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

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Abstract

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

1. Introduction

Biomass burning tracers (e.g., levoglucosan, dehydroabietic, vanillic, p-droxybenzoic, and syringic acids) are ubiquitous in the atmosphere and well deposited on ice sheets as snow particles (i.e., precipitation) (Pokhrel, 2015; Muller-Tautges et al., 2016; Grieman et al., 2018a,b; Shi et al., 2019). Previously, ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) and sulfate (SO_4^{2-}) were used to understand the atmospheric signals of biomass burning and/or the Pioneer Agriculture Revolution (PIA-GREV) in the Northern Hemisphere (Holdsworth et al., 1996; Legrand and Mayewski, 1997; Legrand et al., 2016). For instance, a signal of biomass burning is ammonium (e.g., $[NH_4]_2SO_4$) in snow particles, which is a constituent of forest fire smoke (Holdsworth et al., 1996; Tsai et al., 2013). Biomass burning activities such as forest fires and residential heating may affect climate change (Legrand and De Angelis, 1996; Savarino and Legrand 1998; Gambaro et al., 2008; Keywood et al., 2011).

Ice core records archive the long-term changes in deposition and concentration of organic (e.g., biomass burning tracers, ethane, formate, acetate, dicarboxylic acids, pyruvic acid and α-dicarbonyls) and inorganic species (e.g., NH_3^+, SO_4^{2-}, NO_3^-, K^+ and NO_2^-) (Yang et al., 1995; Legrand and Mayewski, 1997; Andreae and Merlet, 2001; Kaufmann et al., 2010; Lamarque et al., 2010; Wolff et al., 2012; Kawamura et al., 2012; Kehrwald et al., 2012; Legrand et al., 2016; Shi et al., 2019). Many studies have shown that there are some discrepancies of temporal and spatial biomass burning activities in ice core proximity records (Legrand et al., 1992,1996; Kaplan et al., 2010; Kawamura et al., 2012; Grieman et al., 2015; Rubino et al., 2016; Legrand et al.,

2016; Grieman et al., 2017; Zennaro et al., 2018; Li et al., 2018; Grieman et al., 2018a,b; You et al., 2019) in both Northern and Southern Hemisphere (NH/SH).

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

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

There are a few ice core studies of biomass burning-derived specific organic tracers, including levoglucosan that is a pyrolysis product of cellulose and

hemicellulose and other sugar compounds such as mannosan and galactosan, as well as dehydroabietic and vanillic acids which are biomass burning products of resin and lignin, respectively (Kawamura et al., 2012; Legrand et al., 2016; Grieman et al., 2017; Zennaro et al., 2018; Li et al., 2018; Grieman et al., 2018a,b; You et al., 2019). Kawamura et al. (2012) reported specific biomass burning tracers (levoglucosan, dehydroabietic and vanillic acid) for an ice core (1693-1997 A.D.), collected from the Kamchatka Peninsula (56º04'N, 160º28'E, Elevation: 3,903 m) in the western North Pacific Rim.

In this paper, we report levoglucosan, dehydroabietic acid and vanillic acid in an ice core collected from Aurora Peak of southern Alaska, an inland site facing to the northeast of Pacific Ocean (Fig. 1). This study covers 1665-2008 A.D., which can help to better understand the historical variability in the atmospheric transport of biomass burning tracers between the western North Pacific (Kawamura et al., 2012) and eastern North Pacific (this study). We also compare the present results with other ice core studies from Greenland, Svalbard and Akademii Nauk in the NH. The results of this study can further disclose the data base of levoglucosan, dehydroabietic and vanillic acids from the alpine glacier in the North Pacific Rim to explore their possible sources, origin, long- and short-range atmospheric transport, ecological changes and climate variability in the NH.

2. Materials and Methods

An ice core (180.17 m deep, 343 years old) was drilled in the saddle of the Aurora Peak of southern Alaska (location: 63.52°N, 146.54°W, elevation: 2,825 m, see Figure 1 for sampling site). The annual mean temperature at the site was minus 2.2°C, which matched to the temperature of 10 m depth in the borehole-ice. The

annual accumulation rate of snow is 8 mm yr^{-1} since 19 century and 23 mm yr^{-1} after the Great Pacific Climate Shift (GPCS, cold water masses were replaced by warm water since 1977, e.g., Meehl et al, 2009) This 180 m long core was divided into ~50 cm pieces and directly transported to the laboratory of the Institute of Low Temperature Science (ILTS), Hokkaido University, Japan and stored in a dark, cold room at - 20ºC until analysis.

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

These melted ice core samples (150 mL) were concentrated to almost dryness using a rotary evaporator under a vacuum in a pear shaped flask (300 ml) and extracted by a mixture of DCM/MeOH (2:1) using an ultrasonic bath. The extracts were transferred to 1.5 mL glass vial and dried under a nitrogen stream. Extracts were derivatized with 99% N, O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) +1% trimethylchlorosilane (TMCS) and 10 µl of pyridine at 70°C for three hours (Fu et al., 2011; Kawamura et al., 2012). Before injection to gas chromatography (GC)/mass spectrometry (MS), known volume of internal standard (n-C_{13} alkane) was added. GC peaks were analyzed by GC/MS: a Hewlett–Packard Model 5973 MSD coupled to a HP 6890 GC using a capillary column (HP-5MS, 30 m×0.32 mm I.D., 0.25 µm film thickness) installed with a split/splitless injector. The GC oven temperature was programmed from 50°C (2 min) to 120°C at 30°C/min, and then to 300°C at 6°C/min and maintained at 300°C for 20 min. Helium was used as a carrier gas. The GC/MS was operated on a scan mode (m/z=50-650) with an electron impact mode at 70 eV (Pokhrel et al., 2016).

Fragment ions at m/z = 217, 204 and 333 for levoglucosan, m/z = 239 for dehydroabietic acid and m/z = 297/312/267 for vanillic acid were processed on the Chemistation software and used for quantification. Peaks were further confirmed by comparing the mass spectra with those of authentic standards and the mass spectral data in the NIST/Willey library. An aliquot of authentic standard solution (10 µL) containing levoglucosan, dehydroabietic acid, vanillic acid and syringic acid (5.5, 4.7 and 4.2 ng/µL, respectively) was spiked to organic free Milli-Q water (200 ml) placed in the pear-shaped flask. The water sample was concentrated and dried by the procedure described above. The concentrates were derivatized with BSTFA and peaks were analyzed by GC/MS. The recoveries of the spiked samples of levoglucosan,

157 dehydroabietic acid, and vanillic acid were more than 83%. Duplicate analyses was
158 conducted to check analytical error of target compounds, which were less than 9%.
159 Laboratory blanks was measured using Milli-Q water (200 ml). The procedural blanks
160 showed no detectable peaks of these compounds. Detection limits of these species
161 were 0.002-0.005 ng/kg-ice.

