

1           **Organic tracers of fine aerosol particles in central Alaska:**  
2                           **summertime composition and sources**

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11 **Abstract**

12 PM<sub>2.5</sub> aerosols were collected at Fairbanks (64.51°N and 147.51°W) in central  
13 Alaska during the summer of 2009 and analyzed for organic tracer compounds using gas  
14 chromatograph-mass spectrometer. The organic compounds were grouped into fourteen  
15 classes based on their functional groups and sources. Concentrations of total organics  
16 measured ranged from 113 to 1664 ng m<sup>-3</sup> (ave. 535 ng m<sup>-3</sup>). Anhydrosugars (ave. 186 ng m<sup>-3</sup>)  
17 and *n*-alkanoic acids (ave. 185 ng m<sup>-3</sup>) were two major classes among the 14 compound  
18 classes. The similar temporal trends and strong positive correlations among anhydrosugars  
19 and *n*-alkanoic acids demonstrated that biomass burning (BB) is the major source of organic  
20 aerosols (OAs) in central Alaska. The dominance of higher molecular weight *n*-alkanoic acids  
21 over lower molecular weight homologues and their carbon preference index (5.6-9.8)  
22 confirmed that they were mostly emitted from plant waxes during BB in central Alaska. The  
23 mass concentration ratios of levoglucosan to mannosan denoted that softwood is the main  
24 biomass burned. The rainfall event distinctly enhanced the levels of mannitol and arabitol due  
25 to the growth of fungi and active discharge of fungal spores in the subarctic region. Molecular  
26 compositions of biogenic secondary organic aerosol (BSOA) tracers inferred that isoprene is a  
27 crucial precursor of BSOA over central Alaska. Our results suggest forest fires and plant  
28 emissions to be the crucial factors controlling the levels and molecular composition of OAs in  
29 central Alaska. We propose that PM<sub>2.5</sub> laden with OAs derived in central Alaska may  
30 significantly impact on the air quality and climate in the Arctic via long-range atmospheric  
31 transport.

32 **Keywords:** Primary organic aerosol, Secondary organic aerosol, Molecular composition,  
33 Biomass burning, Temporal trends, Central Alaska.

## 34 **1 Introduction**

35 Atmospheric aerosols can absorb and scatter solar radiation and alter the radiative forcing of  
36 the atmosphere (Seinfeld and Pandis, 1998; Wilkening et al., 2000). Fine aerosol particles  
37 have a diameter size close to the wavelengths of visible lights and thus are expected to have a  
38 stronger climatic impact than coarse particles (Kanakidou et al., 2005). They can also be  
39 transported far away from the source regions and thus their climatic and environmental effects  
40 are delocalized compared to the emission areas. Aerosol particles that are hydrophilic can act  
41 as cloud condensation nuclei (CCN) and have an indirect climatic effect through modification  
42 of cloud properties (Novakov and Penner, 1993; Novakov and Corrigan, 1996).

43 Organic aerosols (OAs) that are comprised of thousands of organic compounds  
44 contribute about 20 to 50% of total mass of fine particles in the continental mid-latitude  
45 atmosphere (Saxena and Hildemann, 1996) whereas it is around 90% in tropical forest areas  
46 (Crutzen and Andreae, 1990; Andreae and Rosenfeld, 2008). They are derived from  
47 anthropogenic and natural sources. They can alter the physical and chemical properties of  
48 atmospheric particles depending on the meteorological conditions. OAs are highlighted for  
49 the past decade because they are related to the changes of global and regional climate and  
50 chemical composition of the atmosphere as well as public health. Primary organic aerosols  
51 (POA) are directly emitted as particulate forms whereas secondary organic aerosols (SOA)  
52 refer to particulate organic matters that are transformed to aerosol-phase via gas-phase  
53 oxidation of organic precursors. Emissions of POA particles and SOA precursors can be  
54 released from numerous sources near the ground surface and subsequently mixed in the  
55 boundary layer and to a lesser extent in the free troposphere. The dry depositional removal of  
56 OAs mainly depends on the sizes of the aerosol particles.

57 The molecular composition of OAs can be used as tracer to better understand the  
58 sources and formation pathways. Advances were made during the last decade to better  
59 understand the formation of OAs and their precursors in the atmosphere. On a global scale,  
60 the emission of biogenic volatile organic compounds (VOCs) is one order of magnitude  
61 higher than that of anthropogenic VOCs (Seinfeld and Pandis, 1998). It is notable that  
62 biogenic VOCs are comprised of unsaturated hydrocarbons with double bonds and are more  
63 reactive towards the atmospheric oxidants such as hydroxyl (OH) radical and ozone (O<sub>3</sub>) than  
64 anthropogenic VOCs that are largely comprised of aromatic hydrocarbons. This specific  
65 feature of biogenic VOCs further enhances their significance as a conceivable supplier to the  
66 global burden of OAs in the atmosphere. Laboratory and chamber experiments have also

67 documented that biogenic VOCs are the potential precursor for SOA formation in the  
68 atmosphere (Kavouras et al., 1998; Jaoui et al., 2007).

69 Although early Arctic explorers had noticed atmospheric haze (Nordenskiöld, 1883),  
70 the remote Arctic atmosphere was believed to be extremely clean. Pilots flying over the North  
71 American Arctic in the 1950s observed widespread haze that could be seen every winter and  
72 early spring (Mitchell, 1957). It took until the 1970s for scientists to realize that the haze was  
73 air pollution transported from the middle latitudes (Barrie, 1986). Over the past three decades  
74 there has been much research on the climate consequences of this pollution that is also present  
75 in summer. Surface air temperature has increased more than the global average over the past  
76 few decades and is predicted to warm by about 5 °C over a large part of the Arctic by the end  
77 of the twenty-first century (IPCC, 2001). The arctic atmosphere is considered as a unique  
78 natural laboratory for photochemical reactions and transformations during the polar sunrise  
79 (Kawamura et al., 1996). Arctic atmosphere is influenced by marine-derived OAs from the  
80 Arctic Ocean as well as continentally derived OAs and their precursors from mid-latitudes in  
81 Eurasia or North America (Stohl et al., 2006; Law and Stohl, 2007).

82 Previous analyses have reported a substantial contribution of summertime boreal  
83 forest fires to the chemical composition of aerosol over the Arctic (Iziomon et al., 2006;  
84 Kaplan and New, 2006; Stohl et al., 2006). French et al. (2003) proposed that wildfire has  
85 contributed a substantial amount of carbon-based gas from 1950 to 1999 in the atmosphere of  
86 the boreal region of Alaska. Based on the modeling and in-situ observations of black carbon  
87 (BC) and soot during the FROSTFIRE campaign, Kim et al. (2005) revealed that BC and soot  
88 particles of 0.4 to 10 µm in radius can be transported to the Arctic and the whole area of  
89 Alaska in a very short time. The results of Kaplan and New (2006) delivered strong evidence  
90 that high-latitude ecosystems are sensitive to climate change due to the increase in  
91 concentrations of greenhouse gases. Iziomon et al. (2006) examined summertime aerosols  
92 based on column integrated and surface aerosol measurements at Barrow in the North Slope  
93 of Alaska between 1998 and 2003. They noticed high loadings of aerosols at least 8 days each  
94 summer and demonstrated that the pollution events with the highest aerosol loadings were  
95 associated with smoke from wildfires in northwest Canada. Stohl et al. (2006) explored the  
96 impact of boreal forest fire emissions on the light absorbing aerosol levels at the Barrow  
97 Arctic station. They proposed that boreal forest fires could result in elevated concentrations of  
98 light absorbing aerosols throughout the entire Arctic with an impact on the radiation  
99 transmission of the Arctic atmosphere.

