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Ice core records of monoterpene- and isoprene-SOA tracers from Aurora Peak in Alaska since 1660s: Implication for climate change variability in the North Pacific Rim

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Abstract

Monoterpene and isoprene secondary organic aerosol (SOA) tracers are reported for the first time in an Alaskan ice core to better understand the biological source strength before and after the industrial revolution in the Northern Hemisphere. We found significantly high concentrations of monoterpene- and isoprene-SOA tracers (e.g., pinic, pinonic, and 2-methylglyceric acids, 2-methylthreitol and 2-methylerythritol) in the ice core, which show historical trends with good correlation to each other since 1660s. They show positive correlations with sugar compounds (e.g., mannitol, fructose, glucose, inositol and sucrose), and anti-correlations with α-dicarbonyls (glyoxal and methylglyoxal) and fatty acids (e.g., $C_{18:1}$) in the same ice core. These results suggest similar sources and transport pathways for monoterpene- and isoprene-SOA tracers. In addition, we found that concentrations of C_5-alkene triols (e.g., 3-methyl-2,3,4-trihydroxy-1-butene, *cis*-2-methyl 1,3,4-trihydroxy-1-butene and *trans*-2-methyl-1,3,4-trihydroxy-1-butene) in the ice core have increased after the Great Pacific Climate Shift (late 1970s). They show positive correlations with α-dicarbonyls and fatty acids (e.g., $C_{18:1}$) in the ice core, suggesting that enhanced oceanic emissions of biogenic organic compounds through the marine boundary layer are recorded in the ice core from Alaska. Photochemical oxidation process for these monoterpene- and isoprene-/sesquiterpene-SOA tracers are suggested to be linked with the periodicity of multi-decadal climate oscillations and retreat of sea ice in the Northern Hemisphere.

Keywords: Monoterpenes, isoprene, SOA tracers, ice core, Alaska, multi-decadal climate oscillation, climate change

1. Introduction

Organic aerosols (OA) are an important fraction of atmospheric fine particles. They can alter the earch radiation budget directly by scattering sunlight, and indirectly by acting as cloud condensation nuclei (CCN) and ice nuclei (IN) (*Aalto et al., 2001; Kanakidou et al., 2005*). OA are derived from anthropogenic and biogenic sources via primary emissions and secondary photochemical oxidaiton of various precursors (*Claeys et al., 2004*; *Guenther et al., 2006; Kunwar and Kawamura 2014a, b)*. The former can be classified as primary organic aerosols (POA) whereas the latter as secondary organic aerosols (SOA). POA are emitted from plant debris, fungal spore, fossil fuel combustion, biomass burning, and soil particles (*Guenther et al., 2006; Fu et al., 2014*) whereas SOA are photochemically produced by homogeneous (*Claeys et al., 2004*) and heterogeneous (*Limbeck et al., 2003*) oxidations of biogenic volatile organic compounds (BVOCs) and anthropogenic VOCs.

Globally, annual emissions of BVOCs are estimated to be 1150 TgC/yr, where isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) consist 44%, and 11%, respectively. In contrast, emissions of anthropogenic VOCs (110 TgC/yr) are one order of magnitude smaller than those of BVOC; contribution of aromatic hydrocarbon is estimated to be only 13% of total anthropogenic VOCs (*Guenther et al. 1995, references therein*). Particularly, terrestrial and oceanic phytoplankton's isoprene is the largest source of VOCs, contributing ~50% of total global emission of 309–706 TgC/yr (*Acosta Navarro et al., 2014, references therein*). In contrast, α-/β-pinenes can contribute 35% of total global emissions of BVOCs (*Griffin et al., 1999*). These BVOCs could contribute significantly to the formation of SOA in the troposphere.

Isoprene- and monoterpene-oxidation products have been studied using field- (*Claeys et al., 2004; Fu et al., 2011)* and laboratory-based measurements (*Claeys et al., 2007; Hallquist et al., 2009; Surratt et al., 2010; Noziere et al., 2015)*. Being different from the previous assumption made by Limbeck et al. (2003), Claeys et al. (2004) first reported the

presence of 2-methyltetrols in the Amazonian aerosols as oxidation products of isoprene. Based upon the laboratory work, the formation of SOA from isoprene is further confirmed (*Surratt et al., 2010)*. Laboratory experiments showed that the oxidation products of isoprene (e.g., C_5-alkene triols and 2-methyltetrols) are enhanaced in the presence of NO_x, SO_2 and/or H_2SO_4 (*Surratt et al., 2006, 2010*). Moreover, in-cloud aqueous phase oxidation of isoprene is suggested to significantly contribute to the SOA formation (*Carlton et al., 2009; Volkamer et al., 2009; Hallquist et al., 2009*). Thus, these studies (i.e. field and laboratory measurement) provide insight on the sources, spatial and temporal distributions and molecular evolution of SOA.

McNeill et al. (2012) reported that organic compounds in snow/glaciers and/or in ice particles could be biological in origin and deposited from the atmosphere. Isoprene- and monoterpene-oxidation products are rarely studied in ice and snow, although biomass burning products and photooxidation products (i.e., dicarboxylic acids) of various organic precursors have been reported (*Kawamura et al., 2001; 2012a,b*). However, studies of monoterpene- and isoprene-SOA in snow and glacier ice remain poorly explored.

Here, we studied monoterpene- and isoprene-SOA tracers in an ice core from Alaska. Our objectives are to obtain the temporal profiles of monoterpene- and isoprene-SOA tracers that are derived from atmospheric photooxidation of isoprene and α/β-pinenes to better understand the historical changes in biological source strength of BVOCs. In this study, we report for the first time monoterpene- and isoprene-SOA tracers from mountain glaciers in Alaska to better understand both POA and SOA cycles in the North Pacific Rim.

2. Samples and Analytical Procedures

2.1. Site description

We collected a ~180 m deep ice core on the saddle of Aurora Peak in 2008 AD, which is located in the southeast of Fairbanks (63.52°N; 146.54°W, elevation: 2,825 m) (Figure 1).