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

176 **3. Results and Discussion**

177 Anhydrosugars such as levoglucosan are ubiquitous in the atmosphere, which
178 are emitted significantly from biomass burning activities and deposited on the ice
179 crystals, and contribute to water-soluble organic carbon (WSOC) (Gennaro et al.,
180 2015; Verma et al., 2015; Gao et al., 2015; Legrand et al., 2016; Grieman et al., 2017;

Li et al., 2018; Grieman et al., 2018a,b; You et al., 2019). These are produced from the pyrolysis and combustion of cellulose and/or hemicellulose from wildfires and domestic wood fires at temperatures above 300 °C (Shafizadeh, 1984; Fraser and Lakshmanan, 2000; Simoneit et al., 2002) during the smoldering stage of a fire. Recently, Kuo et al. (2011) reported that levoglucosan and its isomers are produced at temperature up to 350°C. Many studies have shown that levoglucosan is the most abundant anhydrous monosaccharide (Engling et al., 2006; Hoffmann et al., 2010; Kuo et al., 2011), which is tracked by other species of anhydromonosaccharides; e.g. mannosan, galactosan and/or dehydroabietic acid. Such specific characters and the sources can make levoglucosan a unique tracer (Simoneit et al., 1999; Jordan et al., 2006) in the southern Alaska as shown in Figure 1.

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

3.1 Levoglucosan

This study showed that average concentration of levoglucosan (range: BDL-20800, average: 543±2340 ng/kg-ice) is 8.6 times higher than that of dehydroabietic acid (range: BDL-556, ave. 62±97 ng/kg-ice) and 400 times higher than that of vanillic acid (range: BDL-18.6, ave. 1.5±2.9 ng/kg-ice) for 1665-2008 A.D. It should

205 be noted that combustion of lignite (lignite includes fossilized cellulose) or
206 hemicellulose emits levoglucosan and its isomers; e.g., mannosan and galactosan
207 (Hoffmann et al., 2010; Kuo et al., 2011). However, we did not detect these isomer
208 compounds (less than DL). In contrast, higher concentrations of these isomers and
209 levoglucosan were reported in aerosol samples collected from the oceans via "round-
210 the-world cruise" (Fu et al., 2011), Mt. Tai in the North China Plain (Fu et al., 2008),
211 and urban tropical India (Fu et al., 2010) using the same method.

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

220 Levoglucosan showed higher concentrations in around 1660s-1830s (Figure
221 2a) with sporadic peaks in 1678 (ice core depth: 174.6 m; concentration: 593 ng/kg-
222 ice), 1692 (172.2 m; 704 ng/kg-ice), 1695 (170.3 m; 1250 ng/kg-ice), 1716 (165.6 m;
223 990 ng/kg-ice), 1750 (156.7 m; 913 ng/kg-ice), 1764 (151.5 m; 1433 ng/kg-ice), 1786
224 (147.3m; 7057 ng/kg-ice), 1794 (146.1 m; 3302 ng/kg-ice) and 1834 (138.4m; 944
225 ng/kg-ice) above its average concentration (542 ng/kg-ice). Source regions of these
226 higher spikes could be East Asia, Eastern Russia, Siberia, higher latitudes of Alaskan
227 regions, and Canadian regions. For instance, Ivanova et al. (2010) reported the
228 frequently occurred heavy forest fires (e.g., boreal forest) in spring, summer and
229 autumn in eastern Siberia in the past, which is a potential source region to Alaska.

230 This study showed higher concentrations of levoglucosan before the 1840s (Figure
231 2a). Marlon et al. (2008) further confirmed that there was intensive biomass burning
232 between the 1750s -1840s on a global scale, which is linked to increasing
233 anthropogenic activities (e.g., population growth and land-use change).

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

245 Mt. Logan Canada, GISP2, and 20D (older than the 1850s) ice core records of
246 Greenland are characterized by higher spikes of NH_4^+ superimposed with relatively
247 uniform summertime and wintertime minimum (Whitlow et al., 1994). We obtained
248 higher spikes of levoglucosan before the 1840s (Figure 2a), which is consistent with
249 higher spikes of NH_4^+ in 1770-1790 and 1810-1830 in the Mt. Logan data (e.g.,
250 Whitlow et al., 1994). This comparison suggests similar source regions of NH_4^+ for
251 different sampling sites before the 1830s. In contrast, Mt. Logan data showed higher
252 spikes of NH_4^+ in the intervals of 1850-1870 and 1930-1980, which is dissimilar
253 (except for two points) to our results from Aurora Peak (Figure 2a). It should be noted
254 that Greenland ice core records (GISP2 and 20D) showed lower spikes of NH_4^+

compared to Mt. Logan (Whitlow et al., 1994) during these intervals (1850-1870 and 1930-1980). This is consistent with the results of Aurora Peak (except for 1966), again suggesting similar source regions (Holdsworth et al., 1992; Davidson et al., 1993; Whitlow et al., 1994). The potential source regions for Greenland ice cores include northern North America, Europe, and Siberia, which are also likely source regions for Mt. Logan (Holdsworth et al., 1992; Davidson et al., 1993; Whitlow et al., 1994; Legrand et al., 2016). These regions may be associated with higher spikes in ice cores from Mt. Logan, Greenland and Aurora Peak of Alaska.

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

Similarly, the sparsity of levoglucosan after the 1840s compared to 1660s to 1840s means low intensity of biomass burning and/or significant deposition before reaching to the saddle of Aurora Peak, except for 1898, 1913, 1947 and 1966 A.D., which could be due to a point source around Alaskan region for levoglucosan rather

than long-range atmospheric transport. For example, higher spikes of NH_4^+ at Mt. Logan during 1900-1990 A.D. are likely originated from central and eastern Siberia (Robock, 1991), which is dissimilar to the source regions in this study. The only exception is 1966 (2000 ng/kg-ice), suggesting that local biomass burning and/or different source regions could be activated for levoglucosan is important in southern Alaska during this period. Moreover, vanillic acid (VA) and p-hydroxybenzoic acid (p-HBA) of Svalbard and Akademii Nauk (Eurasian Arctic) did not show similar trends (Grieman et al., 2017, 2018a). It further suggests that central and eastern Siberian regions did not contribute this compound significantly during this period (1900-1990 A.D.) compared to other ice core studies (e.g., Fig. 6a-e) and/or atmospheric circulations could be shifted.

