Icelandic (e.g., winter air mass circulation) regions
483 in the NH (Mantua and Hare, 2002). This Siberian High-pressure system (the vertical
484 extent is up to 3 km from the surface) is one of the principal sources of polar air mass
485 in the NH and is a principal factor to control air pollution in the Alaskan regions. Ten-
486 day airmass backward trajectories (Fig. 7a-f) supported the same atmospheric
487 transport pathways to southern Alaska. The consequences of such atmospheric
488 circulation in the Alaskan region can be directly observed with the correlations of
489 monthly (annual and seasonal) records of global lower troposphere temperature
490 anomalies (GLTTA) with this study (Fig. 4a-o).

491 These pieces of evidence are further reflected by the Pacific Decadal
492 Oscillation (PDO), which is characterized by relatively high temperature from the
493 west to east coasts of the North Pacific Rim (Mantuna et al., 1997; Mantuna and Hare,
494 2002; MacDonald and Case, 2005; Shen et al., 2006). The similar trend of
495 levoglucosan with five points running average of this PDO cycle, except for few
496 points (e.g., 1750, 1834, 1870, 1913, 1934 and 1966) during the whole period of 1665
497 to 1995, represents ecological changes and/or changes in climate-driven biomass
498 burning activities. These years, that is, 1750, 1834, 1870, 1913, 1934 and 1966 A.D.,
499 are influenced by micro and meso scale rather than synoptic and global scale weather

500 conditions and/or by long spikes represented by single fire events or seasonal biomass
501 burning activities (Fig. 5a,b). Hence, the positive/negative phase of PDO represents
502 zonal and/or meridional flows and elevated/depressed transport of levoglucosan to the
503 eastern North Pacific Rim.

504 In addition, winter precipitation (i.e., snowfall) is higher than usual in the
505 Alaskan coast. The annual precipitation of Aurora is increasing. The positive
506 correlations (R^2 or τ) of levoglucosan (except for few points, 1993, 1997, 1999 and
507 2005), dehydroabietic (except for, 1991 and 1998) and vanillic acids (except for 1998
508 and 2002) with winter temperature (GLTTA) are 0.55, 0.44 and 0.29, respectively,
509 after the Great Pacific Climate Shift (see Fig. 4-o). When the pressure decreases, the
510 temperature decreases, transporting air mass from higher (e.g., East Asia) to lower
511 pressure regions (Alaska). Similarly, we found further evidence of long-range
512 atmospheric transport due to a strong pressure gradient between Alaskan (e.g.,
513 Aleutian Low) and East Asian regions (e.g., Siberian high). For example, the
514 correlations (R^2 and τ) of these three compounds (except for a few points) are all
515 positive with seasonal (i.e., summer, autumn, and spring) and annual records of this
516 temperature (see Fig. 4a-o). In addition, the terrestrial plant derived biomarker such as
517 homologous series of high molecular weight fatty acids ($C_{21:0}$ to $C_{30:0}$) showed
518 increasing trends after the GPCS from the same ice core. These acids are emitted to
519 the source regions by vaporization of leaf waxes during biomass burning processes
520 (Pokhrel et al., 2015). Hence, these tracers are associated with synoptic scale
521 radiative climate forcing (e.g., radiative lapse rate or temperature inversion) from the
522 surface to boundary layer. The down slope winds and drainage of wind in the Alaskan
523 regions may be associated with PDO and El Nino Southern Oscillation (ENSO) in
524 summer (MacDonald and Case, 2005; Shen et al., 2006).

525 The remarkable increasing trend of dehydroabietic acid (ave. 128 ng/kg-ice,
526 range: 6.59-555, SD \pm 126 and median 108.8) has occurred after the GPCS (1977-
527 2007 AD). We found a significant correlation (Fig. 3a) between dehydroabietic acid
528 (except for 2005) and vanillic acid ($\tau=0.60$, $p<0.01$). In contrast, we found
529 insignificant correlations of levoglucosan with dehydroabietic acid (0.30) (except for
530 1981 and 1986) and vanillic acid (0.21) (except for, 1999 and 2005) after the GPCS,
531 that is, 1977-2007 A.D., revealing the local source emission. For example, the
532 biomass burning year of Alaska is 2004, which shows three times higher
533 concentrations of dehydroabietic acid (309 ng/kg-ice) than levoglucosan (95.3 ng/kg-
534 ice), suggesting that short range atmospheric transport enhances the dehydroabietic
535 acid under the local weather condition of Alaska.

536 The historical record of δD of the same ice core is well correlated with the
537 PDO cycle (Tsushima et al., 2015). Levoglucosan levels of this study are also allied
538 with periodicity of PDO (Fig. 5a,b) due to a Aleutian Low of North Pacific Ocean,
539 which is atmospheric air mass convergent near the southeast coast of Alaska (e.g.,
540 Aleutian Low represents the positive PDO). The average annual amplitude of δD
541 from this ice core is 30.9% (Tsushima et al., 2015). This high amplitude of δD could
542 not be conserved, if 100% of snow melting were occurred in the past. The coastal
543 record of climate change (e.g., winter storm development) of the Gulf of Alaska is
544 well correlated to the GPCS (1976 A.D.) in the PDO, suggesting that δD indicates the
545 air temperature of the saddle of the Aurora Peak.

546 The higher spikes of levoglucosan are similar to those of dehydroabietic and
547 vanillic acids from 1660s to 1970s. The positive/negative phases of both PDO
548 (MacDonald and Case, 2005; Trouet et al., 2009) cover all higher/lower spikes of

549 levoglucosan. The corresponding phase (positive/negative) of PDO varies from year
550 to several years and exhibits a tendency to cover historical intervals of these
551 compounds lasting several decades from 1660s to 1970s. The NAO's (wNAO) phase
552 are remain same for several years than PDO as shown in Figure (Fig. 5b). The
553 periodicity of NAO phase (positive/negative) does not represent the historical trends
554 (higher spikes/depression) of levoglucosan, dehydroabietic and vanillic acids (Fig. 5b,
555 c). This NAO represents atmospheric circulation between subtropical High and polar
556 Low (Trouet et al., 2009). In fact, NAO significantly dominates the North Atlantic
557 (e.g., North America) and European winter climate variabilities rather than those of
558 North Asia (i.e., Eurasia/Siberia), which is spontaneously inappropriate in this study.

559 4. Summary and Conclusions

560 This study has been conducted to better understand temporal trends of the
561 forest fire signals depend on the source region and proximity to the source and types
562 of vegetation in the source regions of southern Alaska since the 1660s A.D. Ice core
563 records of dehydroabietic acid, vanillic acid and levoglucosan showed predominant
564 multidecadal trends, suggesting the variations of fire regimes and the proximity to the
565 source, and changes in atmospheric circulation, land-use and/or ecological pattern in
566 the mid to high latitudes ($\geq 30^\circ$ N) at least before and after the 1830s and after the
567 Great Pacific Climate Shift (GPCS). Levoglucosan showed sporadic peaks during the
568 1660s-1830s, and single spikes in the 1898, 1913, 1966, and 2005 A.D. These spikes
569 indicate a significant contribution of biomass and/or biofuel burning attributing to
570 their source-specific emission and atmospheric stability in Alaskan regions.

571 Dehydroabietic and vanillic acids showed similar historical trends with
572 levoglucosan before the 1830s, suggesting that hard wood and conifer trees (e.g., resin

573 and lignin boreal conifer trees, deciduous trees and other higher plants) and perennial
574 grasses (C_3 and C_4 plants) were simultaneously important as burning sources. The
575 gradually increasing concentration trends of dehydroabietic and vanillic acids after the
576 1980s onward show a strong correlation ($\tau=0.60$, $p<0.01$; after the GPCS; 1976),
577 suggesting significant changes in either burning patterns (i.e., new land-use pattern or
578 new ecological pattern) or atmospheric circulation over Alaska by the climate driven
579 forces with exhibiting similar signals of biomass burning tracers compared to
580 insignificant correlation of levoglucosan with these compounds.