100 The results of Hegg et al. (2009) and Warneke et al. (2009) validate that BB causes a  
101 more efficient transport and deposition of BC aerosol in Arctic snow, causing a strong climate  
102 forcing in high latitudes. Based on in-situ measurements in the Arctic and a transport model  
103 of carbon monoxide (CO), Warneke et al. (2010) proposed that BB plumes transported to the  
104 Arctic in spring in 2008 more than doubled the Arctic atmospheric burden in other seasons.  
105 The results of Ward et al. (2012) based on Chemical Mass Balance modeling revealed that  
106 wood smoke was the major source of PM<sub>2.5</sub> particles mainly during the winter months at  
107 several locations in Fairbanks. Ward et al. (2012) and Wang and Hopke (2014) demonstrate  
108 that Arctic air pollution could be so severe that the city of Fairbanks has been labeled as a  
109 serious non-attainment area by the United States Environmental Protection Agency. Biogenic  
110 emissions from boreal forest largely increase during the summertime growing season. The  
111 year-round measurements conducted at Fairbanks by Haque et al. (2016) have shown that  
112 SOA derived from biogenic VOC emissions dominated organic chemical composition of total  
113 suspended particles during summer in central Alaska. They found high contributions of  
114 isoprene oxidation products than monoterpene and sesquiterpene oxidation products to SOA  
115 formation in summer due to the more isoprene emissions and high levels of oxidants. They  
116 estimated isoprene-derived secondary organic carbon (SOC) approximately 5 times higher  
117 than SOA derived from monoterpene and nearly 2 times higher than sesquiterpene-derived  
118 SOA in central Alaska. Because climate change is generally proceeding fastest in the high  
119 latitudes (Serreze et al., 2000; Hinzman et al., 2005), there is an increasing demand for better  
120 understanding of the chemical compositions and sources of OAs in the Arctic atmosphere.

121 We have collected PM<sub>2.5</sub> samples during the summer of 2009 at Fairbanks in central  
122 Alaska. The samples were analyzed for several organic tracer compounds to characterize OAs  
123 in the North American subarctic region. This paper discusses the molecular compositions of  
124 various organic compound classes and the factors controlling temporal changes in their  
125 concentrations in central Alaska. We also discuss the sources of organic compounds detected  
126 and the secondary formation processes as well as atmospheric implications for the burden of  
127 OAs in the arctic and subarctic atmosphere.

## 128 **2 Methodology**

### 129 **2.1 Description of sampling area**

130 Alaska is located in a subarctic zone. Fairbanks is the largest city in central Alaska. It is  
131 situated in the central Tanana Valley connecting the Chena River near the Tanana River. The  
132 location of the sampling site in Fairbanks (64.51°N and 147.51°W) and its surroundings are

133 shown in Figure 1. The altitude of the sampling location is 136 m above sea level. A total area  
134 of Fairbanks is nearly 85 km<sup>2</sup> with a population of 31,500. The sampling site is located at the  
135 downside of Fairbanks where a forest is very close to the campus of the University of Alaska  
136 Fairbanks. The highest levels of atmospheric aerosol burden in the United States have been  
137 recorded in Fairbanks (Ward et al., 2012). The National Emission Inventory database pointed  
138 out that forest fires and combustion of fossil fuels are the two critical sources of air pollution  
139 in Fairbanks (Shakya and Peltier, 2013; Ware et al., 2013).

## 140 **2.2 Sample collection**

141 Atmospheric particle samples of sizes less than 2.5 µm in diameter (PM<sub>2.5</sub>) were collected on  
142 the rooftop of the International Arctic Research Center building of the University of Alaska  
143 Fairbanks during the summer season from June 5 to September 21 in 2009 when a forest fire  
144 was active in the region. The collection of samples was performed using a low-volume air  
145 sampler model URG-2000-39EH (USA) with a flow rate of 16.7 L min<sup>-1</sup>. PM<sub>2.5</sub> particles were  
146 retained on a quartz fiber filter of 47 mm in diameter that was pre-combusted at 450 °C for 6  
147 hours. The sampler was operated for three to several days to get enough aerosol particles on  
148 the filter to detect trace organic species with very low concentrations. We collected 13  
149 samples (Alaska 01 to 13) and 3 field blanks during the campaign. The samples and field  
150 blank filters were individually placed in a pre-heated glass vial with a Teflon-lined screw cap.  
151 We stored the aerosol samples in a dark room at -20 °C to prevent the samples from microbial  
152 degradation and loss of semivolatile organic compounds.

## 153 **2.3 Analysis of organic tracers**

154 We analyzed the samples for organic compounds using a gas chromatograph-mass  
155 spectrometer (GC-MS) system: Hewlett-Packard (HP) model 6890 GC coupled to HP model  
156 5973 mass-selective detector. A 5.0 cm<sup>2</sup> filter area of each aerosol sample was extracted with  
157 a 10 ml dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and methanol (CH<sub>3</sub>OH) mixture (2:1) through  
158 ultrasonication (10 min × 3). The solvent extracts were filtered through a Pasteur pipet packed  
159 with pre-combusted (450 °C for 6 hours) quartz wool to remove particles and filter debris.  
160 The extracts were concentrated by a rotary evaporator and then dried under a stream of pure  
161 nitrogen gas. The hydroxyl (OH) and carboxyl (COOH) groups of organic compounds in the  
162 extracts were derivatized to trimethylsilyl ethers and esters, respectively, by the reaction with  
163 50 µl N,O-bis(trimethylsilyl)trifluoroacetamide including 1% trimethylsilyl chloride and 10  
164 µl pyridine at 70 °C for 3 hours (Schauer et al., 1996; Simoneit et al., 2004a). *n*-Hexane

165 containing 1.43 ng  $\mu\text{l}^{-1}$  of a  $\text{C}_{13}$  *n*-alkane internal standard (40  $\mu\text{l}$ ) was added into the  
166 derivatives before injection of the sample into a GC-MS.