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

Hence, these historical records of levoglucosan before the 1830s suggest that long-range atmospheric transport was significant rather than short-range transport from intense and widespread forest fires. For instance, forest fire intensity in 1660s-1830s A.D. could be induced by lightning during drought seasons in the Siberian regions as well as extensive burning to clear land for agriculture purposes in the NH (Whitlow et al., 1994; Legrand et al., 2016; Grieman et al., 2017; 2018a, b).

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

3.2 Dehydroabietic acid

Dehydroabietic acid is produced by pyrolytic dehydration of abietic acid from conifer resin. In other words, dehydroabietic acid is produced during the burning process of conifer resins (Simoneit et al., 1993; Kawamura et al., 2012;). It can be used as a specific biomass-burning tracer for conifer trees and other resin-containing softwoods in an ice core study. Dehydroabietic acid was detected as the second

328 dominant species (range: BDL-556, ave. 62.4±97.2 ng/kg-ice), whose concentrations
329 are 9 times lower than levoglucosan but more than 46 times higher than vanillic acid
330 (range: BDL-18.6, ave. 1.62±2.96 ng/kg-ice). Dehydroabietic acid showed higher
331 spikes than its average concentration (62.4 ng/kg-ice) in 1678 A.D. (ice core depth in
332 meter, 173.9 m; 200 ng/kg-ice), 1716 (165.3 m; 67.5 ng/kg-ice), 1728 (161.5 m; 139
333 ng/kg-ice), 1732 (159.6 m; 233 ng/kg-ice), 1738 (158.3 m; 113 ng/kg-ice), 1750
334 (156.7 m; 66.9 ng/kg-ice), 1764 (151.5 m; 331 ng/kg-ice), 1786 (147.3 m; 386 ng/kg-
335 ice), 1794 (146.1 m; 78.6 ng/kg-ice), 1913 (114.8 m; 101 ng/kg-ice), and all
336 consecutive year during 1994-2007 A.D. (depth range is 44.8-0.88 m) of 92.8, 199,
337 141, 203, 136, 109, 98.5 , 124, 124, 174, 309, 131, 298, and 555 ng/kg-ice,
338 respectively. Vanillic acid from Svalbard (Grieman et al., 2018a) showed similar
339 spikes with dehydroabietic acid in this study during the 1660s to 1790s A.D. In
340 addition, Svalbard ice core showed relatively lower spikes from 1800s to 1980s as
341 compared to 1660s-1790s A.D. In contrast, p-HBA in this study did not show a
342 similar trend with Svalbard (Figure 6a,b).

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

We found that concentrations of dehydroabietic acid in the Alaskan ice core after the 1980s were higher than those of levoglucosan, which is consistent with Kamchatka records (Kawamura et al., 2012). This further suggests that biomass burning plumes from Siberian boreal conifer trees could be transported to the North Pacific regions including the eastern North Pacific Rim. It also suggests that East Asian regions (broad-leaf trees are common) could be important for levoglucosan rather than dehydroabietic acid (boreal forest fires in Siberia, where pine trees are dominant). For instance, correlation of levoglucosan versus dehydroabietic and vanillic acid from 1660 to 1840 are weak but significant (τ=0.37 and 0.33, $p<0.05$, respectively), suggesting the presence of common source region. Correlation of levoglucosan with dehydroabietic and vanillic acids from 1920 to 1977 are not significant (0.11 and 0.14, respectively). On the other hand, vanillic vs. dehydroabietic acid showed significant correlation (0.41, $p<0.01$), suggesting a different source region for levoglucosan. Backward trajectories analysis (500 hPa) of air masses (2002-2007 A.D.) together with fire counts also showed that sources regions also include Mongolia, China and Japan (Figure 7a-f). Yasunari and Yamazaki (2009) reported that Alaska can receive air masses from East Asia and Japan in the troposphere (>300 hPa). The Kamchatka Peninsula also can receive air masses from these regions (Kawamura et al., 2012).

These results showed some similarity in the records of levoglucosan between Kamchatka and Alaska ice cores (except for few points) and some discrepancies of dehydroabietic acid between two sampling sites. Dehydroabietic acid concentrations gradually increased in the Kamchatka ice core after the 1950s. Alaskan ice core showed an increase after the 1970s (Figure 6e), suggesting that conifer-burning plumes could be transported significantly to Kamchatka as well, but not southern

Alaska in the 1950s-1980s. There is another possibility for this discrepancy between two sites, i.e., dehydroabietic acid could be decomposed during long-range atmospheric transport (Simoneit and Elias, 2001) from Siberia to southern Alaska although it could easily reach to Kamchatka in the western North Pacific Rim. The Kamchatka ice core also did not show high spikes (except 1970) in the 1950s-1970s. Such types of lower spikes and/or sporadic peaks of levoglucosan and dehydroabietic acid after the 1910s (Figure 2a,b) and the correlations suggest that source regions should be different (e.g. east Asian broad leaf trees and Siberian boreal forest/pine trees), or regional transport overwhelms the long range atmospheric transport of dehydroabietic acid rather than levoglucosan over the saddle of Aurora Peak at least after the 1910s. Interestingly, dehydroabietic acid showed an increasing trend from 1980s to onwards with higher concentrations than levoglucosan, being consistent with Kamchatka ice core (Kawamura et al., 2012).

Annual composite maps (Figure 7a-f) of the Moderate Resolution Imaging Spectroradiometer (MODIS) from 2001 to 2007 show a continental outflow of air masses from Eurasia to the Aurora site, generally supporting the above results and implications for the Alaskan ice core. However, we detected higher spikes of levoglucosan (in 2004, 2005 and 2006 A.D. with 95, 598 and 131 ng/kg-ice, respectively), dehydroabietic acid (in 2004, 2006 and 2007 A.D. with 309, 298 and 556 ng/kg-ice, respectively) and vanillic acid (in 2005, 2006 and 2007 A.D. with 18.6, 7.30 and 12.7 ng/kg-ice) within these years, suggesting that they have different sources. It is well known that 2004 is the year of biomass burning in Alaska. The concentration of dehydrobaietic acid in 2004 (309 ng/kg-ice) is three times higher than levoglucosan (95.3 ng/kg, see Fig. 2), suggesting that boreal forest fires

402 associated with conifer trees followed by short- and long-range atmospheric transport
403 are more important in recent decades in the Northern Hemisphere.