581 The significant positive correlations (τ) of these three compounds with lower
582 tropospheric global (annual and seasonal) temperature anomalies (GLTTA) suggest
583 that Alaskan snow precipitation was involved with climate-driven forces at least after
584 the GPCS to onwards. These tracers are allied with synoptic and global scale radiative
585 climate forcing (e.g., radiative atmospheric lapse rate or inversion) from the surface to
586 atmospheric boundary layer. The series of higher (lower) spikes of biomass burning
587 tracers from Aurora Peak represent the positive (negative) phase of PDO periodicity
588 cycles in the North Pacific Rim. The correlation of temperature and comparison with
589 PDO cycle with this study are further covering the excellent signal of periodic cycle
590 of climate-driven regime, that is, atmospheric activities, climate and weather
591 conditions, ecological changes, and individual fire activities of source regions to the
592 Aurora site.

593 The straight-forward historical trends of these three compounds were
594 significant before the 1830s, which differ from the Kamchatka ice core record,
595 suggesting that there are some differences between the western and eastern North
596 Pacific Rim for the emission, frequency, and deposition. The concentrations of these

597 three compounds from Aurora Peak are higher than those from other ice core studies
598 in the NH (e.g., Kamchatka, Svalbard, Tunu, and Akademii Nauk). In contrast, there
599 are similarities of depressed concentration trend of Aurora with other ice core studies
600 at least for one hundred years (e.g., 1890-1980s: Akademii Nauk, 1820-1960: Tunu
601 Greenland), suggesting that sources of biomass burning tracers are further confined
602 within the same regions, traveling from very long distances and are well captured
603 within the snow particles. If it is true, these compounds might be involved as cloud
604 condensation nuclei from the surface to 15.2 km, (i.e., cumulonimbus cloud),
605 transporting thousands kilometers to Aurora. It bounds positive feedback for the
606 climate change and/or climate variability in the North Pacific Rim.

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613 **References**

- 614 Achard, F., Eva, H. D., Mollicone, D., and Beuchleet, R.: The effect of climate anomalies and human
615 ignition factor on wildfires in Russian boreal forests, *Phil. Trans., R. Soc., B.*, 363, 2329e2337, doi:
616 10.1098/rstb.2007.2203, 2008.
- 617 Andreae, M. O. and Merlet, P.: Emission of trace gases and aerosols from biomass burning, *Global*
618 *Biogeochem. Cycle*, 15, 955-966, 2001.
- 619 Balzter, H., Gerard, F., Weedon, G., Grey, W., Combal, B., Bartholome, E., Bartalev, S., and Los, S.:
620 Coupling of vegetation growing season anomalies with hemispheric and regional scale climate
621 patterns in Central and East Siberia, *J. Clim.* 20, 15, 3713e3729, doi: 10.1175/JCLI4226, 2007.
- 622 Cong, Z., Kawamura, K., Kang, S., and Fu, P.: Penetration of biomass-burning emissions from South
623 Asia through the Himalayas: new insights from atmospheric organic acids, *Scientific Reports*, 5,
624 9580, doi: 10.1038/srep09580, 2015.
- 625 Davidson, C. I., Jaffrezo, J.-L., Small, M. J., Summers, P. W., Olson, M. P., and Borys, R. D.:
626 Trajectory analysis of source regions influencing the south Greenland ice sheet during the DYE3 gas
627 and aerosol sampling program, *Atmos. Env.*, 27A, 2739-2749, 1993.
- 628 Divine, D., Isaksson, E., Martma, T., Meijer, H.A.J., Moore, J., Pohjola, V., van de Wal, R.S.W., and
629 Godtliobsen, F.: Thousand years of winter surface air temperature variations in Svalbard and
630 northern Norway reconstructed from ice-core data: *Polar Research*, vol. 30, 7379, 12 p.,
631 doi.10.3402/polar.v30i0.7379, 2011.
- 632 Eichler, A., Brüttsch, S., Olivier, S., Papina, T., and Schwikowski, M.: A 750 year ice core record of
633 past biogenic emissions from Siberian boreal forests, *Geophys. Res. Lett.*, 36, L18813,
634 doi:10.1029/2009GL038807, 2009.
- 635 Eichler, A., Willy, T., Brüttsch, S., Olivier, S., Papina, T., and Schwikowski, M.: An ice-core based
636 history of Siberian forest fires since AD 1250, *Quat. Sci. Rev.* 30, 1027e1034,
637 doi:10.1016/j.quascirev.2011.02.007, 2011.
- 638 Engling, G., Carrico, C. M., Kreidenweis, S. M., Collett, J. L., Day, D. E., Malm, W. C., Lincoln, E.,
639 Hao, W. M., Iinuma, Y., and Herrmann, H.: Determination of levoglucosan in biomass combustion
640 aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection,
641 *Atmos. Environ.*, 40, S299-S311, 2006.
- 642 Fabbri, D., Marynowski, L., Fabianska, M. J., Zaton, M. and Simoneit, B. R. T.: Levoglucosan and
643 other cellulose markers in pyrolysates of miocene lignites: *Geochemical and environmental*
644 *implications*, *Environ. Sci. Technol.* 42, 2957-2963, 2008.
- 645 Fabbri, D., Torri, C., Simoneit, B. R. T., Marynowski, L., Rushdi, A. I. and Fabianska, M. J.:
646 Levoglucosan and other cellulose and lignin markers in emissions from burning of Miocene lignites,
647 *Atmos. Environ.*, 43, 2286-2295, 2009.
- 648 Fraser, M. P. and Lakshmanan, K.: Using levoglucosan as a molecular marker for the long-range
649 transport of biomass combustion aerosols, *Environ. Sci. Technol.*, 34, 4560-4564, 2000.
- 650 Fu P. Q., Kawamura, K., Okuzawa, K., Agarwal, S. G., Wang, G., Kanaya, Y., and Wang, Z.: Organic
651 molecular compositions and temporal variations of summertime mountain aerosols over Mt. Tai,
652 North China Plain, *J. Geophys. Res. Atmos.*, 113, D19107, doi.org/10.1029/2008JD009900, 2008.