The ice core sample was cut into ~50 cm-long pieces and directly transported to the laboratory of the Institute of Low Temperature Science (ILTS), Sapporo, Japan and stored in a dark cold room at -20ºC until analysis. The ice core ages were determined by annual counting of hydrogen isotopes (δD) and Na^+ seasonal cycles and the age control was provided by reference horizons of tritium peaks in 1963 and 1964 (*Tsushima et al., 2015*). The bottom of the sample was estimated to be 343 years old, i.e., 1665 AD (*Tsushima et al., 2015*). 10-day air mass backward trajectory based on Lagrangian tracking method for 1992 – 2002 has been already reported for Alaskan regions in the troposphere (>300 hPa) (*Yasunari and Yamazaki, 2009*).

2.2. Chemical analysis

Total numbers of ice core sections (50 cm long) were 147, which means that sampling frequency is ~40% of the 180 m deep ice core. This sampling frequency is much better than that (8%) of the previous ice core studies in Greenland (Kawamura et al., 2001). Roughly one quarter of each section was used after removing the surface 5-10 mm of the ice section. These ice core samples (ca. 150 mL) were first molten and then transferred to a pear shape flask (300 ml) and concentrated to almost dryness using a rotary evaporator under a vacuum. The total dissolved and particulate organic matters were extracted with a mixture of CH_2Cl_2/CH_3OH (2:1) using ultrasonic bath. The extracts were transferred to a 1.5 mL glass vial, dried under nitrogen stream and then derivatized with 99% N, O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS) and pyridine at 70 °C for three hours (*Fu et al., 2010a, b; Kawamura et al., 2012b; Zhu et al., 2015)*.

The derivatized fractions were diluted with n-hexane containing an internal standard (*n*-C_{13} alkane) prior to the analysis with a gas chromatograph/mass spectrometer (GC/MS) installed with a capillary column (HP-5MS, 30 m × 0.32 mm I.D. × 0.25 μm film thickness) and split/splitless injector (*Kawamura et al., 2012b*). Monoterpene- and isoprene-SOA tracers (Table 1) were determined using GC/MS method which has been reported elsewhere (*Fu et al.,*

117 *2014*). Triplicate analysis of real ice core sample was also conducted. Analytical errors were
118 less than 8%. Laboratory blank using pure water (150 ml), i.e. , Milli-Q water, showed blank
119 levels of less than 3% of real ice core samples. All the data reported here are corrected for the
120 laboratory blank. We believe that the preservation conditions of organic compounds in the ice
121 core is fairly good and thus post-depositional microbial changes in the signals are not
122 important because no ice lense was found in the ice core studied. However, we cannot exclude
123 the posssibility that some oxidants deposited in snow may react with organic species, which
124 may decompose and/or produce some organics.
125
126 **3. Results and Discussion**
127 *3.1. Historical changes of monoterpene-SOA tracers*
128 Table 1 presents ice core concentrations of monoterpene- and isoprene-SOA tracers
129 since 1660s. Pinic and pinonic acids are detected as α/β−pinene oxidation products. These
130 acids are observed in smog chamber experiments (*Glasius et al., 2000*), and are produced from
131 photooxidation of α/β−pinene in the presence of O_3 and OH radicals (*Hoffman et al., 1997*).
132 Pinic acid showed sporadic peaks in 1750 (concentration, 427 ng/L), 1786 (529), 1870 (406),
133 1875 (484), 1875, 1880 (3001), 1913 (630), 1973 (853), 1993 (352), 1998 (295) and 2005
134 (430) compared to its average concentration (157±148 ng/L). Similar spikes were detected for
135 pinonic acid, except for 1980s and 1990s (Figure 2a and b). The periods for the peaks can be
136 considered as significant monoterpene oxidation periods corresponding to the formation of
137 SOA in the North Pacific region.
138 Interestingly, average concentration of pinic acid (157 ng/L) is more than double of that
139 of pinonic acid (70.6 ng/L), which contradicts the trend reported for aerosol studies from Mt.
140 Tai, East China (*Fu et al., 2010a*), tropical India (*Fu et al., 2010b),* central Greece (*Kavouras*
141 *et al., 1999*), Sierra Nevada Mountains of California (*Cahill et al., 2006*) and North Carolina

142 (*Bhat et al., 2007*). It should be noted that vapor pressure of pinonic acid is twice higher than
143 that of pinic acid (*Fu et al., 2010b*). Coniferous forest is common in southern Alaska, being
144 similar to Research Triangle Park, USA and Germany (e.g., *Kleindienst et al., 2007; Plewka et*
145 *al., 2006*). A good correlation between pinonic and pinic acids (R = 0.93) in the ice core
146 indicates a similar sources and formation pathways and/or similar atmospheric fate in southern
147 Alaska for 1660s-1980s (Figure 4a). Interestingly, these compounds show a decrease during
148 the 1800-1850s and after the 1920s (except for 1973) with sporadic peaks during the 1990s,
149 suggesting that source and/or source region could be shifted to this sampling site.
150 We found significant levels of 3-hydroxyglutaric acid (3-HGA), whose historical
151 trends are completely different (Figure 2c) with pinic and pinonic acids. Smog chamber
152 experiment shows that 3-HGA is an oxidation product of α-pinene under UV irradiation in the
153 presence of NO_x (*Claeys et al., 2007*). Average concentration of 3-HGA (22.4±41 ng/L) is
154 several times lower than pinic and pinonic acids (Table1). It should be noted that we didn't
155 detect any β-caryophyllinic acid and related compounds. For instance, many aerosol studies
156 showed higher concentrations of β-caryophyllinic acid in late winter (*e.g., Fu et al., 2010b)*.
157 Correlations (R) of 3-HGA with pinic and pinonic acids are 0.46 and 0.46, respectively. These
158 results suggest that 3-HGA involves other processes than pinic and pinonic acids over the
159 southern Alaska.
160 *3.2. Historical changes of isoprene-SOA tracers*
161 We detected six isoprene-SOA tracers (Table 1 and Figure 3). Isoprene is readily
162 oxidized in the atmosphere by OH, O_3, NO_x, SO_2 and H_2SO_4 (*Carlton et al, 2009; Surratt et al.,*
163 *2010*). There are many key oxidation products of isoprene via methacrolein (a key as an
164 intermediate in SOA fromation) in ambient aereosl has been found (*Noziere et al., 2015;*
165 *Hallquist et al., 2009 and references therein*). Some isoprene oxidation products have less
166 vapor pressures and thus stay in particle phase, leading to the formation of SOA (*Hoffmann et*