167 The separation of compounds was performed on a 30 m long DB-5MS fused silica  
168 capillary column (0.25 mm inner diameter and 0.25  $\mu\text{m}$  film thickness). Helium was used as a  
169 carrier gas at a flow rate of 1.0 ml  $\text{min}^{-1}$ . The GC oven temperature was programmed from 50  
170  $^{\circ}\text{C}$  for 2 min to 120  $^{\circ}\text{C}$  at 30  $^{\circ}\text{C min}^{-1}$  and then 300  $^{\circ}\text{C}$  at 6  $^{\circ}\text{C min}^{-1}$  with a final isotherm hold  
171 at 300  $^{\circ}\text{C}$  for 16 min. The sample was injected on a splitless mode with the injector  
172 temperature of 280  $^{\circ}\text{C}$ . The mass detection was conducted at 70 eV on an electron ionization  
173 mode with a scan range of 50 to 650 Daltons. The organic compounds were determined by the  
174 comparison of the GC retention times and mass fragmentation patterns of a sample with those  
175 of authentic standards and National Institute of Standards and Technology library data. The  
176 mass spectral data were acquired and processed using HP Chemstation software. GC-MS  
177 relative response factor of each compound was calculated using authentic standards or  
178 surrogate compounds. The recoveries of authentic standards or surrogates were above 80%  
179 for target compounds. The data reported here were not corrected for recoveries. The relative  
180 standard deviation of the measurements based on duplicate analyses was within 10%. The  
181 field blank filters were analyzed by the procedure described above. The target compounds  
182 were not detected in the blank filters.

## 183 **2.4 Meteorology and air mass trajectories**

184 Figure 2 shows temporal changes of daily average meteorological parameters at the campaign  
185 site. The daily mean temperature was in a range of 2.0 to 33  $^{\circ}\text{C}$  with an average of 13.9  $^{\circ}\text{C}$   
186 whereas the daily average relative humidity ranged from 19 to 99 % with a mean of 63 %.  
187 The mean wind speed was 5.2  $\text{km h}^{-1}$  and the total rainfall was 122 mm during the sampling  
188 period. The 5-days air mass backward trajectories at the height of 500 m above the ground  
189 level were computed from Hybrid Single Particle Lagrangian Integrated Trajectory model  
190 (Draxler and Rolph, 2013). The air mass backward trajectories arriving over the observation  
191 site during the collection of aerosol samples is presented in Figure 3.

## 192 **3 Results and discussion**

### 193 **3.1 Overview of the molecular composition of organic aerosols**

194 A total of 96 organic compounds were detected in  $\text{PM}_{2.5}$  samples collected at Fairbanks  
195 during the sampling period. We grouped them into fourteen compound classes as listed in  
196 Table 1 together with the mean concentrations and ranges. Figure 4 shows the chemical

197 compositions of OAs in individual samples (Alaska 01 to 13). The levels of all the quantified  
198 organic compounds in Alaskan samples ranged from 113 to 1664 (ave. 535 ng m<sup>-3</sup>) with the  
199 predominance of anhydrosugars (ave. 186 ng m<sup>-3</sup>) and *n*-alkanoic acids (ave. 185 ng m<sup>-3</sup>).  
200 Anhydrosugars are produced by pyrolysis of cellulose and hemicellulose followed by the  
201 subsequent emission to the atmosphere and are widely used as specific tracers of biomass  
202 burning (BB) (Simoneit et al., 1999; Sang et al., 2013). *n*-Alkanoic acids are derived directly  
203 from the surface of plant leaves and marine phytoplankton as well as BB and meat cooking  
204 (Kawamura and Gagosian, 1987; Rogge et al., 1993; Fine et al., 2001). Sugar alcohols were  
205 detected in ample amount in three samples collected during the end of the campaign. We also  
206 detected a substantial amount of isoprene-derived SOA tracers and *n*-alkanols in Alaskan  
207 samples while the concentrations of other compound classes are relatively low.

### 208 **3.2 Anhydrosugars and lignin and resin products: tracers of biomass burning**

209 The combustion of biopolymers including cellulose and hemicellulose as well as lignin and  
210 suberin produces several organic molecules that have been recognized as important source  
211 tracers of OAs. Anhydrosugars and lignin and resin acids are specific tracers of BB among  
212 the pyrolysis products of biopolymers (Simoneit et al., 1999). The pyrolysis of cellulose and  
213 hemicellulose produces anhydrosugars such as levoglucosan and its isomers mannosan and  
214 galactosan (Simoneit et al., 1999; Engling et al., 2009). Figure 5a presents molecular  
215 distributions of anhydrosugars in Alaskan PM<sub>2.5</sub> samples. Levoglucosan is the dominant  
216 anhydrosugar followed by mannosan and galactosan in Alaskan samples. Their concentrations  
217 ranged from 23 to 463 ng m<sup>-3</sup> (ave. 125 ng m<sup>-3</sup>), 4.1 to 180 ng m<sup>-3</sup> (ave. 36 ng m<sup>-3</sup>) and 3.5 to  
218 106 ng m<sup>-3</sup> (ave. 26 ng m<sup>-3</sup>), respectively.

219 Because 90% of levoglucosan exist in the atmospheric particles with aerodynamic  
220 diameter less than 2 μm (Giannoni et al., 2012), it is reasonable to compare the levoglucosan  
221 concentrations of Alaskan PM<sub>2.5</sub> samples with those reported in PM<sub>10</sub> and TSP during  
222 summer or BB season. We found that the concentration levels of levoglucosan in central  
223 Alaska are substantially higher than those from the Bering Sea (10 ng m<sup>-3</sup>) and Arctic Ocean  
224 (5.2 ng m<sup>-3</sup>) (Hu et al., 2013), Chichijima (0.24 ng m<sup>-3</sup>) and Okinawa (0.57 ng m<sup>-3</sup>) Islands in  
225 the western North Pacific (Verma et al., 2015; Zhu et al., 2015), Northern Japan (7.8 ng m<sup>-3</sup>)  
226 (Agarwal et al., 2010), Mt. Everest (47.2 ng m<sup>-3</sup>) (Cong et al., 2015). They are comparable to  
227 those reported at urban site Chennai in India (ave. 111 ng m<sup>-3</sup>) (Fu et al., 2010) but lower than  
228 those reported at rural site Lumbini in Nepal (ave. 771 ng m<sup>-3</sup>) (Wan et al., 2017), forest site  
229 Rondonia in Brazil (ave. 1180 ng m<sup>-3</sup>) (Graham et al., 2002) and Chiang Mai in Thailand  
230 (ave. 1222 ng m<sup>-3</sup>) (Thepnuan et al., 2019).