- 653 Fu, P. Q., Kawamura, K., Pavuluri, C. M., Swaminathan, T., and Chen, J.: Molecular characterization
654 of urban organic aerosol in tropical India: contributions of primary emissions and secondary
655 photooxidation, *Atmos. Chem. Phys.*, 10, 2663-2689, 2010.
- 656 Fu, P., Kawamura, K., and Miura, K.: Molecular Characteristics of Marine Organic Aerosols Collected
657 during a Round-the-World Cruise, *J. Geophys. Res. Atmos.*, 116, D13302, doi:
658 10.1029/2011JD015604, 2011.
- 659 **Gambaro, A., Zangrando, R., Gabrielli, P., Barbante, C., and Cescon, P.: Direct Determination of**
660 **Levogluconan at the Picogram per Milliliter Level in Antarctic Ice by High-Performance Liquid**
661 **Chromatography/Electrospray Ionization Triple Quadrupole Mass Spectrometry, *Anal. Chem.*,**
662 **8051649-1655, 2008.**
- 663 Gao, S., Liu, D., Kang, S., Kawamura, K., Wu, G., Zhang, G., and Cong, Z.: A new isolation method
664 for biomass-burning tracers in snow: measurements of p-hydroxybenzoic, vanillic, and
665 dehydroabietic acids, *Atmos. Environ.*, 122, 142-147, 2015.
- 666 Grieman, M. M., Greaves, J., and Saltzman, E. S.: A method for analysis of **vanillic acid in polar ice**
667 **cores, *Climate of the Past*, 11(2), 227–232, doi:10.5194/cp-11-227, 2015.**
- 668 **Grieman, M. M.,** Aydin, M., Fritzsche, D., McConnell, J. R., Opel, T., Sigl, M., and Saltzman, E. S.:
669 Aromatic acids in a Eurasian Arctic ice core: a 2600-year proxy record of biomass burning, *Climate*
670 *of the Past*, 13(4), 395–410, doi:10.5194/cp-13-395-2017, 2017.
- 671 **Grieman, M. M.,** Aydin, M., Isaksson, E., Schwikowski, M., and Saltzman, E. S.: Aromatic acids in an
672 **Arctic ice core from Svalbard:** a proxy record of biomass burning, *Clim. Past*, 14, 637-651,
673 <https://doi.org/10.5194/cp-14-637-2018>, 2018a.
- 674 **Grieman, M. M.,** Aydin, M., McConnell, J., R., and Saltzman, E. S.: Burning-derived **vanillic acid in**
675 **an Arctic ice core** from Tunu, northeastern Greenland, *Clim. Past* 14(11), 1625-1637, 2018b.
- 676 Hennigan, C. J., Sullivan, A. P., Collett, Jr. J. L., and Robinson, A. L.: Levoglucosan stability in
677 biomass burning particles exposed to hydroxyl radicals, *Geophys. Res. Lett.*, 37, L09806,
678 doi:10.1029/2010GL043088, 2010.
- 679 Hoffmann, D., Tilgner A., Iinuma, Y., and Herrmann, H.: Atmospheric stability of levoglucosan: a
680 detailed laboratory and modeling study. *Environ. Sci. Technol.*, 44, 694–699,
681 doi:10.1021/es902476f, 2010.
- 682 Holdsworth, G., Higuchi, K., Zielinski, G. A., Mayewski, P. A., Wahlen, M., Deck, B., Chylek, P.,
683 Johnson, B., and Damiano, P.: Historical biomass burning: Late 19th century pioneer agriculture
684 revolution in northern hemisphere ice core data and its atmospheric interpretation, *J. Geophys. Res.*,
685 101, 23, 317-23, 334, 1996.
- 686 Holdsworth, G., Krouse, H. R., and Nosal, M.: Ice core climate signals from Mount Logan, Yukon AD.
687 1700-1987. In: *Climate since AD 1500* (ed. R.S. Bradley and P. D. Jones), Routledge, New Yourk,
688 NY, 483-504, 1992.
- 689 Isaev, A. S., Korovin, G. N., Bartalev, S. A., Ershow, D. V., and Janetos, A.: Using remote sensing to
690 assess Russian forest fire carbon emissions. *Climatic Change*, 55, 235e249, doi: 10.1023/A:
691 1020221123884, 2002.
- 692 Ivanova, G. A., Ivanov, V. A., Kukavskaya, E. A., and Soja, A. J.: The frequency of forest fires in
693 Scots pine stands of Tuva, Russia, *Environ. Res. Lett.*, 5, doi.org/10.1088/1748-
694 9326/1085/1081/015002, 2010.

- 695 Ivanova, G. A., Ivanov, V. A., Kukavskaya, E. A., and Soja, A. J.: The frequency of forest fires in
696 Scots pine stands of Tuva, Russia, *Environ. Res. Lett.*, 5, doi.org/10.1088/1748-
697 9326/1085/1081/015002, 2010.
- 698 Jordan, T. B., Seen, A. J., and Jacobsen, G. E.: Levoglucosan as an atmospheric tracer for wood smoke,
699 *Atmos. Environ.*, 40, 5316– 5321, 2006.
- 700 Kaplan, Y., Wake, C. P., Kreutz, K. J., and Whitlow, S. I.: A 1000-yr record of forest fire activity from
701 Eclipse Icefield, Yukon, Canada, *The Holocene*, 16, 2, 200-209, 2006.
- 702 Kaufmann, P., Fundel, F., Fischer, H., Bigler, M., Ruth, U., Udisti, R., Hansson, M., De Angelis, M.,
703 Barbante, C., Wolff, E. W., Hutterli, M., and Wagenbach, D.: Ammonium and non-sea salt sulfate in
704 the EPICA ice cores as indicator of biological activity in the Southern Ocean, *Quate. Science*
705 *Reviews*, 29, 313-323. doi:10.1016/j.quascirev. 2009.11.009, 2010.
- 706 Kawamura K., Yokoyama, K., Fujii, Y., and Watanabe, O. A.: Greenland ice core record of low
707 molecular weight dicarboxylic acids, ketocarboxylic acids, and dicarbonyls: A trend from Little Ice
708 Age to the present (1540 to 1989 A.D.), *J. Geophys. Res.*, D1, 106, 1331-1345, 2001.
- 709 Kawamura, K. and Pavuluri, C. M.: New Directions: Need for better understanding of plastic waste
710 burning as inferred from high abundance of terephthalic acid in South Asian aerosols, *Atoms.*
711 *Environ.*, 44, 5320-5321, 2010.
- 712 Kawamura, K., Izawa, Y., Mochida, M., and Shiraiwa, T.: Ice core records of biomass burning tracers
713 (levoglucosan and dehydroabietic, vanillic and p-hydroxybenzoic acids) and total organic carbon
714 for past 300 years in the Kamchatka Peninsula, Northeast Asia, *Geochimica. Cosmochimica. Acta.*,
715 99, 317-329, doi: 10.1016/j.gca.2012.08.006, 2012.
- 716 Kehrwald, N., Zangrando, R., Gabrielli, P., Jaffrezo, J.L., Boutron, C., Barbante, C., and Gambaro, A.:
717 Levoglucosan as a specific marker of fire events in Greenland snow, *Tellus B, Chemical and*
718 *Physical Meteorology*, 64(1), 18196, 2012.
- 719 Keywood, M., Kanakidou, M., Stohl, A., Dentener, F., Grassi, G., Meyer, C. P., Torseth, K., Edwards,
720 D., Thompson, A. M., Lohmann, U., and Burrows, J.: Fire in the Air: Biomass burning impacts in a
721 changing climate, *Crit. Rev. Environ. Sci. Technol.* doi.org/10.1080/10643389.10642011.10604248,
722 2011.
- 723 Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: Molecular distributions of
724 dicarboxylic acids, ketocarboxylic acids and dicarbonyls in biomass burning aerosols: implications
725 for photochemical production and degradation in smoke layers, *Atmos. Chem. Phys.*, 10, 2209-2225,
726 2010.
- 727 Kunwar, B., Kawamura, K., Fujiwara, S., Fu, P., Miyazaki, Y., and Pokhrel, A.: Dicarboxylic acids,
728 oxocarboxylic acids and α -dicarbonyls in atmospheric aerosols from Mt. Fuji, Japan: Implication for
729 primary emission versus secondary formation, *Atmos Res.*, 221, 58-71, 2019.
- 730 Kuo, L. J., Louchouart, P., and and Herbert, B. E.: Influence of combustion conditions on yields of
731 solvent-extractable anhydrosugars and lignin phenols in chars: Implications for characterizations of
732 biomass combustion residues, *Chemosphere*, 85, 797-805, 2011.
- 733 Lamarque, J. F., Bond, T. C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse, C.,
734 Mieville, A., Owen, B., Schultz, M. G., Shindell, D., Smith, S. J., Stehfest, E., Van Aardenne, J.,
735 Cooper, O. R., Kainuma, M., Mahowald, N., McConnell, J. R., Naik, V., Riahi, K., and van Vuuren,
736 D. P.: Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive

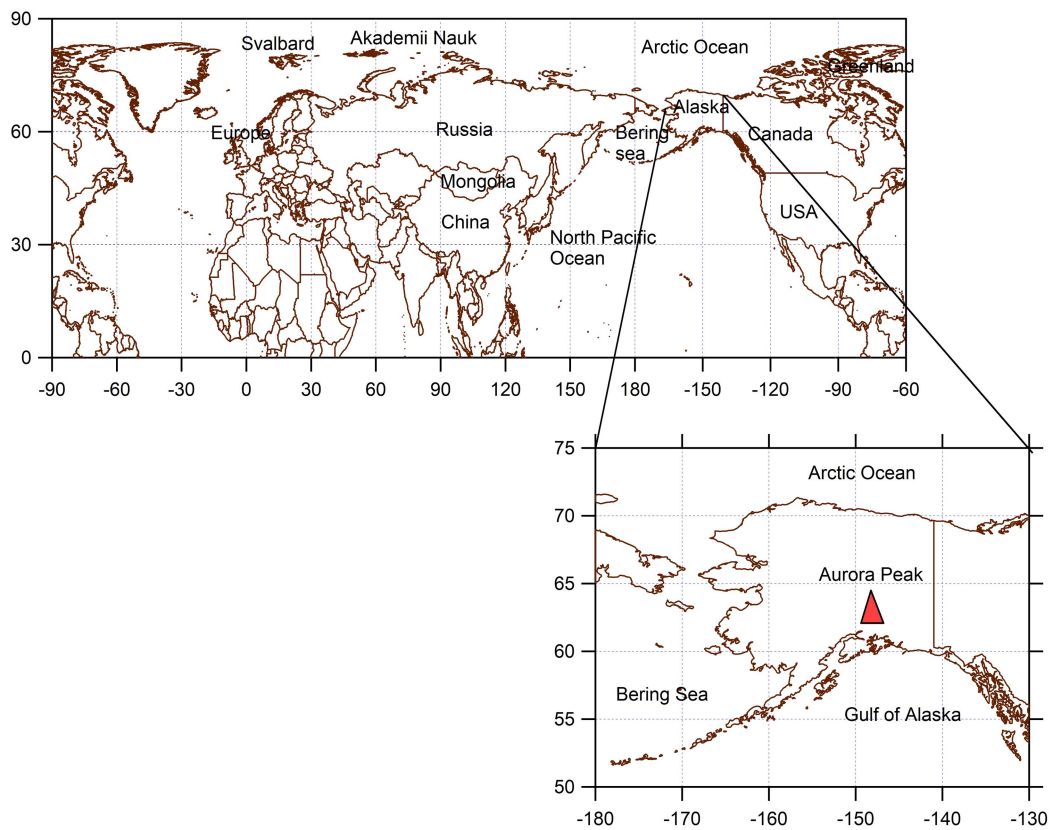
- 737 gases and aerosols: methodology and application, *Atmos. Chem. Phys.*, 10, 7017–7039,
738 doi:10.5194/acp-10-7017-2010, 2010.
- 739 Lazaar, M. and Kawamura, K.: Size distribution of low molecular weight dicarboxylic acids,
740 ketocarboxylic acids and α -dicarbonyls in the marine aerosols collected over Okinawa Island, the
741 western North Pacific, In H.-J. Ceccaldi et al. (eds.), *Glocal Change: Mankind-Marine Environment*
742 *Interactions*, doi 10.1007/978-90-481-8630-3, 67, 373-375, 2011.
- 743 Legrand, M. and Mayewski, P. A.: Glaciochemistry of polar ice cores: A review, *Reviews of*
744 *Geophysics*, 35, 219-143, 1997.
- 745 Legrand, M., and De Angelis, M.: Light carboxylic acids in Greenland ice: A record of past forest fires
746 and vegetation emissions from the boreal zone, *J. Geophys. Res.*, 101, 4129-4145, 1996.
- 747 Legrand, M., De Angelis, M., Staffelbach, T., Neftel, A., and Stauffer, B.: Large perturbations of
748 ammonium and organic acids content in the Summit Greenland ice core, fingerprint from forest
749 fires ?, *Geophys. Res. Lett.*, 19, 473-475, 1992.
- 750 Legrand, M., McConnell, J., Fischer, H., Wolff, E. W., Preunkert, S., Arienzo, M., Chellman, N.,
751 Leuenberger, D., Maselli, D., Place, P., Sigl, M., Schüpbach, S., and Flannigan, M.: Boreal fire
752 records in Northern Hemisphere ice cores: A review, *Clim. Past*, 12, 2033-2059, doi: 10.5194/cp-12-
753 2033-2016, 2016.
- 754 Lai, C., Liu, Y., Ma, J., Ma, Q., He, H.: Degradation kinetics of levoglucosan initiated by hydroxyl
755 radical under different environmental conditions, *Atmospheric Environment*, 91, 32-39,
756 <https://doi.org/10.1016/j.atmosenv.2014.03.054>, 2014.
- 757 MacDonald, G. M. and Case, R. A., Variations in the Pacific Decadal Oscillation over the past
758 millennium, *Geophys. Res. Lett.*, 32, L08703, doi: 10.1029/2005GL022478, 2005
- 759 Marlon, J. R., Bartlein, P. J., Carcaillet, C., Gavin, D. G., Harrison, S. P., Higuera, P. E., Joos, F.,
760 Power, M. J., and Prentice, I. C.: Climate and human influences on global biomass burning over the
761 past two millennia, *Nat. Geosci.*, 1, 697-702, doi: 10.1038/ngeo313, 2008.
- 762 Mantua, N. J. and Hare, S. R. : The Pacific Decadal Oscillation, *Jour of Oceanography*, vol, 58, 35-44,
763 2002.
- 764 Mantua, N. J., Hare, S. R., Zhang, Y., Wallace, J. M, and Francis, R. C.: A Pacific interdecadal climate
765 oscillation with impacts on salmon production, *American Meteorological Society*, 78 (6), 1069–79,
766 1997.
- 767 Mann, M.E., Zhang, Z., Rutherford, S., Bradley, R., Hughes, M.K., Shindell, D., Ammann, C., Faluvegi,
768 G., and Ni, F.: Global signatures and dynamical origins of the Little Ice Age and Medieval Climate
769 Anomaly, *Science*, 326, 1256-1260, doi:10.1126/science.1177303, 2009.
- 770 Mayewski, P. A., Meeker, L. D., Morrison, M. C., Twickler, M. S., Whitlow, S. I., Ferland, K. K.,
771 Meese, D., Legrand, M. R., and Stefessen, J. P.: Greenland ice core signal characteristics: An
772 expanded view of climate change, *J. Geophys. Res.*, 98, 12839-12847, 1993.
- 773 McConnell, J. R., Edwards, P. R., Kok, G. L., Flanner, M. G., Zender, C. S., Saltzman, E. S., Banta, J.
774 R., Pasteris, D. R., Carter, M. M., and Kahl, J. D. W.: 20th Century industrial black carbon
775 emissions altered Arctic climate forcing, *Science*, DOI: 10.1126/science.1144856, 2007.
- 776 Meehl, A. G., Hu, A., and Santer, D. B.: The mid-1970s climate shift in the Pacific and the relative
777 roles of forced versus inherent decadal variability, *J., Climate*, 780-792, 22, doi:
778 10.1175/2008JCLI2552.1, 2008.