167 *al., 1997*). 2-Methylglyceric acid can be formed by the oxidation of methacrolein and
168 methacrylic acid from two major gas-phase oxidation products of isoprene (*Surrat et al., 2007;*
169 *Hu et al., 2008*), which can be altered and/or associated with land sea breeze atmospheric
170 circulation (*Claeys et al., 2007; Fu et al., 2010b and references therein*).

171 2-Methylglyceric acid showed higher concentrations in 1750 (74.8 ng/L), 1786 (175),
172 1870 (83.4), 1875 (93.1), 1880 (73.1), 1913 (166), 1973 (144), 1977 (67.3), 1993 (230), 1998
173 (65.9), 1999 (71.8) and 2005 (282), whose concentrations are much higher than its average
174 (35.6±48 ng/L). These periods are consistent with those of 2-methylthreitol (ave. 349±383
175 ng/L) and 2-methylerythritol (692±709 ng/L) as shown in Figure 3a, b and c. Interestingly,
176 historical trends are similar to those of pinic and pinonic acids and isoprene-SOA tracers
177 (Figure 2a, b, and 3a, b, c) before 1990s. Correlation coefficients (R) of pinonic and pinic acids
178 with 2-methylglyceric acid are 0.71 and 0.83, respectively whereas that of 2-methylglyceric
179 acid and 3-HGA is 0.67 (Figure 4b, c and d). Correlation coefficients of pinonic and pinic
180 acids with 2-methylthreitol are 0.73 and 0.77, respectively (Figure 5a, b). In addition, those of
181 pinonic and pinic acids with 2-methylerythritol are 0.71 and 0.75 (Figure 5c, d) and correlation
182 coefficients (R) of 2-methylglyceric with 2-methylthreitol and 2-methylerythritol are 0.82 and
183 0.67, respectively (not shown in figure).

184 The source strength of these SOA tracers is somewhat higher before the industrial
185 revolution than in recent years in the southern Alaskan ice core (Figure 3a-c). It should be
186 noted that 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) was reported during smog
187 chamber experiments of α-pinene with UV irradiation in the presence of NO_x (*Claeys et al.,*
188 *2007*). But we didn't detect MBTCA from the 1660's till 2008, suggesting that anthropogenic
189 contributions are insignificant for the last 3 centuries. In contrast, C_5-alkene triols showed
190 similar historical trends each other (Figure 3d,e and f), with somewhat different trends to other
191 SOA tracers (e.g., Figure 3a, b and c). Particularly, 3-methyl-2,3,4-trihydroxy-1-butene

192 showed higher concentrations in 1786 (13.8 ng/L), 1947 (12.0), 1973 (30.2), 1989 (41.1), 1993
193 (93.5), 1998 (23.0), 1999 (31.7), 2004 (35.1), 2005 (140.7) and 2006 (46.4) compared to its
194 average concentration (6.99±17 ng/L-ice). These periods are also consistent with those for the
195 reaction products of *cis* and *trans* hydroxy alkenes (e.g., Figure 3d, e and f). Correlation
196 coefficients (R) of 3-methyl-2,3,4-trihydroxy-1-butene with pinonic and pinic acids in the ice
197 core are 0.51 and 0.63, whereas those of cis 2-methy-l 1,3,4-trihydroxy-1butene with pinonic
198 and pinic acids are 0.49 and 0.52, respectively.
199 Moreover, correlations of 2-methylglyceric acid with 3-methyl-2,3,4-trihydroxy-1-
200 butene, trans-2-methyl-1,3,4-trihydroxy-1-butene and cis 2-methyl 1,3,4-trihydroxy-1-butene
201 are 0.83, 0.77 and 0.75, respectively. Correlations of 2-methylthreitol to 2-methylerythritol, 3-
202 methyl-2,3,4-trihydroxy-1-butene, cis 2-methyl 1,3,4-trihydroxy-1-butene and trans-2-methyl-
203 1,3,4-trihydroxy-1-butene are positive (R=0.87, 0.65, 0.54 and 0.57, respectively). Hence, we
204 consider that atmospheric fate could be strongly involved with local or regional meteorological
205 conditions with an insignificant influence of anthropogenic activities. The most prevalent SOA
206 precursors on a global scale are terpenoids emitted from vegetations (*Claeys et al., 2007;*
207 *Faiola et. al., 2014*). It should be noted that more than 100 organic compounds including many
208 numbers of SOA precursors are emitted from leaf litter and/or soil, although they are less
209 significant than direct emission from plant leaves (*Faiola et. al., 2014*). SOA formation in the
210 forest environment (i.e., from leaf litter and/or forest soil) is also important in spring to fall
211 (*Faiola et. al., 2014).* For instance, rate of particle formation was high during spring from soil
212 and leaf litter in a boreal forest of southern Finland (*Makela et al., 2000; Bigg et al., 2004*). In
213 addition, emissions of SOA precursors (i.e., terpenoids) are high during late spring and autumn
214 in boreal pine forest floor (e.g., *Aaltonen et al., 2011 and references therein*). These results
215 suggest the additional sources for higher spikes in an ice core.
216 *3.3. Responses of monoterpene- and isoprene-SOA tracers to tropospheric temperature*

We found that monoterpene- (Figure 2a-b) and isoprene-SOA tracers (Figure 3a-c) inversely correlate with marine biogenic tracers, i.e., even carbon numbered fatty acids (e.g., $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$) (*Pokhrel et al., 2015*). In contrast, those SOA tracers show a positive correlation with sugar compounds (e.g., mannitol, fructose, glucose, inositol and sucrose) from the same ice core, suggesting the continental sources (unpublished data, Pokhrel and Kawamura, 2015). Hence, emissions of isoprene and monoterpenes from vegetations could be controlled by biological activity of the ocean and continents in different years, which could be linked to histrorical variations of thermohaline circulation (*Boyce et al., 2010 and references therein*).