404 **3.3 Vanillic acid**

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

419 The higher concentrations and similarity of vanillic and dehydroabietic acids
420 in the Alaskan ice core after the 1990 suggests an enhanced emission of biomass
421 burning products of conifer trees and lignin in the boreal forests in Alaska, which
422 could be imprinted in the southern Alaska ice core. Interestingly, we found a
423 significant correlation (Fig. 3a) between dehydroabietic acid (except for 2005 A.D.)
424 and vanillic acid (τ= 0.60, $p<0.01$) after 1990s, whose period corresponds to the Great
425 Pacific Climate Shift (GPCS, 1977-2007 A.D.). Being consistent with the warmer sea

surface temperature in the eastern North Pacific Rim during the GPCS periods (Meehl et al., 2009), southern Alaska is influenced by the warmer temperature and dryness, which triggered more chance of forest fires in the boreal forests, causing more emissions of conifer and lignin tracers over the southern Alaskan atmosphere (Figs. 2 and 6). Interestingly, Kamchatka ice core also showed an increased concentration of these tracers after 1970s (Kawamura et al., 2012).

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

These results suggest that Alaskan glacier showed non-stationary multi-decadal variability of biomass burning tracers from tundra grasses and peat species. Notably, during the 1660s to 1820s, vanillic acid, dehydroabietic acid, and levoglucosan have higher spikes (Fig. 6a,b,c) at 4 to 9 points, which are common in other ice cores (Fig. 6a-d) in the NH. After these higher spikes, global (at least Tunu, Akademii Nauk and Aurora) depression of vanillic acid and p-HBA (1830s-1950) can be observed (e.g., Fig. 6a-d) in the NH, suggesting that similarity and variability of

these acids are temporally and spatially heterogeneous in the NH under the climate driven forces. Historical trends of biomass burning tracers from this and other ice core studies, together with backward trajectories (Figure 7a-f), suggest a common potential source region of North Asia and North America, which are characterized by fire activities of boreal tundra woodlands, boreal conifer forests and peat.

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

Moreover, the historical trend of vanillic acid from 1800-2000 in Greenland ice core (McConnell et al., 2007) is entirely different from that of this study. Besides, the historical trend of vanillic acid shows many higher sporadic peaks during the Little Ice Age (LIA) and extended LIA (ELIA), which is somewhat similar to concentration trends of 10-year bin averages of p-HBA and vanillic acid from Svalbard ice core (Grieman et al., 2018a). These similarities could be due to a similar source and source regions. In contrast, dissimilarity of historical records of these compounds before and after ELIA suggests that shifting of atmospheric circulation or different spatial pattern of biomass burning and/or that climate-driven effects are

475 deeply involved (Pokhrel et al., 2015). Hence these results further support a snap of
476 biomass burning periodic cycles of Alpine glacier in the North Pacific Rim

477 **3.4 Biomass burning tracers, temperature and climate: Atmospheric**
478 **consequences**

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

493 These pieces of evidence are further reflected by the Pacific Decadal
494 Oscillation (PDO), which is characterized by relatively high temperature from the
495 west to east coasts of the North Pacific Rim (Mantuna et al., 1997; MacDonald and
496 Case, 2005; Shen et al., 2006). The similar trend of levoglucosan with five points
497 running average of this PDO cycle, except for few points (e.g., 1750, 1834, 1870,
498 1913, 1934 and 1966) during the whole period of 1665 to 1995, represents ecological

499 changes and/or changes in climate-driven biomass burning activities. These years, that
500 is, 1750, 1834, 1870, 1913, 1934 and 1966 A.D., are influenced by micro and meso
501 scale rather than synoptic and global scale weather conditions and/or by long spikes
502 represented by single fire events or seasonal biomass burning activities (Figure 5a,b).
503 Hence, the positive/negative phase of PDO represents zonal and/or meridional flows
504 and elevated/depressed transport of levoglucosan to the eastern North Pacific Rim.

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

524 wind in the Alaskan regions may be associated with PDO and El Nino Southern
525 Oscillation (ENSO) in summer (MacDonald and Case, 2005; Shen et al., 2006).

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

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

The higher spikes of levoglucosan are similar to those of dehydroabietic and vanillic acids from 1660s to 1970s. The positive/negative phases of both PDO (MacDonald and Case, 2005; Trouet et al., 2009) cover all higher/lower spikes of levoglucosan. The corresponding phase (positive/negative) of PDO varies from year to several years and exhibits a tendency to cover historical intervals of these compounds lasting several decades from 1660s to 1970s. The NAO's (wNAO) phase are remain same for several years than PDO as shown in Figure (Figure 5b). The periodicity of NAO phase (positive/negative) does not represent the historical trends (higher spikes/depression) of levoglucosan, dehydroabietic and vanillic acids (Figure 5b, c). This NAO represents atmospheric circulation between subtropical High and polar Low (Trouet et al., 2009). In fact, NAO significantly dominates the North Atlantic (e.g., North America) and European winter climate variabilities rather than those of North Asia (i.e., Eurasia/Siberia), which is spontaneously inappropriate in this study.

4. Summary and Conclusions

This study has been conducted to better understand temporal trends of the forest fire signals depend on the source region and proximity to the source and types of vegetation in the source regions of southern Alaska since the 1660s A.D. Ice core records of dehydroabietic acid, vanillic acid and levoglucosan showed predominant multidecadal trends, suggesting the variations of fire regimes and the proximity to the source, and changes in atmospheric circulation, land-use and/or ecological pattern in the mid to high latitudes (≥ 30° N) at least before and after the 1830s and after the Great Pacific Climate Shift (GPCS). Levoglucosan showed sporadic peaks during the 1660s-1830s, and single spikes in the 1898, 1913, 1966, and 2005 A.D. These spikes

571 indicate a significant contribution of biomass and/or biofuel burning attributing to
572 their source-specific emission and atmospheric stability in Alaskan regions.

573 Dehydroabietic and vanillic acids showed similar historical trends with
574 levoglucosan before the 1830s, suggesting that hard wood and conifer trees (e.g., resin
575 and lignin boreal conifer trees, deciduous trees and other higher plants) and perennial
576 grasses (C_3 and C_4 plants) were simultaneously important as burning sources. The
577 gradually increasing concentration trends of dehydroabietic and vanillic acids after the
578 1980s onward show a strong correlation (τ= 0.60, $p< 0.01$; after the GPCS; 1976),
579 suggesting significant changes in either burning patterns (i.e., new land-use pattern or
580 new ecological pattern) or atmospheric circulation over Alaska by the climate driven
581 forces with exhibiting similar signals of biomass burning tracers compared to
582 insignificant correlation of levoglucosan with these compounds.