- 779 Muller-Tautges, C., Eichler, A., Schwikowski, M., Pezzatti, G. B., Conedera, M., and Hoffmann,
780 T.: Historic records of organic compounds from a high Alpine glacier: influences of biomass
781 burning, anthropogenic emissions, and dust transport, *Atmos. Chem. Phys.*, 16, 1029-1043,
782 <https://doi.org/10.5194/acp-16-1029-2016>, 2016.
- 783 Olivier, S., Blaser, C., Brüttsch, S., Frolova, N., Gäggeler, H. W., Henderson, K. A., Palmer, A. S.,
784 Papina, T., and Schwikowski, M.: Temporal variations of mineral dust, biogenic tracers, and
785 anthropogenic species during the past two centuries from Belukha ice core, Siberian Altai., *J.*
786 *Geophys. Res.*, 111, D05309, doi: 10.1029/2005JD005830, 2006.
- 787 Pavuluri, C. M., Kawamura, K., and Swaminathan, T.: Water-soluble organic carbon, dicarboxylic
788 acids, ketoacids and α -dicarbonyls in the tropical Indian aerosols, *J. Geophys. Res.-Atmosphere*,
789 Vol. 115, doi: 10.1029/2009JD012661, 2010.
- 790 Pokhrel, A., Kawamura, K., Ono, K., Seki, O., Matoba, S., Shiraiwa, T. and Fu, P.: Ice core records of
791 monoterpene- and isoprene-SOA tracers from Aurora Peak in Alaska since 1660s: Implication for
792 climate change variability in the North Pacific Rim, *Atmospheric Environment*, doi:
793 10.1016/j.atmosenv.2015.09.063, 2016.
- 794 Pokhrel, A., Kawamura, K., Ono, K., Seki, O., Matoba, S., and Shiraiwa, T.: Ice core profiles of
795 saturated fatty acids (C_{12:0} - C_{30:0}) and oleic acid (C_{18:1}) from southern Alaska since 1734 AD: A link
796 to climate change in the Northern Hemisphere, *Atmos. Environ.*, 100, 201-209, 2015.
- 797 Pokhrel, A.: Studies on ice core records of dicarboxylic acids, ω -oxocarboxylic acids, pyruvic acid, α -
798 dicarbonyls and fatty acids from southern Alaska since 1665 AD: A link to climate change in the
799 Northern Hemisphere, Ph. D thesis, Hokkaido University, HUSCAP 11786,
800 <http://hdl.handle.net/2115/59331>, 2015.
- 801 Robock, A.: Surface cooling due to smoke from biomass burning, In: *Global biomass burning* (ed. J. S.
802 levine), MIT press, Cambridge, Mass., 463-476, 1991.
- 803 Rubino, M., D'Onofrio, A., Seki, O., and Bendle, J.A.: Ice-core records of biomass burning, *The*
804 *Anthropocene Review*, vol. 3(2), 140-162, doi: 10.1177/2053019615605117, 2016.
- 805 Savarino, J., and Legrand, M.: High northern latitude forest fires and vegetation emissions over the last
806 millenium inferred from the chemistry of a central Greenland ice core, *J. Geophys. Res.*, 103, 8267-
807 8279, 1998.
- 808 Shafizadeh, F.: The chemistry of pyrolysis and combustion, *Adv. Chem. Ser.*, 491-529, 1984.
- 809 Shen, C., Wang, W. C. Gong, W., and Hao, Z.: A Pacific Decadal Oscillation record since 1470 AD
810 reconstructed from proxy data of summer rainfall over eastern China, *Geophys. Res. Lett.*, vol. 33,
811 L03702, doi:10.1029/2005GL024804, 2006.
- 812 Shi, G., Wang, X C., Li, Y., Trengove, R., Hu, Z., Mi, M., Li, X., Yu, J., Hunter, B., and He, T.:
813 Organic tracers from biomass burning in snow from the coast to the ice sheet summit of East
814 Antarctica, *Atmos. Environ.*, 201, 231-241, 2019.
- 815 Simoneit, B. R. T., Kobayashi, M., Mochida, M., Kawamura, K., Lee, M., Lim, H. J., Turpin, B. J., and
816 Komazaki, Y.: Composition and major sources of organic compounds of aerosol particulate matter
817 sampled during the ACE-Asia campaign, *J. Geophys. Res. Atmos.*, 109, D19S10,
818 doi.org/10.1029/2004JD004598, 2004.
- 819 Simoneit, B. R. T. and Elias, V. O.: Detecting organic tracers from biomass burning in the atmosphere,
820 *Mar. Pollut. Bull.*, 42, 805-810, 2001.

- 821 Simoneit, B. R. T., Rogge, W. F., Mazurek, M. A., Standley, L. J., Hildemann, L. M., and Cass, G. R.:
822 Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions
823 from biomass combustion, *Environ. Sci. Technol.*, 27, 2533-2541, 1993.
- 824 Simoneit, B. R. T.: Biomass burning-a review of organic tracers for smoke from incomplete
825 combustion, *Appl. Geochem.*, 17, 129-162, 2002.
- 826 Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R. and Elias, V. O., Fraser, M. P., Rogge, W.
827 F., and Cass, G. R.: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric
828 particles, *Atmos. Environ.*, 33, 173-182, 1999.
- 829 Tsai, Y. I., Sopajaree, K., Chotruksa, A., Wu, H. C., and Kuo, S. C.: Source indicators of biomass
830 burning associated with inorganic salts and carboxylates in dry season ambient aerosol in Chiang
831 Mai Basin, Thailand, *Atmos. Environ.*, 78, 93-104, doi: 10.1016/j.atmosenv.2012.09.040,
832 2013. Trouet, V., Esper, J., Graham, N. E., Baker, A., Scourse, J. D., and Frank, D. C.: Persistent
833 Positive North Atlantic Oscillation mode dominated the medieval Climate anomaly, *Science*, vol.
834 324, pp. 78-80, 2009, doi: 10.1126/science.1166349.
- 835 Tsushima, A.: A study on reconstruction of paleo-environmental changes in the northern North Pacific
836 region from an alpine ice core, A Doctor's thesis, Hokkaido University, pp.78, 2015a,
837 doi:10.14943/doctoral.k11790.
- 838 Tsushima, A., Matoba, S., Shiraiwa, T., Okamoto, S., Sasaki, H., Solie, D., Yoshikawa, K.:
839 Reconstruction of recent climate change in Alaska from the Aurora Peak ice core, central Alaska.
840 *Clim. Past*, 11, 217-226, 2015.
- 841 Verma, S. K., Kawamura, K., Chen, J., Fu, P., and Zhu, C.: Thirteen years of observations on biomass
842 burning organic tracers over Chichijima Island in the western North Pacific: An outflow region of
843 Asian aerosols, *J. Geophys. Res. Atmos.*, 120, 4155-4168, doi: 10.1002/2014JD022224, 2015.
- 844 Wallenius, T. H., Pitkänen, A., Kuuluvainen, T., Pennanen, J., and Karttunen, H.: Fire history and
845 forest age distribution of an unmanaged *Picea abies* dominated landscape, *Can. J. For. Res.*, 35,
846 1540e1552, doi: 10.1139/x05-050, 2005.
- 847 Wang, G., Kawamura, K., Xie, M., Hu, S., Cao, J., An, Z., Waston, J. G., and Chow, J. C.: Organic
848 Molecular Compositions and Size Distributions of Chinese Summer and Autumn Aerosols from
849 Nanjing: Characteristic Haze Event Caused by Wheat Straw Burning, *Environ. Sci. Technol.*, 43
850 (17), 6493-6499, 2009.
- 851 Whitlow, S., Mayewski, P., Dibb, J., Holdsworth, G., and Twickler, M.: An ice-core-based record of
852 biomass burning in the Arctic and Subarctic, 1750-1980, *Tellus*, 46, 234-242, issn 0280-6509, 1994.
- 853 Wolff, E. W.: Chemical signals of past climate and environment from polar ice cores and firn air,
854 *Chem. Soc. Rev.*, 41, 6247-6258, doi: 10.1039/c2cs35227c, 2012.
- 855 Yang, Q., Mayewski, P. A., Whitlow, S., Twickler, M., Morrison, M., Talbot, R., Dibb, J. E., and
856 Linder, E.: Global perspective of nitrate flux in ice cores, *J. Geophys. Res.*, 100, D3, 5113-5121,
857 94JD03115, 1995.
- 858 Yasunari, T. J. and Yamazaki, K.: Origins of air mass over an Alaskan glacier and implications for ice
859 core studies in the North Pacific regions, *SOLA*, 5, 077-080, doi: 10.2151/sola.2009-020, 2009.
- 860 Zennaro, P., Kehrwald, N., McConnell, J. R., Schüpbach, S., Maselli, O. J., Marlon, J., Vallelonga, P.,
861 Leuenberger, D., Zangrando, R., Spolaor, A., Borrotti, M., Barbaro, E., Gambaro, A., and Barbante,
862 C.: Fire in ice: two millennia of boreal forest fire history from the Greenland NEEM ice core, *Clim.*
863 *Past*, 10, 1905-1924, <https://doi.org/10.5194/cp-10-1905-2014>, 2014.