Reconstructed air temperatures from the Gulf of Alaska (GOA) using tree ring showed a sharp drop in June to September since 1800 to1875 except for 1830s (e.g., Wilson et al., 2007b), whose historical trend is similar to lower concentrations of monoterpene- and isoprene-SOA tracers (Figure 2a-b and Figure 3a-c). It should be noted that sampling sites for the tree ring data are located close to coastal range of the GOA and/or south of the Brooks Range at about 68 °N. This GOA temperature expresses a strong consistency with multi-decadal climate oscillation and short-term atmospheric activities (e.g., ENSO/El-Nino and/or Aleutian Low). Interestingly, reconstructed Northern Hemisphere annual temperature since 1671 based on high-latitude tree-ring data from North America (*Jacoby and D'Arrigo, 1989*) is also similar histrorical trend (except for few decades). In addition, tree-ring growth data and inferred temperature variability at the North American Arctic tree line (*D'Arrigo et al., 2009*) are also consistent with the trends of ice core SOA tracers.

Based on 10 day backward trajectory analyses for the years of 1992-2002, *Yasunari and Yamazaki* (2009) reported that Alaskan regions can receive significant air parcels from adjacent North Pacific Regions, East Asia, Eastern Russia, Siberia, the Okhotsk and Bering Seas, higher latitudes of Alaskan regions, the Gulf of Alaska, Japan, Canada, the Arctic Ocean

and Europe in the troposphere (>300 hPa). These areas are represented by extra tropical Northern Hemispheric temperature (ENHT). ENHT is the robust temperature trends for the Northern Hemisphere, which is calculated with more than 25 different sampling sites from tree ring proxy records of the world. ENHT shows the positive correlations (R) with the ambient temperatures in European Alps (0.67), western Siberia (0.61), Mongolia (0.70), Nepal (0.49), Northern Yukon (0.60), Wrangell Mountains (0.60), British Columbia (0.77), Idaho (0.41) and Northern Quebec (0.42) (e.g., *Wilson et al., 2007a*).

Lower concentrations of monoterpene- and isoprene-SOA tracers (Figures 2 and 3) during this period are further supported by historical trend of ENHT (Figure 3h). For instance, decreasing trends for all these SOA tracers showed positive correlations with decreasing historical trends of ENHT during 1800-1860. Particularly, correlation coefficients (R) of each 11 points running mean (11-RM) of pinonic, pinic and 3-HGA with 11-RM of ENHT are 0.84, 0.86 and 0.54, respectively. Similarly, correlation coefficients (R) of 11-RM of each isoprene-SOA tracers (e.g., Figure 3a - f) with 11-RM of ENHT are 0.84, 0.95, 0.94, 0.82, 0.89, and 0.67, respectively. It should be noted that NH temperature departure and reconstructed solar irradiance are well correlated with many climate periodicity and non-periodicity cycles in the NH, which are reported elsewhere (*Wang et al., 2012; Lean et al., 2005 and refererences therein*).

Aleutian Low (AL) can easily alter air parcel flow and heat exchange between the Arctic and mid-latitudinal region (*Wang et al., 2012*). *Mantua et al.* (1997) pointed out that the AL was significantly correlated with the Pacific Decadal Oscillation (PDO), which can be described as a long-lived El Niño-like pattern of Pacific climate variability. For instance, the warm phase of PDO corresponds to the strong AL, while the cold phase of PDO corresponds to the weak AL. The AL would have mixed continental and marine air mass, and more drive prevailing winds from the northwestern Pacific regions to northeastward in North America,

267 which can intensify the positive North Pacific Index (NPI) over American west (*Trouet and*
268 *Taylor, 2010*). It represents the region of 30°N-65°N, 160°E-140°W for decadal variations in
269 the atmospheric circulation (https://climatedataguide.ucar.edu). Moreover, on a decadal scale,
270 the AL has been consistently strong and drifted eastward since 1970s (*Wang et al, 2012*).
271 These monoterpene- and isoprene-SOA tracers (Figure 2a-b and Figure 3a-c,
272 respectively) showed decreased trends since 1920s, which are similar to the trend of NPI.
273 Historical trends of C_5-alkene triols (Figure 3d-f) showed anti-correlation with those of other
274 compounds. Particularly, large-scale atmospheric circulation (or relatively local) is associated
275 with the AL system in the Bering Sea (or Alaskan regions) (*Sasaki and Minobe, 2005*). If this
276 is the case, it is important to understand the historical variations of atmospheric circulation
277 over the Bering Sea, Gulf of Alaska and Alaskan regions. The climatic oscillations can
278 represent the atmospheric transport in the lower latitudes. The effect of climatic oscillations
279 can be observed using NPI (*Trouet and Taylor, 2010*). For instance, relations between 7-RM of
280 C_5-alkene triols, i.e., 3-methyl-2,3,4-trihydroxy-1-butene, cis 2-methyl 1,3,4-trihydroxy-1-
281 butene and trans-2-methyl-1,3,4-trihydroxy-1-butene (Figure 3d-f), anti-correlate with 7-RM
282 of NPI since 1899-2007 (R = 0.31, 0.32 and 0.29, respectively). These results suggest that
283 decadal variability (or atmospheric stability) may be involved with the alteration in the
284 concentrations of SOA tracers.
285 *Tsushima et al.* (2015) reported that concentrations of Na^+ in the same ice core
286 increased after the 1970s. This increase could be resulted from changes in the position and/or
287 strength of winter storms in the Gulf of Alaska, which is associated with the PDO shift in 1976.
288 We obtained higher concentrations of all the compounds around 1975 (Figures 2 and 3), being
289 similar to Na^+ cycle of same ice core, rapid change of sea ice concentrations (SIC) and
290 temporal wind pattern (TW) over the Bering Sea (*Sasaki and Minobe, 2005*). Moreover,
291 historical trends C_5-alkene triols (Figure 3d-f) are similar to changes of SIC and TW over the