231 The emission strength of BB products and their long-range atmospheric transport  
232 influence the atmospheric levels of anhydrosugars. The backward trajectories reveal that air  
233 masses mostly came from the ocean during the campaign (Fig. 3). This result shows that  
234 anhydrosugars present in the Alaskan aerosols were mainly associated with the local and  
235 regional BB during the campaign. The higher level of levoglucosan in Fairbanks than other  
236 sites in the Arctic implies a possible effect of BB on the air quality and climate in the arctic  
237 region. Stocks et al. (2000) and Grell et al. (2011) proposed that the frequency of boreal forest  
238 fires recently increased in summer due to global warming. Figure 6a-c show the temporal  
239 trends of anhydrosugars in the Alaskan aerosols. The levels of anhydrosugars expressively  
240 alter during the campaign period. The lower levoglucosan levels were found at the beginning  
241 of the campaign whereas they became very high (241 to 463 ng m<sup>-3</sup>) in 4-23 July (Fig. 6a).  
242 Another peak of levoglucosan was found in 30 July to 4 August (169 ng m<sup>-3</sup>). The  
243 concentrations of levoglucosan decreased towards the end of the campaign (23 to 50 ng m<sup>-3</sup>).  
244 Forest fires smokes were seen during 4-23 July and 30 July to 4 August over central Alaska.  
245 This observation demonstrates that levoglucosan levels became high due to the local forest  
246 fire in central Alaska. Mannosan and galactosan presented similar temporal variations with  
247 levoglucosan (Fig. 6b and c). The chemical reaction of anhydrosugars with OH radicals could  
248 also influence their concentrations in the atmosphere. Although previous studies have  
249 reported that levoglucosan can remain stable in the atmosphere for around 10 days with no  
250 substantial degradation (Fraser and Lakshmanan, 2000; Schkolnik and Rudich, 2006), recent  
251 findings (Hoffmann et al., 2009; Hennigan et al., 2010; Gensch et al., 2018) reported  
252 significant chemical reactivity of levoglucosan and have raised a question over the stability of  
253 levoglucosan in the atmosphere. Hennigan et al. (2010) carried out a smog chamber  
254 experiment and reported the lifetime of atmospheric levoglucosan to be 0.7 to 2.2 days when  
255 exposed to  $1 \times 10^6$  molecules of OH cm<sup>-3</sup>. This lifetime is within the range of 0.5 to 3.4 days  
256 predicted by Hoffmann et al. (2009) using the Spectral Aerosol Cloud Chemistry Interaction  
257 Model. Lai et al. (2014) found that the atmospheric lifetime of levoglucosan ranged from 1.2  
258 to 3.9 days by the control experiment integrating OH in a flow reactor under different  
259 environmental conditions and different mixing states. Nevertheless, Bai et al. (2013) reported  
260 an atmospheric lifetime of levoglucosan to be 26 days when exposed with OH level of  $2 \times 10^6$   
261 molecules cm<sup>-3</sup> that is much longer than other predictions.

262 It is notable from the above discussion that the degradation of levoglucosan is mostly  
263 induced by photochemical aging via oxidation by OH radicals during long-range transport.  
264 Therefore, the degradation of levoglucosan could be insignificant if the receptor site is close

265 to the source region. As discussed previously, anhydrosugars detected in Alaskan aerosols  
266 during the campaign originated from local and regional BB, we consider that the degradation  
267 of anhydrosugars may not be important to explain the low levels of BB tracers in the samples  
268 collected at the beginning and end of the campaign. The low concentrations of anhydrosugars  
269 during the beginning and end of the campaign might be caused by the decreased emission rate  
270 of BB tracers due to lower BB activities in the source region. Wet deposition may be another  
271 cause to lower the level of anhydrosugars in aerosol samples collected at the beginning and  
272 end of the campaign because we observed rainfall especially in 5 June to 3 July and 6 August  
273 to 17 September in Fairbanks (Fig. 2). Although the concentrations of both mannosan and  
274 galactosan are much lower than levoglucosan (Fig. 5a), we observed strong positive  
275 correlations ( $r = 0.94-0.97$ ) among these tracers (Table 2). This result indicates that they  
276 might have originated from similar types of biomass via the burning in central Alaska.

277 Levoglucosan (L) is largely produced by thermal decomposition of cellulose while  
278 mannosan (M) is mainly a pyrolysis product of hemicellulose (Simoneit et al., 1999). Klemm  
279 et al. (2005) investigated that hardwood contains almost 55 to 65 % of cellulose and 20 to 30  
280 % of hemicellulose. Accordingly, in a laboratory chamber analysis, Schmidl et al. (2008)  
281 found the L/M ratios of nearly 2.5 to 3.9 for softwoods and around 14 to 15 for hardwoods  
282 burning. It is worth to use the L/M ratio to identify the relative contribution of biomass types:  
283 hardwood vs. softwood in central Alaska. The L/M ratios in Alaskan samples ranged from 2.2  
284 to 6.8 (ave. 4.6), which are much lower than the ratios found in smoke samples derived from  
285 the burning of hardwoods but almost similar to the ratios found in samples derived from the  
286 burning of softwoods. The L/M ratios found in Alaskan aerosol samples are also much lower  
287 than the ratios reported for the samples derived from burning of rice straw (12.3 to 55.0)  
288 (Sheesley et al., 2003; Sullivan et al., 2008; Engling et al., 2009), cereal straw (55.7)  
289 (Zhang et al., 2007), wheat straw (12.7) and corn straw (19.5) (Cheng et al., 2013).

290 Fine et al. (2001, 2002, 2004) presented the concentrations of BB tracers in fine  
291 particles derived from the burning of several wood species collected from the United States.  
292 Bases on their data, we calculated the L/M ratios to be 3.4 to 6.7 for softwood burning and  
293 10.7 to 83.4 for hardwood burning. Our values from the Alaskan aerosol (2.2 to 6.8) are well  
294 within the range of L/M ratios for softwood burning from the United States. The ratios in  
295 Alaskan aerosol samples are comparable to those for marine aerosols collected from the  
296 Arctic Ocean (ave. 3.5) (Fu et al., 2013), South China Sea (6.4) and western North Pacific  
297 (ave. 4.6) (Fu et al., 2011). Our values are also similar to those found in aerosol samples  
298 collected at Montana in the USA (4.6) (Ward et al., 2006), Vienna (4.1 to 6.4) and Salzburg

299 (5.4 to 5.7) sites in Austria (Caseiro et al., 2009) and Moitinhos in Portugal (ave. 3.5) (Pio et  
300 al., 2008), where BB was dominated by burning of softwoods but lower than the ratios  
301 estimated in aerosol samples collected at Chennai in India (ave. 11.2) (Fu et al., 2010),  
302 Karachi in Pakistan (ave. 17.5) (Sahid et al., 2016), Lumbini in Nepal (ave. 15.1) (Wan et al.,  
303 2017), Morogoro in Tanzania (9 to 13) (Mkoma et al., 2013), Chiang Mai in Thailand (14.1 to  
304 14.9) (Tsai et al., 2013) and Rondonia in Brazil (ave. 14.2) (Claeys et al., 2010), where  
305 hardwoods and crop residues were the major sources of biomass burning. Our results and  
306 above comparison imply that softwood is most likely biomass burned in central Alaska during  
307 the campaign.

308 Burning of lignin produces phenolic compounds such as 4-hydroxybenzoic (4-HBA),  
309 vanillic and syringic acids whereas dehydroabietic acid (DHAA) is a specific pyrolysis  
310 product of resin present in the bark surface and needle leaves and woody tissues of conifers  
311 (Simoneit et al., 1993). We detected 4-HBA and DHAA in the Alaskan aerosols although  
312 their concentrations were much lower than BB tracers produced from cellulose and  
313 hemicellulose burning (Fig. 5b). The concentrations of 4-HBA and vanillic acid ranged from  
314 0.4 to 6.4 ng m<sup>-3</sup> (ave. 1.7 ng m<sup>-3</sup>) and 0.1 to 8.6 (ave. 1.8 ng m<sup>-3</sup>), respectively whereas those  
315 of syringic acid ranged from 0.02 to 1.1 ng m<sup>-3</sup> (ave. 0.2 ng m<sup>-3</sup>). Shakya et al. (2011) and  
316 Myers-Pigg et al. (2016) reported that syringic to vanillic acid ratios for the burning of woody  
317 and non-woody angiosperm range from 0.1 to 2.4 whereas the ratios of softwood are 0.01 to  
318 0.24. The concentration ratio of syringic to vanillic acid can therefore be used as a marker to  
319 distinguish the type of vegetation burned. We found that syringic to vanillic acid ratios in  
320 Fairbanks aerosols ranged from 0.02 to 0.5 (ave. 0.2), suggesting that softwood is more  
321 important biomass burned in central Alaska during the campaign. This conclusion is  
322 consistent with the observation on the L to M ratios as discussed above. The temporal  
323 variation of 4-HBA is very similar to that of anhydrosugars whereas vanillic and syringic  
324 acids presented rather similar temporal trends with DHAA in Alaskan aerosols (Fig. 6d-g).  
325 Simoneit et al. (1993) proposed that the emission of DHAA is different than those of lignin  
326 and cellulose burning products and therefore it is a more specific molecular marker of the  
327 burning of conifer trees. The concentrations of DHAA ranged between 0.9 and 19 ng m<sup>-3</sup>  
328 (ave. 6.1 ng m<sup>-3</sup>), which are higher than those of lignin pyrolysis products (Fig. 5b). This  
329 result suggests that the burning of conifer is a common source of OAs in central Alaska.