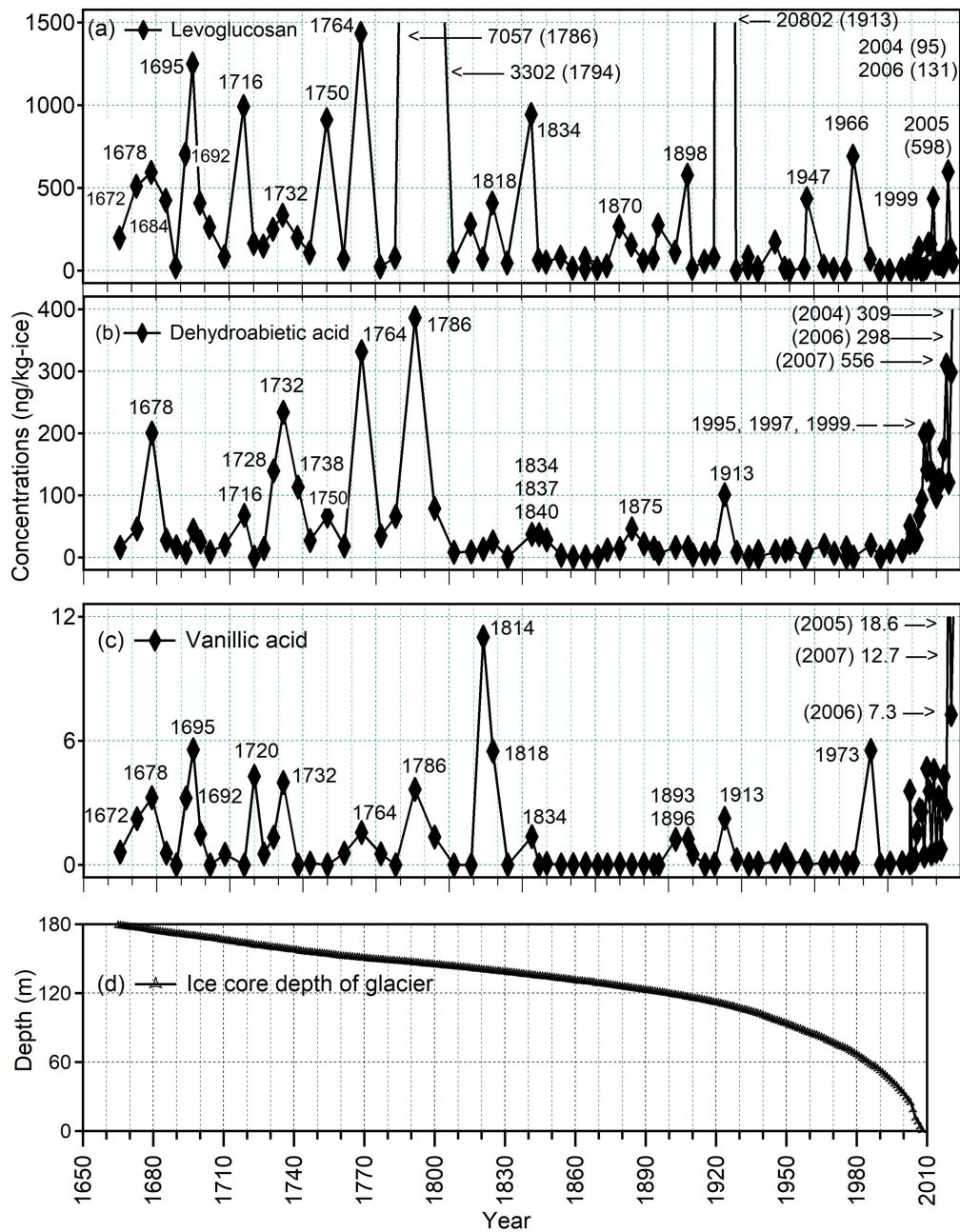
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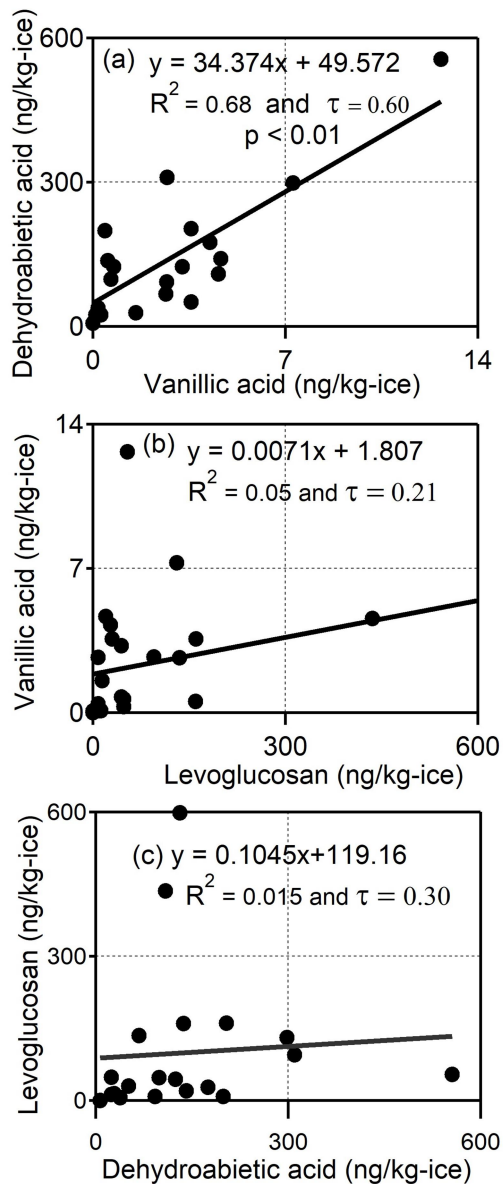
867 Figure 1. Geographical location of Aurora Peak in Alaska, where a 180-meter long ice
 868 core was drilled on the saddle of this peak in 2008



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870 Figure 2. Concentration changes of (a) levoglucosan, (b) dehydroabietic, (c) vanillic
 871 acids in the ice core, and (d) depth of the ice core collected from Aurora Peak in
 872 Alaska for 1665-2008 A.D.