292 Bering Sea for spring season after 1950s. It should be noted that SOA formation in forest
293 environment is important during spring and fall season compared to summer season (*Faiola et*
294 *al., 2014)*. *Makela et al.* (2000) and *Bigg et al.* (2004) reported that particle formation rate was
295 high during spring season in the boreal forest of southern Finland. SOA precursors and/or
296 terpenoids are also high during late spring and autumn in boreal pine forest floor (*Aaltonen et*
297 *al., 2011 and references therein*).

298 In contrast, all other compounds in the ice core (Figure 2a-c and 3a-c) exhibit similar
299 trends with wintertime SIC and TW over the Bering Sea during the same periods. These results
300 indicate that different pattern of wind circulations can alter the temporal trends of these
301 compounds in ice core, further suggesting that the first case is linked with local circulation
302 over the North Pacific Rim compared to regional wind circulation for the latter case. These
303 results may suggest that climatic variations could be recorded in the ice core profile of SOA
304 tracers. Similarly, we can explain another process for vaiable concentrations of SOA tracers
305 since 1660s. For instance, we found lower concentrations of SOA-tracers around 1650-1700s
306 and 1800-1850s, which are known as cooling period of Maunder and Dalton minima and a part
307 of Little Ice Age (Figure 3h, i), respectively (*Krivova, et al., 2010*), suggesting lower emission
308 of isoprene and monoterpenes during the cold periods. Our ice core records of SOA tracers can
309 be further supported by air-sea and oceanic heat fluxes of the northern Gulf of Alaska (*Janout*
310 *et al., 2013*). Net heat flux and/or heat flux anomalies in winter are significantly increased
311 during 1975-2010 (except around 1998) compared to 1950-1975 (*Janout et al., 2013*), which is
312 consistent with historical trends of C_5-alkene triols.

313 These considerations suggest that concentrations of SOA tracers are controlled by
314 temperature, pressure and wind field of the Gulf of Alaska and/or Northern North Pacific Rim.
315 These three parameters alter the atmospheric transport (e.g., the AL can alter the atmospheric
316 transport), which are correlated with ENHT and NPI elsewhere (NPI has negative correlation

317 with C_5-alkenes) (*Wilson et al., 2007a,b; Wang et al., 2012 and references therein*). We found
318 that C_5-alkene triols positively correlate with ENHT during the 1750s to 1980s. Particularly,
319 correlation coefficients (R) between 5 points running mean (5-RM) of C_5-alkene triols (Figure
320 3d, e and f) with ENHT are 0.73, 0.80 and 0.78 for individual species (3-methyl-2,3,4-
321 trihydroxy-1-butene, cis 2-methyl 1,3,4-trihydroxy-1-butene and trans-2-methyl-1,3,4-
322 trihydroxy-1-butene), respectively. It is likely that BVOC emissios could be associated with
323 type and density of vegetation in landscape, temperature and radiation, having a significant
324 impact on SOA formation (*Pokhrel, 2015*).

325 In addition, C_5-alkene triols have increasing trends of the concentrations since 1920s,
326 which is similar to sea surface temperature (SST) over the past century (*Boyce et al., 2010 and*
327 *references therein)*. Hence, these increasing trends of C_5-alkene triols (see Figure 3d-f) could
328 be involved with climatic and oceanographic variability. Particularly, an increased SST over
329 the past century since 1920s (except for few points) is similar to historical trends of SOA
330 tracers, suggesting that an enhanced ocean warming could cause a restructuring of marine
331 ecosystems and/or likely ocean circulation (*Boyce et al., 2010; and references therein*),
332 followed by intensified production of SOA in southern Alaska. In the same ways, we may
333 explain other historical trends since 1660s, which could be altered by complex mechanisms of
334 thermohaline circulation and productivity of marine biota, which are reported elsewere (*Boyce*
335 *et al., 2010; and references therein*).

336 Moreover, C_5-alkene triols have positive correlations with α-dicarbonyls (i.e., glyoxal
337 and methylglyoxal) and even-carbon numbered low molecular weight fatty acids (e.g., $C_{16:0}$
338 and $C_{18:0}$) including unsaturated fatty acids ($C_{18:1}$), which are originated from marine
339 phytoplankton (*Pokhrel et al., 2015)*. Increased historical trends of C_5-alkenes after 1920s are
340 somewhat similar to the reconstructed solar total irradiance (Figure 3i) (*Krivova et al., 2010;*
341 *Ball et al., 2012*). In addition, historical concentrations of C_5-alkene triols are

changed/increased significantly after the Great Pacific Climate Shift. In contrast, other compounds (Figure 2a-c and 3a-c) show negative correlation with α-dicarbonyls and fatty acids including oleic acid (e.g., $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$). But they have positive correlations with sugar compounds (e.g., mannitol, fructose, glucose, inositol and sucrose) from same ice core sample (unpublished data, Pokhrel and Kawamura, 2015). These results all suggest that an increased biogenic emission capacity and/or source could be changed, being recorded in a clear historical profile of dual sources; marine phytoplankton and terrestrial plants.

4. Summary and Conclusions

We report for the first time historical records of monoterpene- and isoprene-derived secondary organic aerosols (SOA) tracers in glacier ice core from Aurora Peak in Alaska since 1660s, which could be derived from dual biogenic sources (marine and continental). Positive correlations of monoterpene tracers with 2-methylglyceric acid and 2-methyltetrols are found to be strong, indicating the shared source regions and transport. In contrast, correlations of monoterpene tracers with C_5-alkene triols are weak, suggesting the different source regions and transport pathways.