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

595 The straight forward historical trends of these three compounds were
596 significant before the 1830s, which differ from the Kamchatka ice core record,
597 suggesting that there are some differences between the western and eastern North
598 Pacific Rim for the emission, frequency, and deposition. The concentrations of these
599 three compounds from Aurora Peak are higher than those from other ice core studies
600 in the NH (e.g., Kamchatka, Svalbard, Tunu, and Akademii Nauk). In contrast, there
601 are similarities of depressed concentration trend of Aurora with other ice core studies
602 at least for one hundred years (e.g., 1890-1980s: Akademii Nauk, 1820-1960: Tunu
603 Greenland), suggesting that sources of biomass burning tracers are further confined
604 within the same regions, traveling from very long distances and are well captured
605 within the snow particles. If it is true, these compounds might be involved as cloud
606 condensation nuclei from the surface to 15.2 km, (i.e., cumulonimbus cloud),
607 transporting thousands kilometers to Aurora. It bounds positive feedback for the
608 climate change and/or climate variability in the North Pacific Rim.

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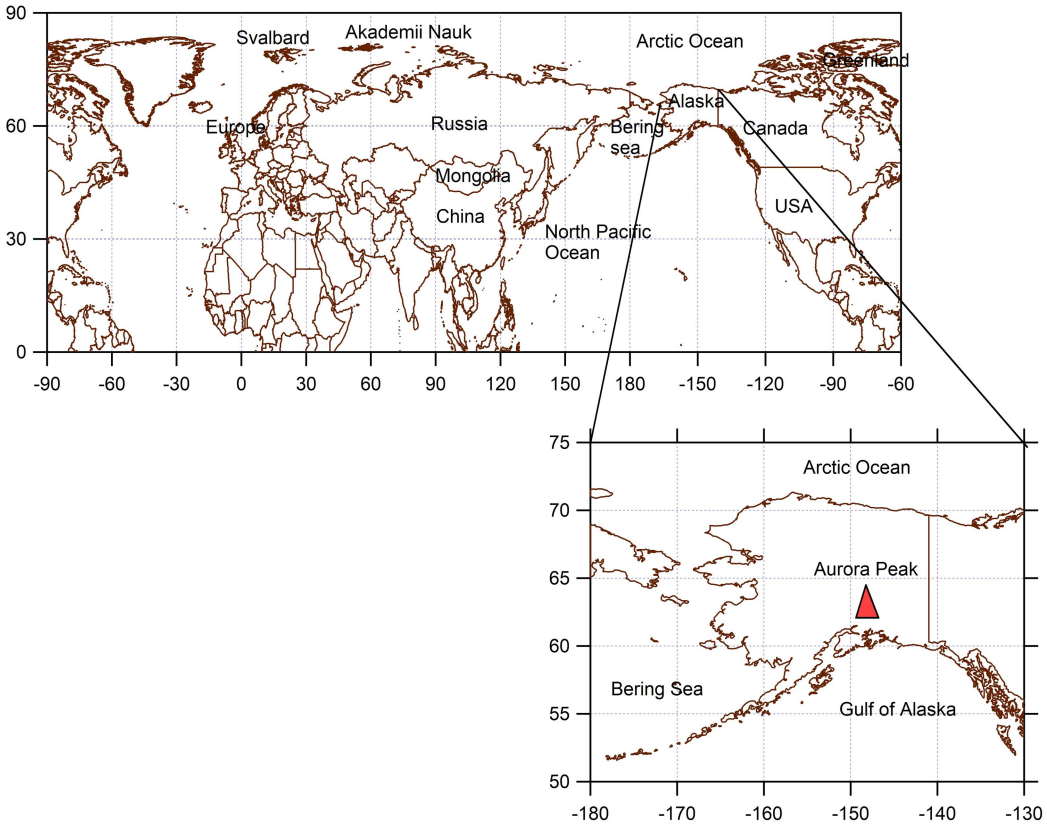
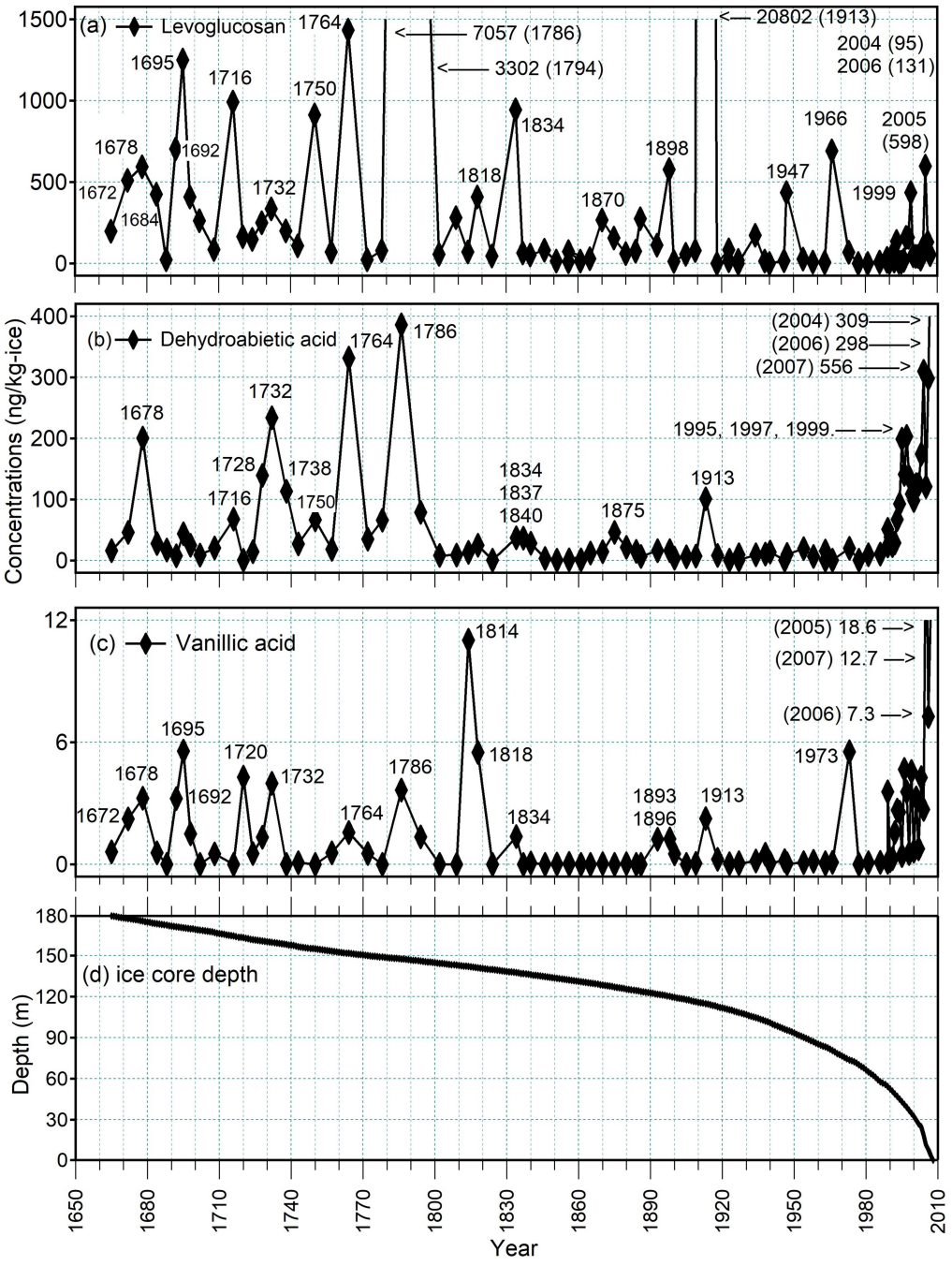