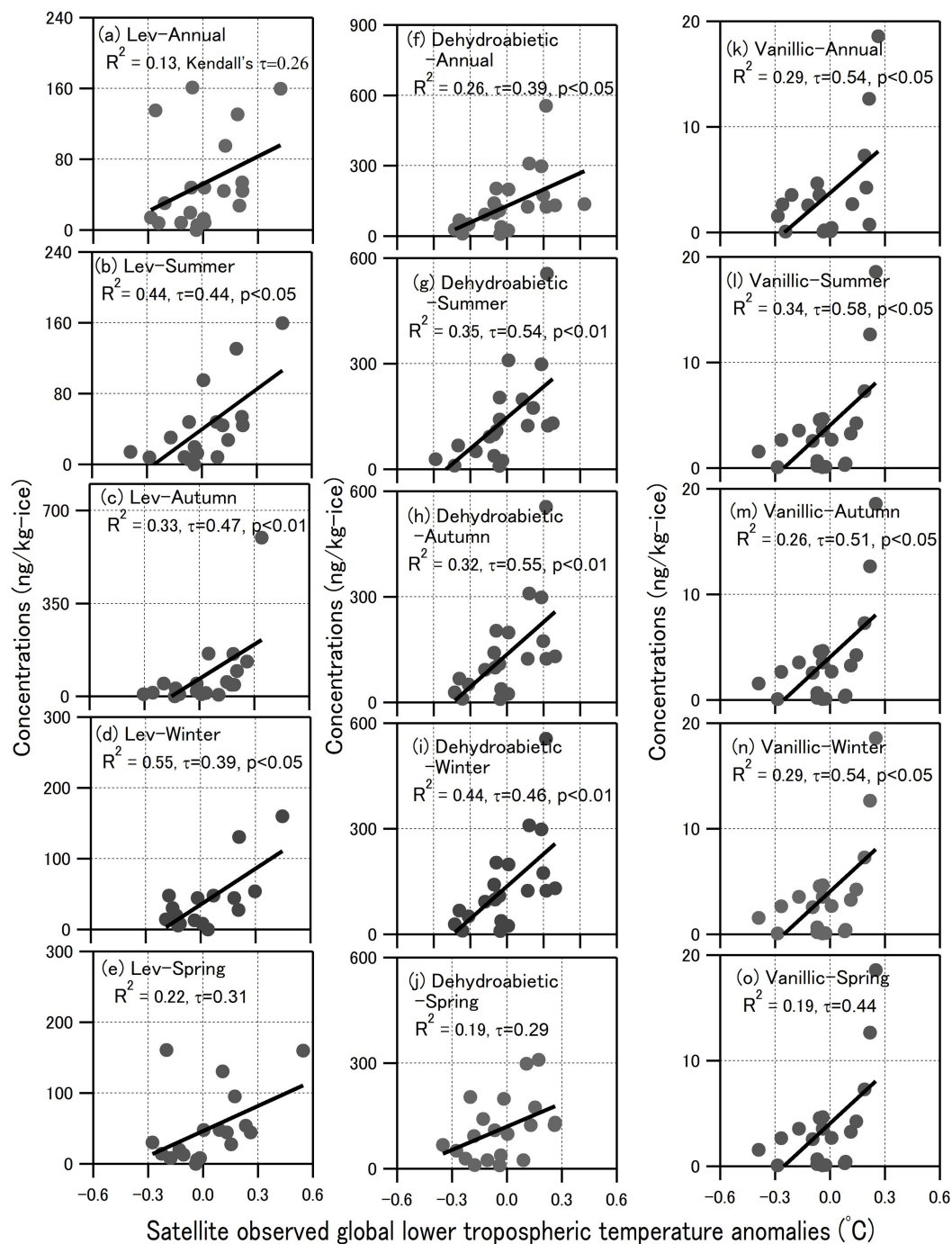
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875 **Figure 3.** Correlations (Pearson: R^2 and Kendall: τ) plots between the concentrations
 876 of (a) dehydroabiestic and vanillic acids, (b) vanillic acid and levoglucosan, and (c)
 877 levoglucosan and dehydroabiestic acid. In (b) and (c), correlations are insignificant in
 878 the Alaska ice core records from the saddle of Aurora Peak after the Great Pacific
 879 Climate Shift (1977-2007 A.D.).

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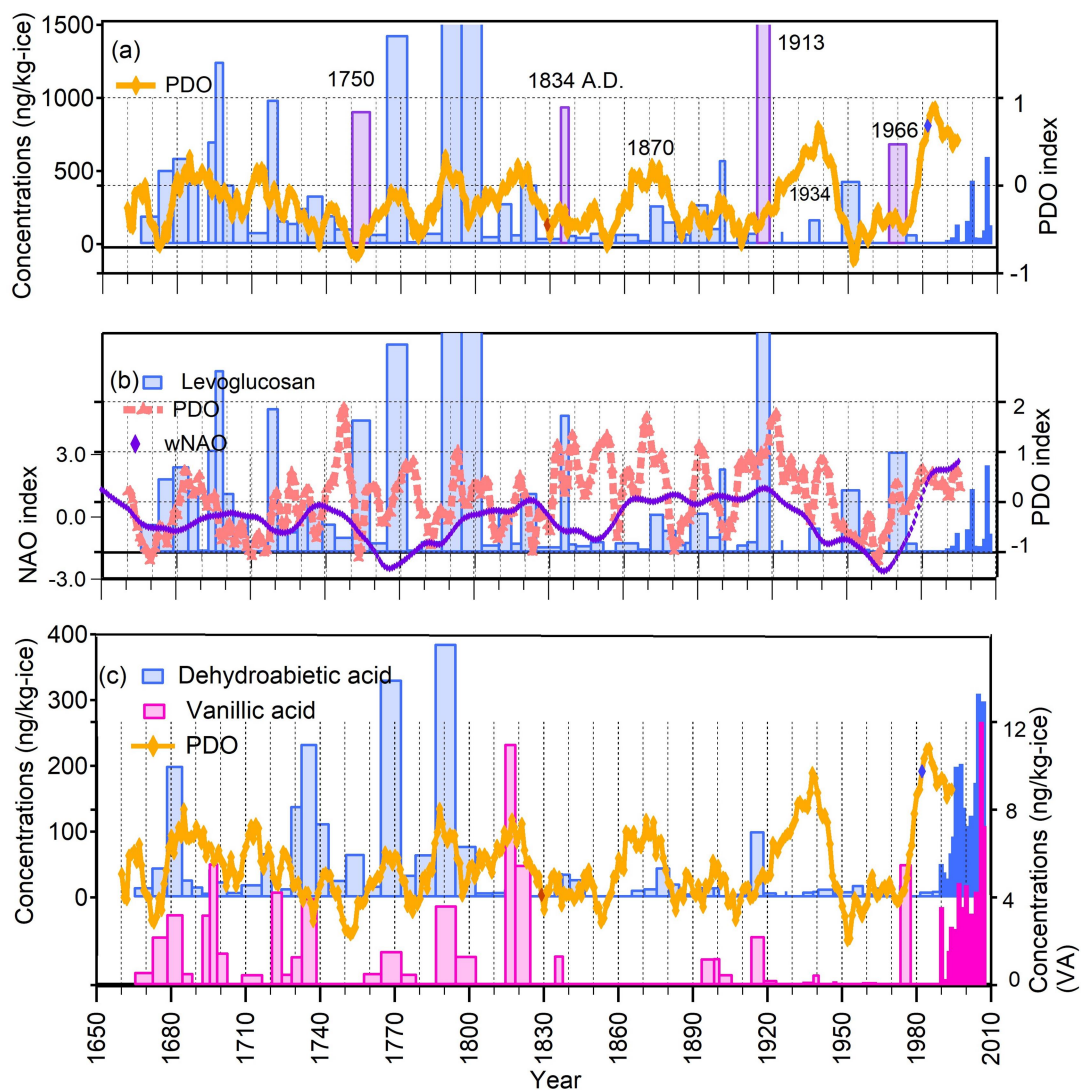


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882 **Figure 4.** Correlation (Pearson: R^2 and Kendall: τ) plots between satellite-observed
 883 global lower tropospheric temperature anomalies (i.e., microwave sounding unit
 884 temperature anomalies ($^{\circ}\text{C}$) of annual and seasonal records) and annual concentrations
 885 of (a-e) levoglucosan, (f-j) dehydroabietic acid, and (k-o) vanillic acid after the Great
 886 Pacific Climate Shift in the Northern Hemisphere.