Ice core concentrations of monoterpene- and isoprene-SOA tracers showed lower levels during 1800-1860, which are similar to temperature trends of the Gulf of Alaska and showed a positive correlation with extra-tropical Northern Hemisphere temperature (ENHT). In addition, C_5-alkene triols showed positive correlations with α-dicarbonyls, ENHT and fatty acids, and their historical trends are increased after the Great Pacific Climate Shift. In contrast, all other compounds (i.e., monoterpene-SOA tracters) have negative correlation with α-dicarbonyls and fatty acids including oleic acid ($C_{18:1}$). But they have positive correlations with sugar compounds (e.g., mannitol, fructose, glucose, inositol and sucrose) in the same ice core.

These results suggest that source could be changed significantly after the Great Pacific Climate Shift and exhibit a clear historical dual sources likely to be marine boundary layer. This study reveals that ice core records of SOA tracers and atmospheric oxidizing capability or emission of monoterpenes and isoprene are associated with multi-decadal climate oscillation periodicity in the North Pacific Rim, which are associated with the Northern Hemispheric temperature signals.

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565 Table 1. Concentrations of monoterpene and isoprene secondary organic tracers in ice core
566 samples from southeast Alaska in 1665 – 2008.

	Concentrations (ng/L)			
Name	Ave.	Min.	Max.	SD
α/β-Pinene-SOA tracers				
Pinic acid	157	BDL	853	148
Pinonic acid	70.6	BDL	300	68
3-HGA	22.4	BDL	234	41
Isoprene-SOA tracers				
2-methylglyceric acid	35.6	BDL	282	48
2-methylthreitol	349	BDL	1740	383
2-methylerythritol	692	BDL	3509	709
3-methyl-2,3,4-trihydroxy-1-butene	6.99	BDL	141	17
cis-2-methyl-1,3,4-trihydroxy-1-butene	23.1	BDL	384	52
trans-2-methyl-1,3,4-trihydroxy-1-butene	36.5	BDL	786	98

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

568

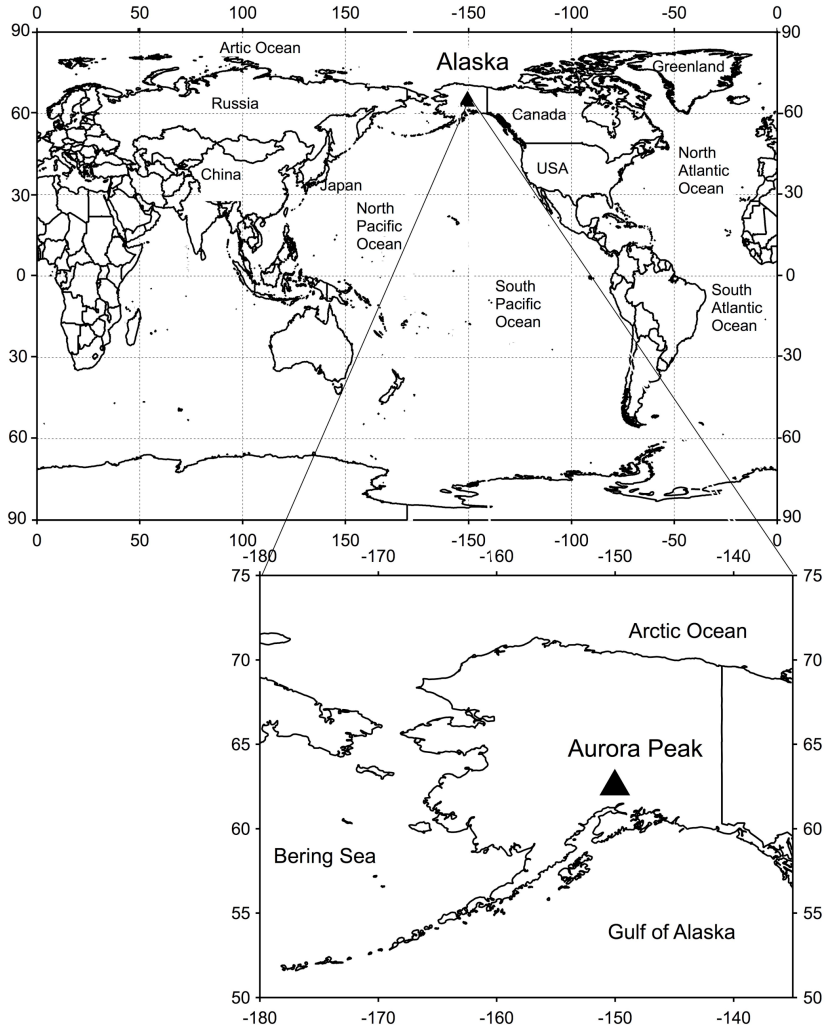
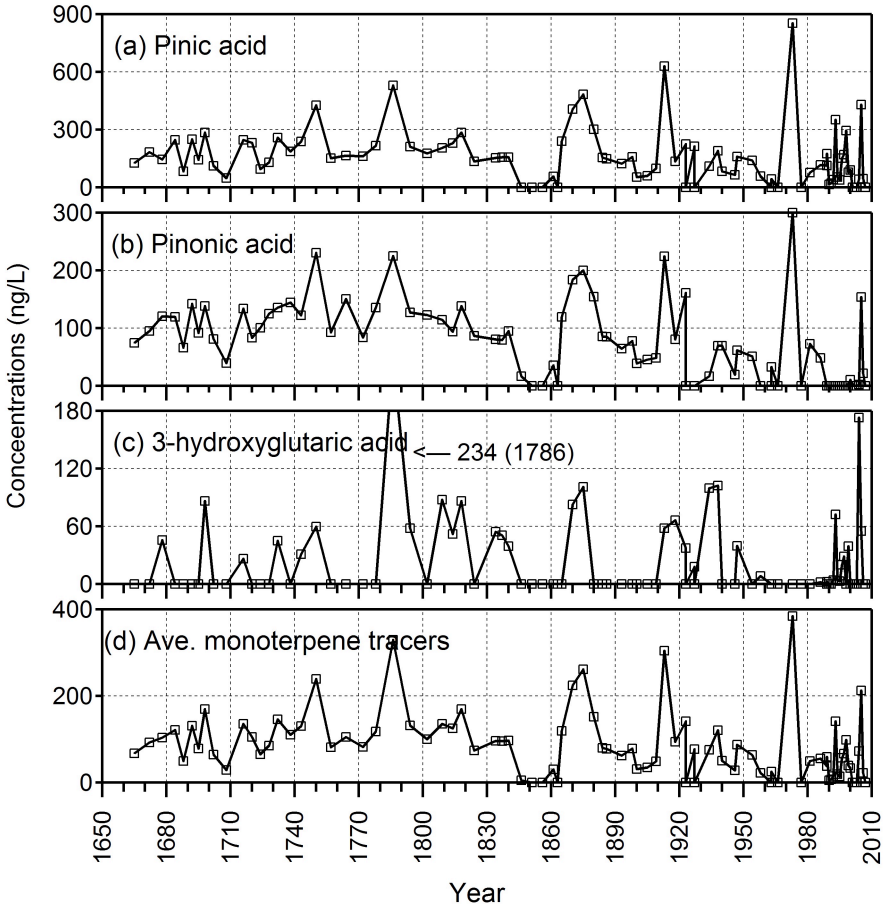