### 330 **3.3 Lipids: tracers of leaf waxes and marine sources**

331 Series of lipid class compounds, including *n*-alkanes (C<sub>21</sub> to C<sub>33</sub>), *n*-alkanols (C<sub>8</sub> to C<sub>30</sub>) and  
332 *n*-alkanoic acids (C<sub>12</sub> to C<sub>32</sub>) were detected in Alaskan aerosols. *n*-Alkanoic acids are the

333 major lipid class compounds in Alaskan aerosols (ave. 185 ng m<sup>-3</sup>), which is several times  
334 higher than those of *n*-alkanols (ave. 46 ng m<sup>-3</sup>) and *n*-alkanes (ave. 24 ng m<sup>-3</sup>) (Table 1).  
335 Figure 7a-c show the average molecular distributions of lipid compounds in Alaskan aerosols.  
336 The molecular distribution of *n*-alkanes is characterized by an odd-carbon-number  
337 predominance with maxima at heptacosane (C<sub>27</sub>: ave. 6.8 ng m<sup>-3</sup>). Low molecular weight  
338 (LMW) *n*-alkanes are dominated in particles derived from fossil fuel combustion whereas  
339 those derived from leaf waxes are enriched with high molecular weight (HMW) *n*-alkanes  
340 (Rogge et al., 1993; Hays et al., 2005; Wang et al., 2009). A remarkable feature in the  
341 molecular signature of *n*-alkanes is the presence of only the HMW species (C<sub>21</sub> to C<sub>33</sub>) in  
342 Alaskan aerosols. This molecular signature in the PM<sub>2.5</sub> samples suggests that leaf waxes are  
343 the major source of *n*-alkanes in central Alaska with no significant contribution from fossil  
344 fuel combustion. This feature is different from the result of marine aerosols collected over the  
345 Arctic Ocean (Fu et al., 2013), in which *n*-alkanes were mostly of fossil fuel origin. We  
346 conclude that fossil fuel combustion is not an important source of OAs over central Alaska  
347 during the summer campaign. This remark is consistent with the fact that the fossil fuel  
348 biomarkers such as hopanes and steranes (Ding et al., 2009; Wang et al., 2009) were not  
349 detected in the Alaskan samples. These results demonstrate that biogenic *n*-alkanes emitted  
350 from boreal forest fires largely overwhelmed fossil fuel combustion-derived *n*-alkanes in  
351 central Alaska.

352 The carbon preference index (CPI) is a powerful tool to characterize the  
353 anthropogenic versus biogenic sources of lipid compounds (Simoneit et al., 1991;  
354 Kawamura et al., 2003). The CPI value of *n*-alkanes in fossil fuel emission is usually close to  
355 unity while it is more than 5 for leaf waxes (Peltzer and Gagosian, 1989). The calculated CPI  
356 values of *n*-alkanes in the Alaskan aerosols are in the range of 5.2 to 9.9 with an average of  
357 6.6. These values are significantly higher than those reported in urban aerosols from  
358 megacities in China (0.9 to 1.8) (Wang et al., 2006), India (1.2 to 2.3) (Fu et al., 2010) and  
359 Japan (1.1 to 2.8) (Kawamura et al., 1994), where aerosol particles were seriously affected by  
360 fossil fuel combustion. The broader range of CPI values was found in aerosol particle samples  
361 collected over Mt. Tai (1.1 to 8.0) (Fu et al., 2008) and the western North Pacific (1.8 to 15)  
362 (Kawamura et al., 2003), where the input of plant waxes overwhelms the contribution of  
363 fossil fuel combustion. Together with these assessments our results strongly infer that  
364 *n*-alkanes over the Alaskan atmosphere mainly originated from plant leaf waxes. The wax  
365 covering the external surface of a plant leaf is composed of a mixture of long-chain aliphatic  
366 compounds. Kollattukudy (1976) investigated that odd carbon number *n*-alkanes (C<sub>25</sub> to C<sub>33</sub>)

367 are one of the most abundant compound classes in the leaf wax. Simoneit et al. (1991)  
368 considered the excess of odd homologues minus the neighboring even homologues as the  
369 abundance of plant derived *n*-alkanes in atmospheric samples. The contribution of estimated  
370 plant-derived *n*-alkanes in total *n*-alkanes ranged from 53 to 70 % (ave. 61 %), implying that  
371 leaf wax is a major source of *n*-alkanes in the Alaskan aerosols.

372 The average molecular characteristics of *n*-alkanols and *n*-alkanoic acids displayed  
373 even-carbon-number predominance (Fig. 7b and c). *n*-Alkanols presented maxima at  
374 docosanol (C<sub>22</sub>: ave. 9.2 ng m<sup>-3</sup>) whereas *n*-alkanoic acids demonstrated a peak at  
375 tetracosanoic acid (C<sub>24</sub>: ave. 63 ng m<sup>-3</sup>). Microbes and marine phytoplankton are the sources  
376 of LMW *n*-alkanols and *n*-alkanoic acids while their HMW homologues are specifically  
377 derived from higher plant waxes (Kawamura et al., 2003; Wang and Kawamura, 2005).  
378 Simoneit (2002) has proposed that BB also emit a large extent of *n*-alkanols and *n*-alkanoic  
379 acids into the atmosphere. The average concentrations of HMW *n*-alkanols (C<sub>21</sub> to C<sub>30</sub>: 31  
380 ng m<sup>-3</sup>) and HMW *n*-alkanoic acids (C<sub>21</sub> to C<sub>32</sub>: 122 ng m<sup>-3</sup>) are twice higher than those of  
381 LMW *n*-alkanols (C<sub>8</sub> to C<sub>20</sub>: 15 ng m<sup>-3</sup>) and LMW *n*-alkanoic acids (C<sub>12</sub> to C<sub>20</sub>: 58 ng m<sup>-3</sup>) in  
382 the Alaskan aerosols. This result shows that locally derived plant waxes might be the source  
383 of HMW *n*-alkanols and *n*-alkanoic acids in central Alaska. The CPI values of *n*-alkanols and  
384 *n*-alkanoic acids are in the range of 3.0 to 10 (ave. 6.2) and 5.6 to 9.8 (ave. 7.9), respectively,  
385 suggesting a large contribution of plant waxes to lipid class compounds in central Alaskan  
386 aerosols.