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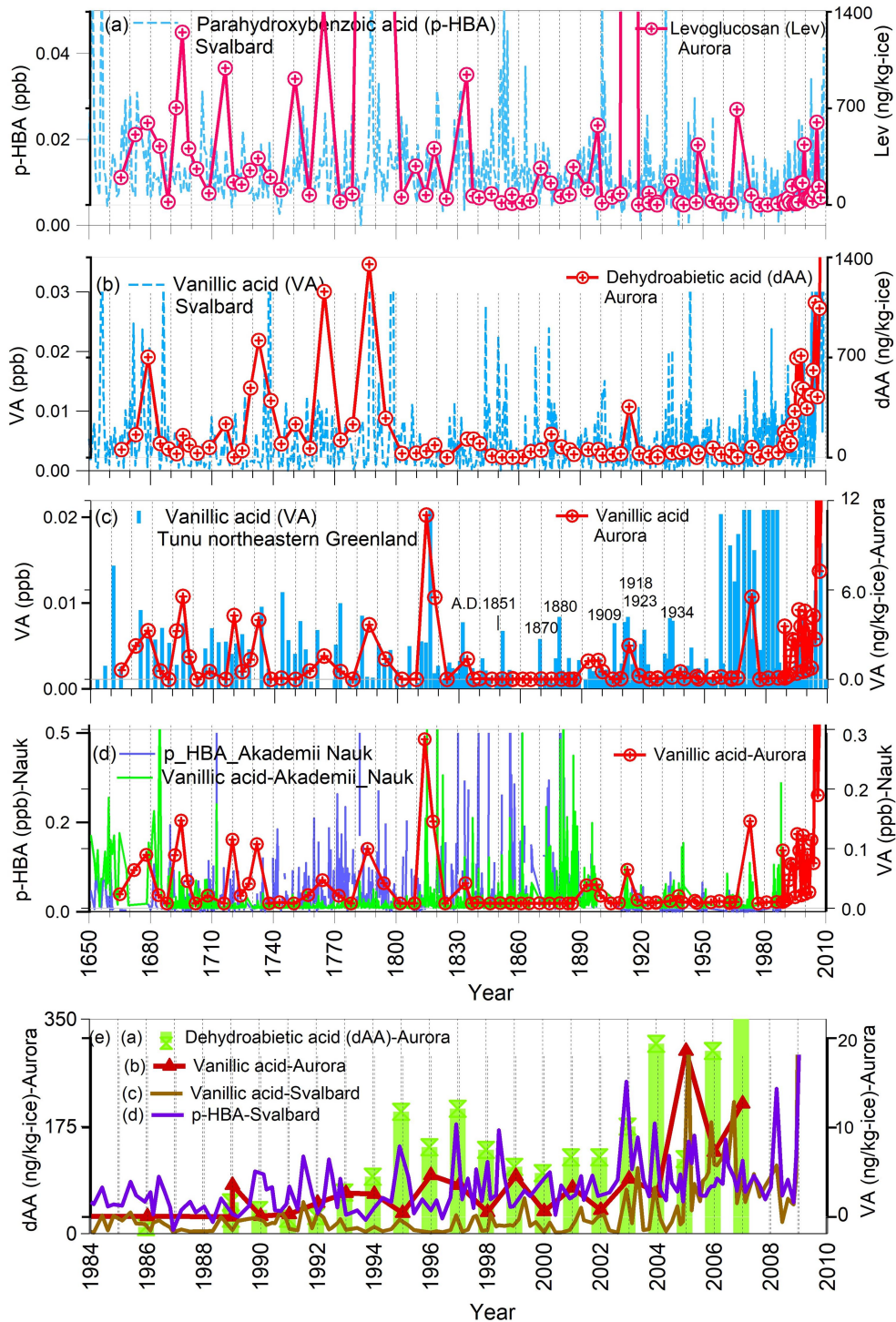
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890 **Figure 5.** Historical trends in the concentrations of (a) levoglucosan (Aurora Peak) and
 891 Pacific Decadal Oscillation (5 year mean PDO) index (Shen et al., 2006), (b) levoglucosan
 892 (Aurora Peak), PDO-5 year mean index (MacDonal and Case, 2005) and Multi-decadal winter
 893 North Atlantic index (wNAO) (Trouet et al., 2009), and (c) dehydroabietic and vanillic acids
 894 and PDO for 1665-2008 A.D.

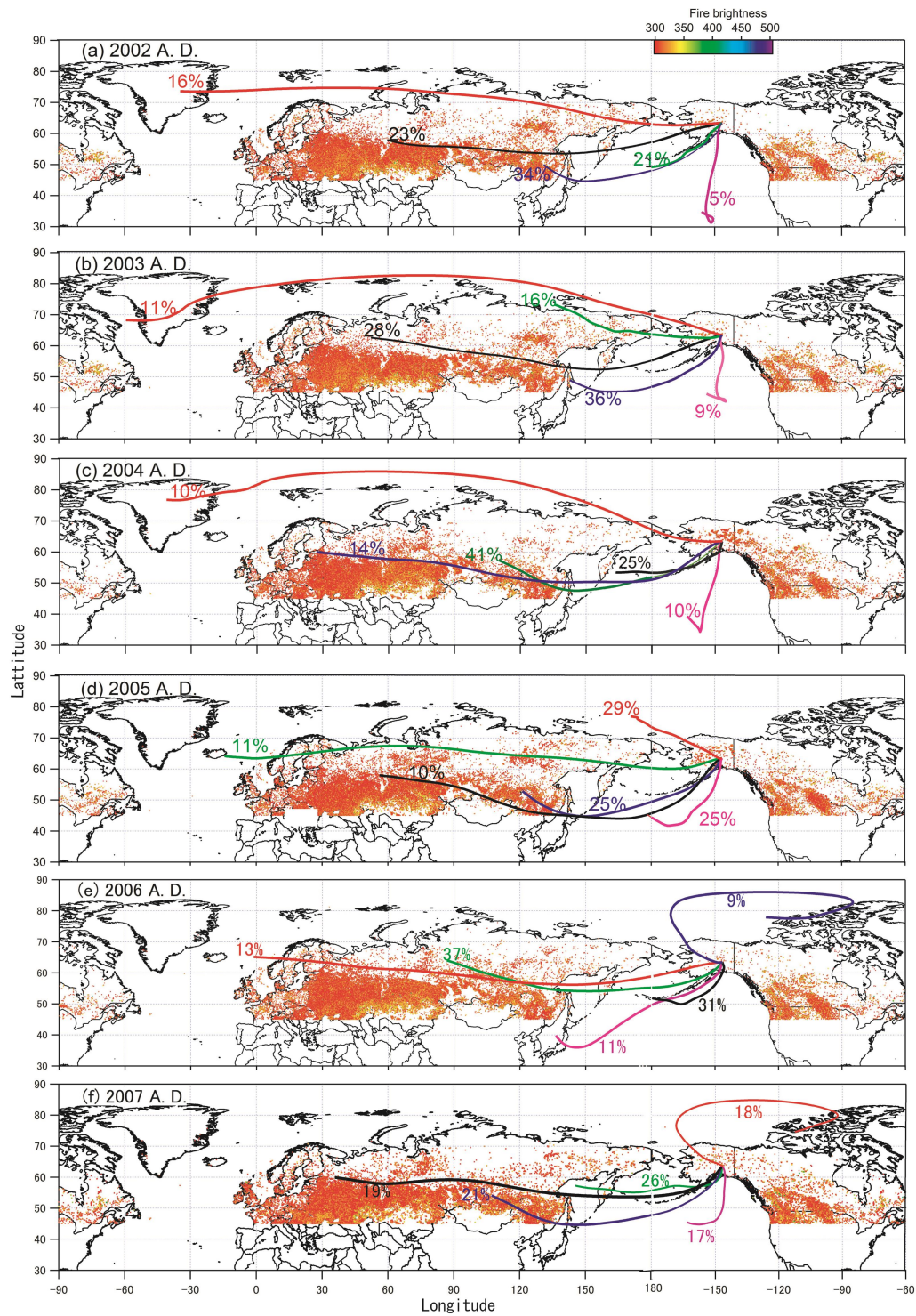
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897 **Figure 6.** Historical trends of (a) p-hydroxybenzoic acid (p-HBA) of Svalbard, (b) vanillic
 898 acid (VA) of Svalbard, (c) VA of Tunu Greenland, (d) p-HBA and VA of Akademii Nauk,
 899 with levoglucosan (Lev), dehydroabietic acid (dAA) and VA of Aurora Peak, respectively,
 900 and (e) historical trends of dAA and VA of Aurora and VA and p-HBA of Svalbard after the
 901 Great Pacific Climate Shift (1977-2007 A.D.).

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903

904 **Figure 7. The MODIS fire spots together with 10 days back trajectories analysis (a-f)**905 **of Alaskan regions since 2001 to 2007.**