Figure 1. Map showing the geographical location of Aurora Peak of Alaska, from which 180-meter long ice core sample was drilled in 2008 (*Pokhrel et al., 2014*).

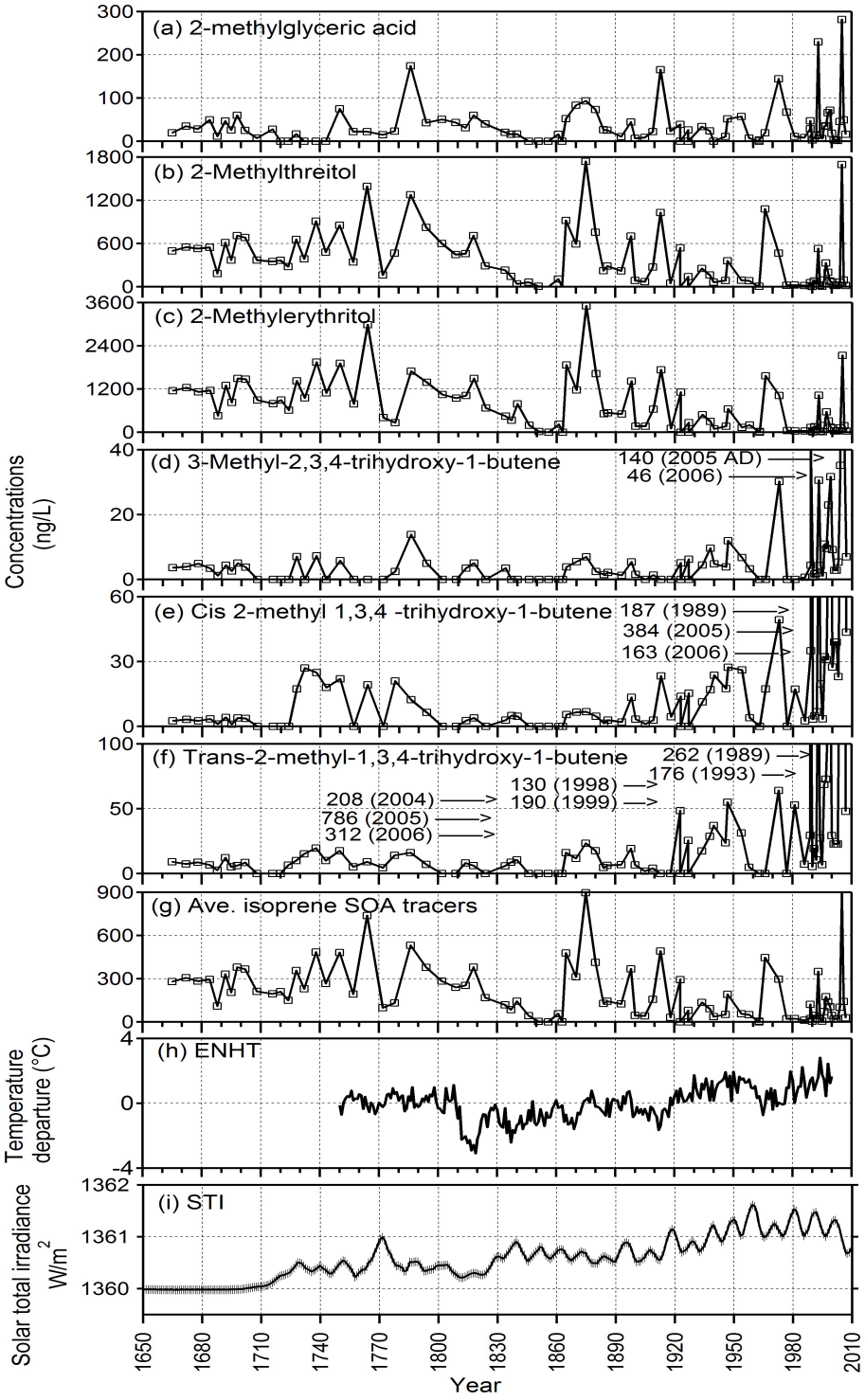


581

582 Figure 2. Concentration changes of (a) pinic acid, (b) pinonic acid (c) 3-hydroxyglutaric acid
583 (3-HGA) and (d) average concentration changes of monoterpene tracers (a)-(c) in the Alaska
584 ice core records collected from Aurora peak.