387 The concentrations of *n*-alkanes and *n*-alkanols slightly decreased from June 05-12  
388 to late June samples (June 25 to July 04) and then dramatically increased in July 04-06  
389 sample (Fig. 6h and i). The concentration peaks of *n*-alkanes and *n*-alkanols were also  
390 observed in sample of July 14-23 whereas their concentrations constantly decreased from July  
391 30 to the end of the campaign. The levels of *n*-alkanoic acids were low at the beginning of the  
392 campaign and then increased drastically in July 04-06 sample and remained high in two  
393 samples collected in July 06-23 (Fig. 6j). Concentrations of *n*-alkanoic acids decreased from  
394 July 30 to September 21. Fascinatingly, the temporal variations of lipid class compounds were  
395 similar to those of anhydrosugars (Fig. 6a-c and h-j). Figure 8a-c show the linear regression  
396 analysis of lipid compounds with levoglucosan. We found strong correlations ( $r = 0.90-0.96$ )  
397 of lipid compounds with levoglucosan in Alaskan aerosols. These results suggest that forest  
398 fires significantly control the atmospheric levels of lipids in central Alaska via the evaporative  
399 ablation of leaf-waxes of terrestrial plants.

400 We also detected unsaturated *n*-alkanoic acids in Alaskan aerosol samples. Oleic  
401 (C<sub>18:1</sub>) and linoleic (C<sub>18:2</sub>) acids are major constituents of the cell membranes in terrestrial  
402 plants. They are released into the atmosphere directly from the leaf surface by wind action  
403 (Yokouchi and Ambe, 1986; Nouredini and Kanabur, 1999). Fine et al. (2001) and Hays et  
404 al. (2005) proposed that BB also emits significant amounts of C<sub>18:1</sub> and C<sub>18:2</sub> to the  
405 atmosphere. They are subjected to photochemical oxidation in the atmosphere. C<sub>18:1</sub> and C<sub>18:2</sub>  
406 are more reactive due to a double bond than C<sub>18:0</sub> in the atmosphere with oxidants such as OH  
407 radical and O<sub>3</sub>. The ratio of C<sub>18:1</sub>+C<sub>18:2</sub> to octadecanoic acid (C<sub>18:0</sub>) is thus used as an indicator  
408 of photochemical processing of OAs (Kawamura and Gagosian, 1987). The ratios ranged  
409 from 0.03 to 0.3 with an average of 0.2 in Alaskan aerosols. Because average concentrations  
410 of C<sub>18:1</sub> (0.9 ng m<sup>-3</sup>) and C<sub>18:2</sub> (0.5 ng m<sup>-3</sup>) in Alaskan samples are significantly lower than that  
411 of C<sub>18:0</sub> (10 ng m<sup>-3</sup>), C<sub>18:1</sub> and C<sub>18:2</sub> may be rapidly degraded in the atmosphere by  
412 photochemical oxidations.

### 413 3.4 Sugar compounds: tracers of primary biological particles

414 Nine sugar compounds were detected in Alaskan aerosol samples with five primary sugars  
415 and four sugar alcohols (Fig. 9). The concentrations of primary sugars were in the range of  
416 0.3 to 44 ng m<sup>-3</sup> (ave. 13 ng m<sup>-3</sup>) whereas those of sugar alcohols ranged from 1.0 to 24 ng m<sup>-3</sup>  
417 (ave. 14 ng m<sup>-3</sup>). The concentrations of total sugar compounds ranged from 1.3 to 62 ng m<sup>-3</sup>  
418 (27 ng m<sup>-3</sup>), in which sugar alcohols contributed more to the total sugars (ave. 54.2 %) than  
419 primary sugars (ave. 45.8 %) in Alaskan aerosols. Primary sugars are abundantly present in  
420 vascular plants. They are produced during the photosynthetic process in leaves and then  
421 accumulated in growing plants (Medeiros et al., 2006). Figure 9a presents the average  
422 molecular distributions of primary sugars in Alaskan aerosols. Primary sugars are  
423 characterized by the predominance of glucose in Alaskan samples with the concentration  
424 range of 0.1 to 19 ng m<sup>-3</sup> (ave. 6.8 ng m<sup>-3</sup>) followed by trehalose (ave. 2.6 ng m<sup>-3</sup>). Although  
425 sucrose (ave. 1.6 ng m<sup>-3</sup>) and fructose (ave. 1.3 ng m<sup>-3</sup>) are not abundant (Fig. 9a), glucose  
426 showed strong positive correlations with fructose ( $r = 0.91$ ) and sucrose ( $r = 0.82$ ) (Table 2).  
427 Fructose also presented a strong correlation with sucrose ( $r = 0.94$ ) (Table 2). These  
428 correlations indicate their similar source and origin in the atmosphere of central Alaska.

429 Glucose and fructose are carbohydrates enriched in tree barks as well as branches  
430 and leaves (Medeiros et al., 2006; Li et al., 2016). They are present in plant nectars and fruits  
431 as well as pollen and fern spores (Baker et al., 1998; Graham et al., 2002). Dust and BB  
432 derived particles have also been reported as major sources of glucose and fructose in the  
433 atmosphere (Nolte et al., 2001; Rogge et al., 2007). Sucrose is produced in plant leaves and

434 distributed to several portions of the plant body (Jia et al., 2010). Sucrose has also been  
435 reported in airborne pollen grains produced from blooming plants (Pacini, 2000), surface soil  
436 and associated microbiota (Simoneit et al., 2004b) and dehydrated plant materials  
437 (Ma et al., 2009). We found that glucose shows moderate correlation ( $r = 0.48$ ) with  
438 levoglucosan (Fig. 8d). Shafizadeh and Fu (1973) documented that glucose is a minor  
439 product of cellulose pyrolysis. The predominance of glucose among primary sugars together  
440 with a moderate correlation with levoglucosan suggests that pyrolysis of cellulose and  
441 hemicellulose is not the source of glucose in central Alaska. Pullman and Buchanan (2008)  
442 investigated that soluble carbohydrates such as glucose are a major component of conifers  
443 where it can be stored in a large amount as deposited or dissolved free molecules. The  
444 temporal trend of glucose showed a peak in the sample collected during July 14-23 (Fig. 6k).  
445 Interestingly, **the same sample showed** a high loading of DHAA that is a unique tracer of the  
446 burning of conifer trees (Fig. 6g). This result suggests that the burning of conifer plants is the  
447 source of glucose in central Alaska.