861

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



864

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

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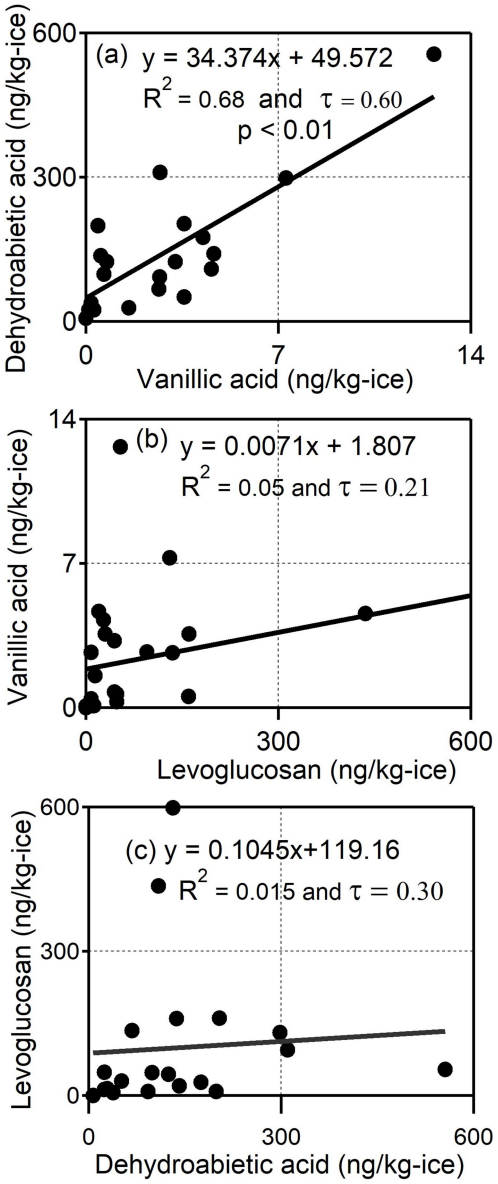
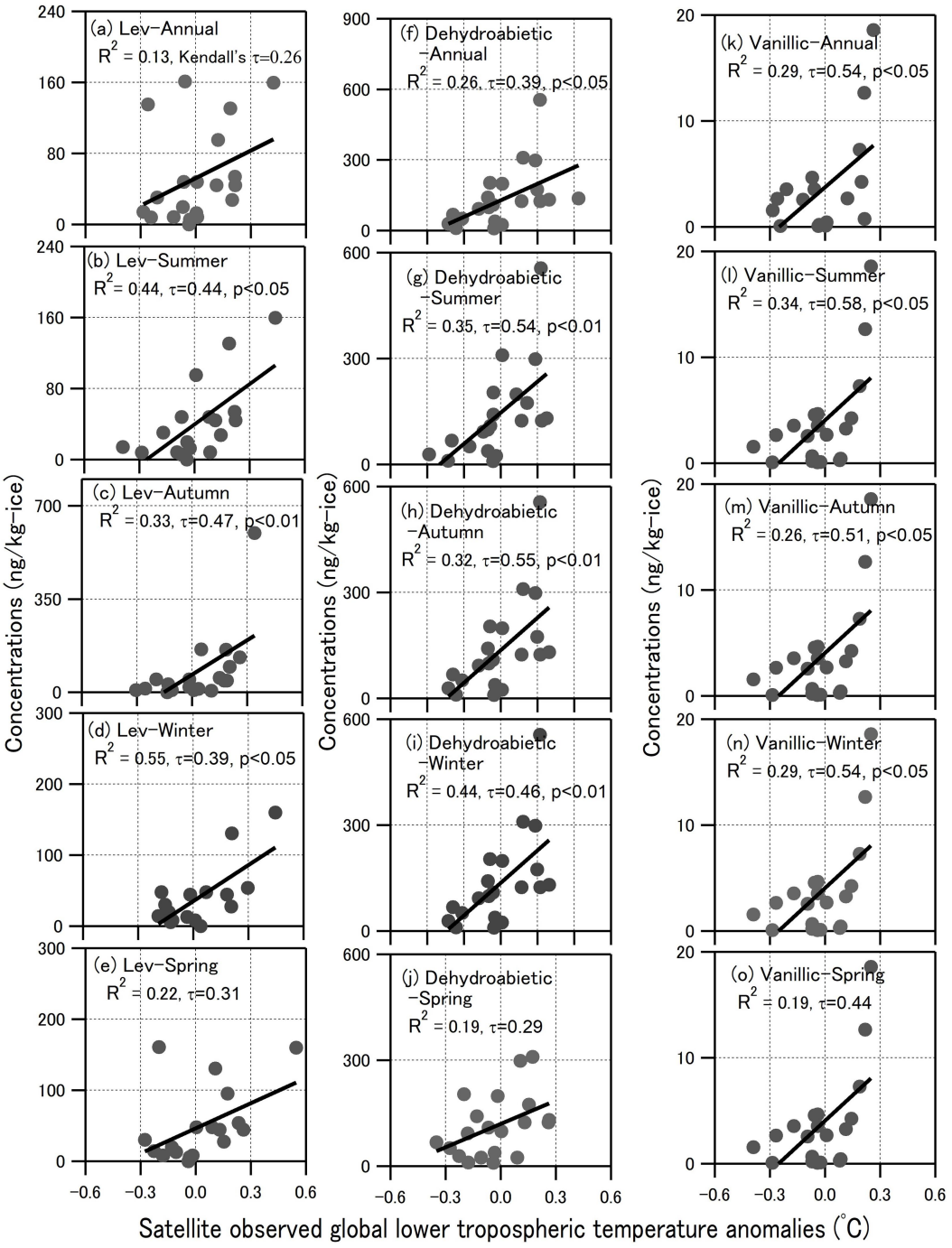


869

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

875



876

877 **Figure 4.** Correlation (Pearson: R^2 and Kendall: τ) plots between satellite-observed
878 global lower tropospheric temperature anomalies (i.e., microwave sounding unit
879 temperature anomalies (°C) of annual and seasonal records) and annual concentrations
880 of (a-e) levoglucosan, (f-j) dehydroabietic acid, and (k-o) vanillic acid after the Great
881 Pacific Climate Shift in the Northern Hemisphere.