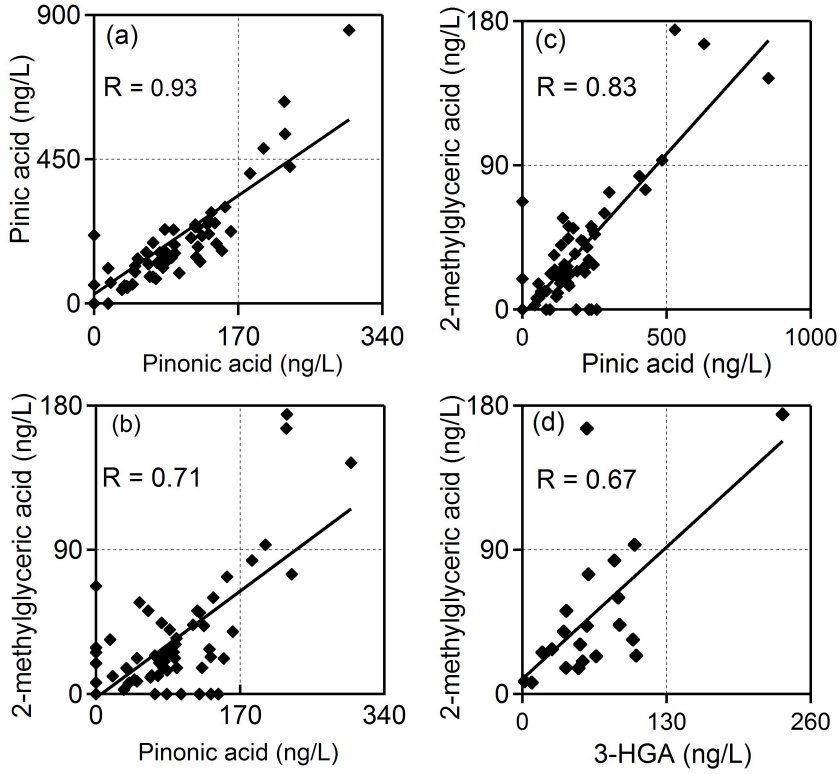
585

586



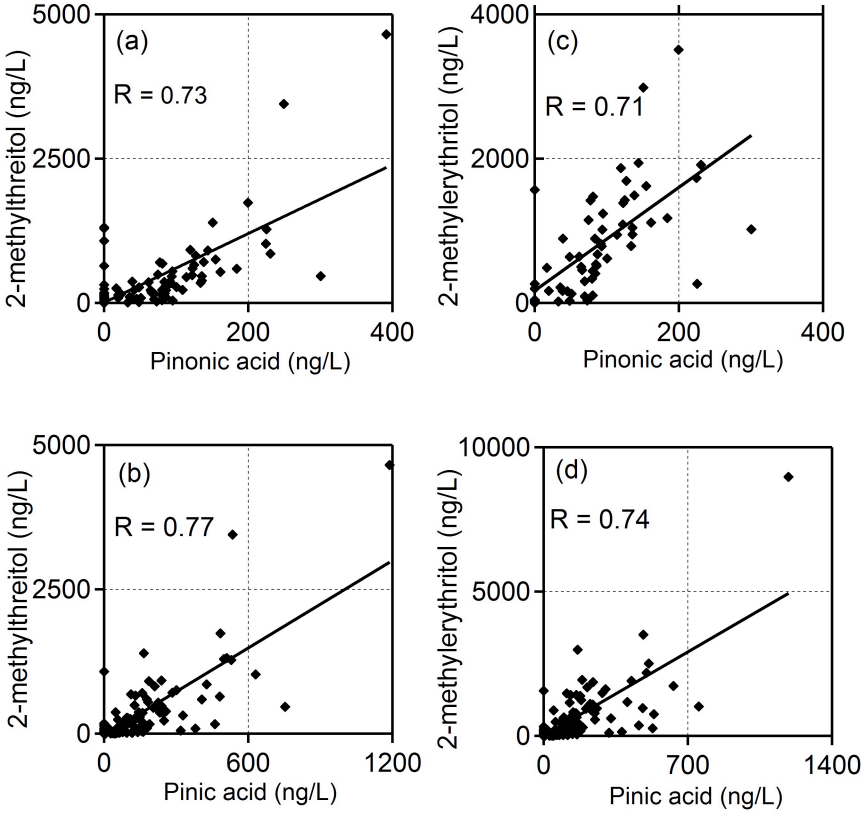
587

588 Figure 3. Concentration changes of (a) 2-methylglyceric (b) 2-methylthreitol (c) 2-methylerythritol (d) cis 2-
589 methyl 1,3,4-trihydroxy-1-butene (e) 3-methyl-2,3,4-trihydroxy-1-butene (f) trans-2-methyl-1,3,4-trihydroxy-1-
590 butene and (g) total annual average concentrations of all these isoprene SOA tracers (a – f) in the Alaska ice core
591 records collected from Aurora peak (h) extra tropical Northern Hemispheric temperature (ENHT) departure, e.g.,
592 Wilson et al. (2007a) and (i) 7 years running mean of reconstructed solar total irradiance (STI) from IPCC AR5
593 based on Krivova et al. (2010) and Ball et al. (2012).
594



595

596 Figure 4. Correlation between the concentrations of (a) pinonic and pinic (b) pinonic acid and
597 2-methylglyceric (e) pinic acid and 2-methylglyceric and (f) 2-methylglyceric and 3-
598 hydroxyglutaric acid (3-HGA) in the Alaska ice core records collected from saddle of Aurora
599 Peak.



600

601 Figure 5. Correlation between the concentrations of (a) pinonic and 2-methylthreitol (b) pinic
602 and 2-methylthreitol, (c) pinonic and 2-methylerythritol, and (d) pinic and 2-methylerythritol
603 in the Alaskan ice core records collected from saddle of Aurora Peak.

604

605 **Highlights**

606 1. Monoterpene-SOA tracers in south Alaskan ice core are associated with continental sources.

607 (80 with space)

608 2. Isoprene-SOA tracers in the ice core are derived from both continental and marine sources.

609 (75 with space)

610 3. Monoterpene- and isoprene-SOA tracers are linked with climate oscillations of Aleutian Low.

611 (80 with space)