448 Trehalose is a well-known constituent of microbes and fungal spores as well as plant  
449 species and suspended soil particles (Graham et al., 2003; Medeiros et al., 2006). The levels  
450 of trehalose stayed constant from June 05 to July 14 and dramatically decreased in July 23 to  
451 August 08 and then increased towards the end of the campaign when rainfall occurs in central  
452 Alaska (Fig. 2 and Fig. 6m). This result shows that the major source of trehalose might be the  
453 fungi in the surface soil of central Alaska that was emitted after the rainfall event. Terrestrial  
454 plants and marine phytoplankton as well as soil dust particles and associated microorganisms  
455 release xylose into the atmosphere (Cowie and Hedges, 1984). Although xylose is a minor  
456 primary sugar in Alaskan aerosols (ave.  $1.1 \text{ ng m}^{-3}$ ), its temporal trend is very similar to that  
457 of anhydrosugars (Fig. 6a-c and n). This result together with a strong positive correlation of  
458 xylose with levoglucosan ( $r = 0.92$ ) implies its BB origin in central Alaska (Fig. 8g). This  
459 **finding** is similar to that of Sullivan et al. (2011), who documented that atmospheric levels of  
460 xylose in the Midwestern United States were attributed to BB emission.

461 Sugar alcohols presented the predominance of arabitol (ave.  $6.6 \text{ ng m}^{-3}$ ) and mannitol  
462 (ave.  $6.2 \text{ ng m}^{-3}$ ) (Fig. 9b). The concentration levels of erythritol (ave.  $1.0 \text{ ng m}^{-3}$ ) and inositol  
463 (ave.  $0.3 \text{ ng m}^{-3}$ ) are much lower than those of arabitol and mannitol in Alaskan aerosols.  
464 Arabitol and **mannitol concentrations were higher during** the beginning and end of the  
465 campaign than those during the middle of the campaign (Fig. 6o and p). We found that  
466 arabitol and mannitol are strongly correlated ( $r = 0.95$ ), implying their similar source in the  
467 Alaskan aerosols (Table 2). The major sources of arabitol and mannitol are airborne fungal

468 spores (Pashynska et al., 2002; Bauer et al., 2008). Debris from mature leaves has also been  
469 proposed as a source of arabinol and mannitol in the forest areas (Pashynska et al., 2002;  
470 Zhang et al., 2010). Guasco et al. (2013) and Prather et al. (2013) proposed that bubble  
471 bursting of seawater contributes bacteria and dissolve organic species along with sea-salts to  
472 aerosol particles. Although air masses mostly originated from the ocean (Figure 3), the  
473 altitude of most of the air masses dropped at several places and went on to Fairbanks by  
474 maintaining low height. Therefore, we presume a negligible input of marine sources to sugar  
475 alcohols in Alaskan fine aerosol samples. Arabitol and mannitol were also detected in aerosol  
476 particles derived from BB (Fu et al., 2012; Yang et al., 2012; Nirmalkar et al., 2015). We  
477 found insignificant correlations of arabinol ( $r = 0.16$ ) and mannitol ( $r = 0.27$ ) with  
478 levoglucosan (Fig. 8h and i). This result suggests that BB is not an important source of  
479 arabinol and mannitol in the Alaskan aerosols.

480 The source of arabinol and mannitol might be fungi in the surface soil of Fairbanks  
481 whose activities were high during the campaign. Elbert et al. (2007) suggested that the active  
482 ejection of fungal spores demands water from the nearby atmosphere and release through  
483 osmotic pressure and surface tension effects. As shown in Figure 2 and Figures 6o and 6p,  
484 arabinol and mannitol concentrations in Alaskan samples are well connected with the rainfall  
485 event. We found that the levels of arabinol and mannitol are high during and after the rainfall.  
486 The rainfall increases the moisture contents in surface soil and thus fungal and microbial  
487 activities are enhanced in central Alaska. This study implies that the precipitation stimulates  
488 the release of fungal spores to increase the arabinol and mannitol levels in Alaskan samples.  
489 Gottwald et al. (1997), and Burch and Levetin (2002) reported that passive discharge of  
490 spores is enhanced under windy conditions. This consideration further implying that fungal  
491 spores are actively ejected in the atmosphere of central Alaska. Our finding is consistent with  
492 the result of Elbert et al. (2007) from Amazonia rainforest where the ambient fungal spores  
493 were controlled by the active discharge. It is noteworthy that primary sugar trehalose  
494 presented significant positive correlations with arabinol ( $r = 0.85$ ) and mannitol ( $r = 0.74$ )  
495 (Table 2), documenting that trehalose is also produced from surface soil under wet conditions  
496 in central Alaska.

### 497 3.5 Phthalate esters: tracers of plastic burning

498 Phthalates are widely used as a plasticizer in synthetic polymers and as a softener in  
499 polyvinylchloride (Thuren and Larsson, 1990; Wang et al., 2006). They can be emitted into  
500 the atmosphere by evaporation from polymers because they are not chemically bonded  
501 (Staples et al., 1997). The compositions of phthalate esters are the subject of scientific



502 discussion and public concern due to their potential carcinogenic and endocrine disrupting  
503 properties (Sidhu et al., 2005; Swan et al., 2005). We detected four phthalate esters in  
504 Alaskan aerosols, including diethyl phthalate (DEP), dibutyl phthalate (DBP), diisobutyl  
505 phthalate (DiBP) and diethylhexyl phthalate (DEHP).

506 The ambient concentrations of total phthalate esters ranged from 0.4 to 6.6 ng m<sup>-3</sup>  
507 (ave. 1.7 ng m<sup>-3</sup>), which are slightly higher than those from the North Sea to the high Arctic  
508 (0.4 to 1.0 ng m<sup>-3</sup>) (Xie et al., 2007), comparable to or slightly lower than those observed in  
509 the North Pacific (0.72 to 4.48 ng m<sup>-3</sup>) (Atlas and Giam, 1981), Great Lakes (0.1 to 10 ng m<sup>-3</sup>)  
510 (Eisenreich et al., 1981), Canadian High Arctic (0.28 to 11 ng m<sup>-3</sup>) (Fu et al., 2009), but much  
511 lower than those reported in Sweden (0.5 to 127 ng m<sup>-3</sup>) (Thuren and Larsson, 1990),  
512 mountainous aerosols (9.6 to 985 ng m<sup>-3</sup>) (Fu et al., 2008) and urban aerosols from megacities  
513 in India and China (62 to 2200 ng m<sup>-3</sup>) (Wang et al., 2006; Fu et al., 2010). Figure 10a shows  
514 the average molecular distributions of phthalate esters in Alaskan aerosols. We found DEP  
515 (ave. 0.8 ng m<sup>-3</sup>) as a dominant phthalate followed by DBP and DEHP (ave. 0.4 ng m<sup>-3</sup>),  
516 whereas DiBP was less abundant (ave. 0.2 ng m<sup>-3</sup>). The predominance of DEP among  
517 phthalate esters in Alaskan aerosol is different than those found in marine aerosol from the  
518 Arctic Ocean (Xie et al., 2007; Fu et al., 2013) and urban aerosols from India and China  
519 (Wang et al., 2006; Fu et al., 2010), where DEHP was the dominant species. We found  
520 similar temporal variations with significant positive correlations among detected phthalate  
521 esters ( $r = 0.71-0.88$ ) (Fig. 11a-d and Table 2), suggesting that they have similar sources in  
522 central Alaska.