882

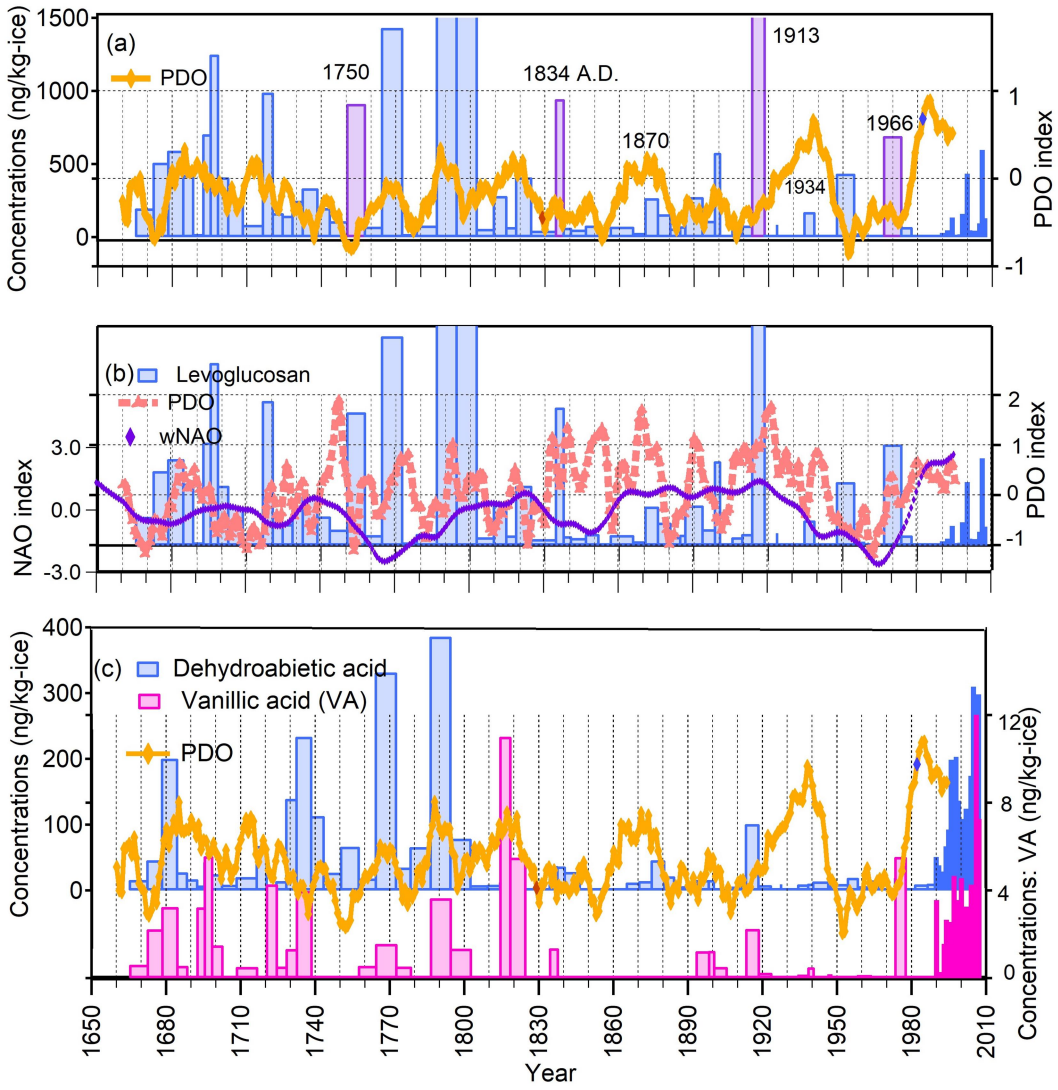
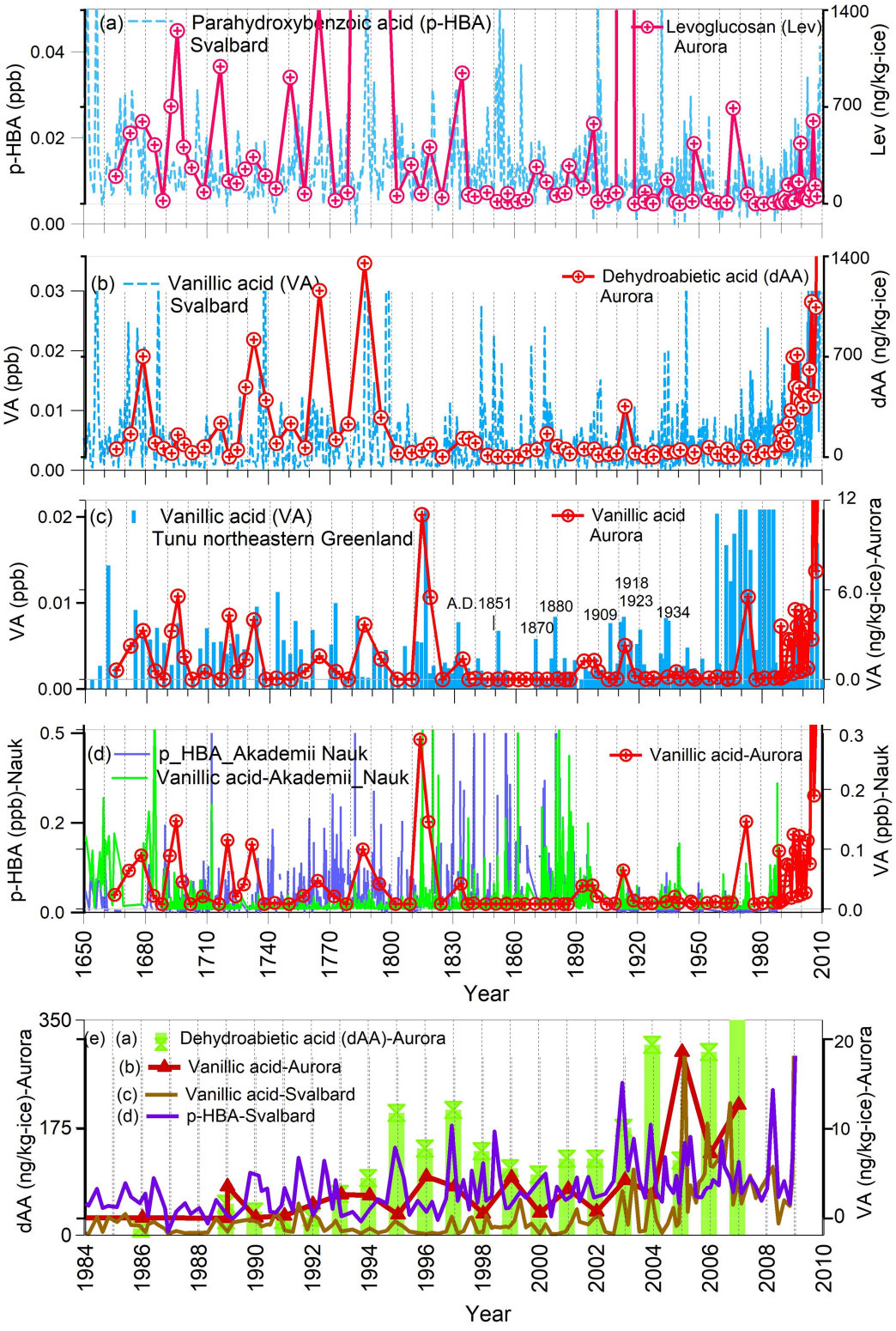


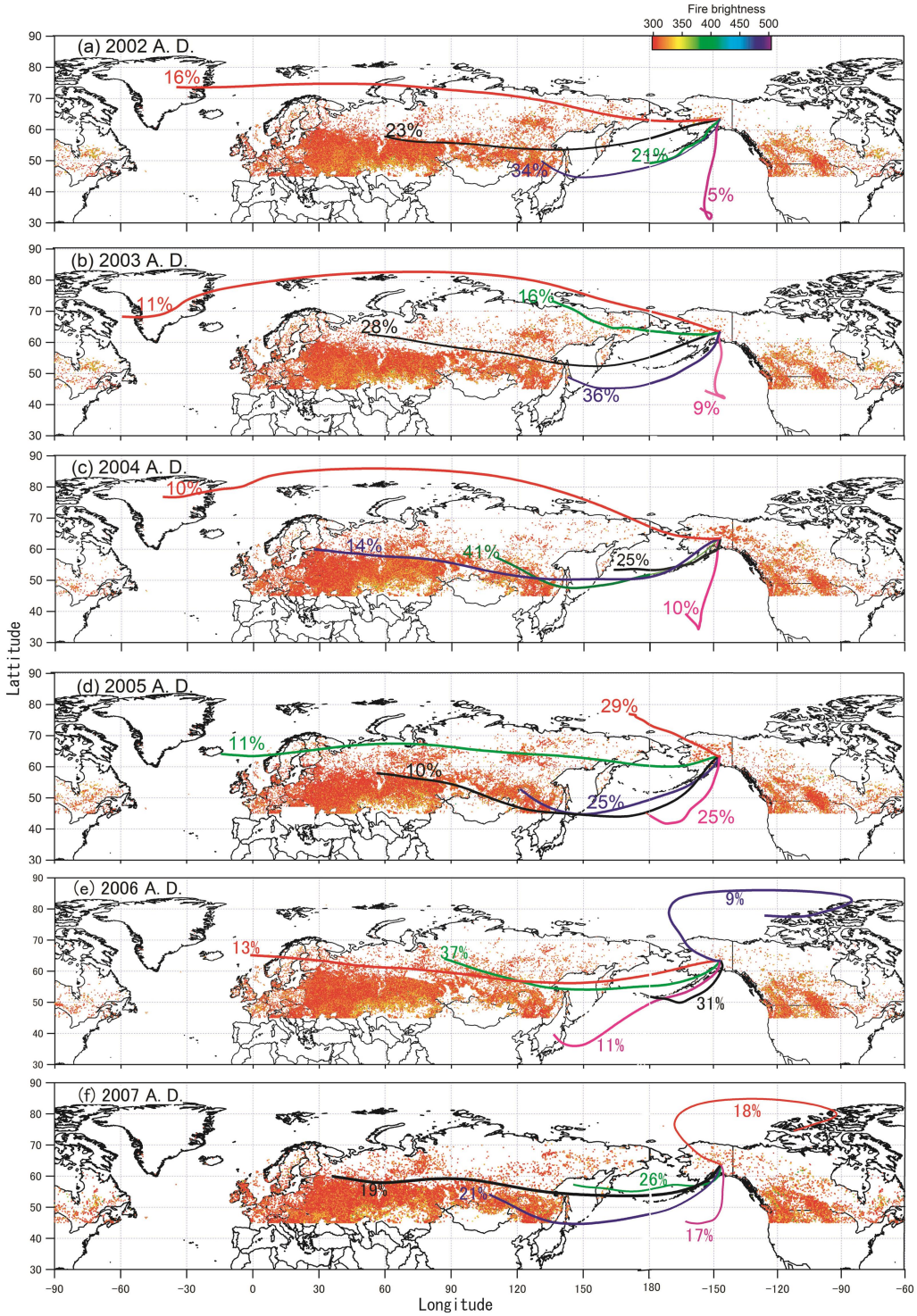
Figure 5. Historical trends in the concentrations of (a) levoglucosan (Aurora Peak) and Pacific Decadal Oscillation (5 year mean PDO) index (Shen et al., 2006), (b) levoglucosan (Aurora Peak), PDO-5 year mean index (MacDonal and Case, 2005) and Multi-decadal winter North Atlantic index (wNAO) (Trouet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



891

892 **Figure 6**. Historical trends of (a) p-hydrobenzoic acid (p-HBA) of Svalbard, (b) vanillic acid
893 (VA) of Svalbard, (c) VA of Tunu Greenland, (d) p-HBA and VA of Akademii Nauk, with
894 levoglucosan (Lev), dehydroabietic acid (dAA) and VA of Aurora Peak, respectively, and (e)

historical trends of dAA and VA of Aurora and VA and p-HBA of Svalbard after the Great Pacific Climate Shift (1977-2007 A.D.).



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