### 523 **3.6 Tracers of biogenic SOA**

524 Significant progress has been made in the last decade to better understand SOA formation  
525 from BVOCs such as isoprene, monoterpenes and sesquiterpenes (Carlton et al., 2009;  
526 Ding et al., 2014; Jathar et al., 2014; Sarkar et al., 2017). SOA is a crucial component of  
527 the atmosphere that has an impact on the radiation budget directly by scattering sunlight and  
528 indirectly by acting as CCN (Kanakidou et al., 2005; Carlton et al., 2009). Isoprene has  
529 conjugated double bonds and thus it is more reactive towards oxidants such as O<sub>3</sub> and NO<sub>x</sub> to  
530 result in various intermediates and stable products via a series of oxidative reactions in the  
531 atmosphere. We detected six organic compounds including 2-methylglyceric acid (2-MGA),  
532 three C<sub>5</sub>-alkene triols and two 2-methyltetrols (2-MTLs) as isoprene-SOA tracers in the  
533 Alaskan aerosols. Their total concentrations ranged from 2.0 to 142 ng m<sup>-3</sup> (ave. 41 ng m<sup>-3</sup>),  
534 which are significantly higher than those reported over the North Pacific (0.11 to 0.48 ng m<sup>-3</sup>)  
535 (Fu et al., 2011), Canadian High Arctic (ave. 0.30 ng m<sup>-3</sup>) (Fu et al., 2009), North Pacific to

536 Arctic (ave. 0.62 ng m<sup>-3</sup>) (Ding et al., 2013), western North Pacific (0.05 to 7.22 ng m<sup>-3</sup>)  
537 (Zhu et al., 2016), forest site in western Germany (ave. 20.5 ng m<sup>-3</sup>) (Kourtchev et al., 2008a),  
538 and Mumbai in India (ave. 1.1 ng m<sup>-3</sup>) (Fu et al., 2016) but lower than those in Mt. Changbai  
539 (22 to 280 ng m<sup>-3</sup>) (Wang et al., 2008) and Mt. Fuji (ave. 69 ng m<sup>-3</sup>) (Fu et al., 2014),  
540 Research Triangle Park in USA (19.9 to 384 ng m<sup>-3</sup>) (Lewandowski et al., 2007) and several  
541 sites in China (8.65 to 554 ng m<sup>-3</sup>) (Ding et al., 2014).

542 Molecular compositions of isoprene-SOA tracers are characterized by the  
543 predominance of C<sub>5</sub>-alkene triols (ave. 20 ng m<sup>-3</sup>) and 2-MTLs (ave. 19 ng m<sup>-3</sup>) in Alaskan  
544 aerosols (Fig. 12). Surratt et al. (2010) proposed that C<sub>5</sub>-alkene triols and 2-MTLs are higher  
545 generation products from the photooxidation of epoxydiols of isoprene under low-NO<sub>x</sub>  
546 conditions. C<sub>5</sub>-Alkene triols were strongly correlated with 2-MTLs ( $r = 0.97$ ) in the Alaskan  
547 aerosols (Table 2). The abundant co-presence of C<sub>5</sub>-alkene triols and 2-MTLs suggest their  
548 similar sources and formation pathways in central Alaska. 2-Methylerythritol (ave. 13 ng m<sup>-3</sup>)  
549 is twice more abundant than 2-methylthreitol (ave. 5.9 ng m<sup>-3</sup>), being similar to previous  
550 studies (Ion et al., 2005; Cahill et al., 2006). The concentration of 2-MGA is significantly  
551 lower (ave. 2.2 ng m<sup>-3</sup>) than C<sub>5</sub>-alkene triols and 2-MTLs (Fig. 12). Surratt et al. (2006)  
552 suggested that 2-MGA is produced by the oxidation of methacrolein and methacrylic acid and  
553 has been detected as an important gas-phase intermediate in the SOA formation from isoprene  
554 under high-NO<sub>x</sub> conditions. Temporal variations of isoprene-SOA tracers were very similar to  
555 each other in Alaskan aerosols (Fig. 11e-g). Their concentrations increased in the sample of  
556 June 12-25 to July 06-14 and decreased in the sample of July 14-23 and July 23-30. They  
557 increased significantly in July 30 to August 04 sample and quickly reduced in August 04-08  
558 sample and then remain comparable at the end of the campaign.

559 Four organic acids were identified as monoterpenes-SOA tracers in Alaskan  
560 aerosols. They include 3-hydroxyglutaric acid (3-HGA), pinonic acid (PNA), pinic acid (PA)  
561 and 3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA). Hallquist et al. (2009) suggested  
562 that these acids are produced by the oxidation of pinenes through reactions with OH radical  
563 and O<sub>3</sub>. Their total concentrations ranged from 1.0 to 36 ng m<sup>-3</sup> (ave. 9.2 ng m<sup>-3</sup>), which are  
564 higher than those reported in the North Pacific (0.02 to 0.22 ng m<sup>-3</sup>) (Fu et al., 2011),  
565 Canadian High Arctic (ave. 1.6 ng m<sup>-3</sup>) (Fu et al., 2009), North Pacific to Arctic (ave. 0.05  
566 ng m<sup>-3</sup>) (Ding et al., 2013), western North Pacific (0.04 to 10.8 ng m<sup>-3</sup>) (Zhu et al., 2016), and  
567 comparable to those reported at several sites in China (3.09 to 33.8) (Ding et al., 2014) but  
568 lower than those reported at Mt. Fuji in Japan (ave. 39 ng m<sup>-3</sup>) (Fu et al., 2014), forest site in  
569 Germany (ave. 25.6 ng m<sup>-3</sup>) (Kourtchev et al., 2008a) and Finland (11.1 to 217 ng m<sup>-3</sup>)

570 (Kourtchev et al., 2008b). PA is most abundant (ave.  $3.4 \text{ ng m}^{-3}$ ) among monoterpene-SOA  
571 tracers followed by PNA (ave.  $2.3 \text{ ng m}^{-3}$ ) (Fig. 12). The dominance of PA over PNA in  
572 summertime can be explained by the much lower vapor pressure of PA than that of PNA.  
573 However, this pattern is different from those found in summertime aerosols at the summit of  
574 Mt. Tai in China (Fu et al., 2008) and other sites in Europe (Kavouras and Stephanou, 2002)  
575 and North America (Cahill et al., 2006), in which PNA is more abundant than PA.

576 PA and PNA are the initial photooxidation products of monoterpenes that can be  
577 further photooxidized to 3-MBTCA in the atmosphere (Gomez-Gonzalez et al., 2012). The  
578 concentration ratio (3-MBTCA to PA+PNA) can therefore be used to differentiate the fresh  
579 and photochemically processed monoterpene-SOA tracers in the atmosphere. We found the  
580 ratios to be 0.1 to 1.4 (ave. 0.5), demonstrating that monoterpene-SOA are mostly fresh in  
581 central Alaska. The ratios of 3-HGA to 3-MBTCA are mostly lower when they are produced  
582 from  $\alpha$ -pinene as compared to  $\beta$ -pinene. Lewandowski et al. (2013) documented a major  
583 contribution of  $\alpha$ -pinene to monoterpene-SOA tracers based on the 3-HGA/3-MBTCA ratio  
584 of about 1 in the southeastern United States than those observed in California (1.8 to 3.8).  
585 Ding et al. (2014) also suggested  $\alpha$ -pinene as the major precursor in China based on the low  
586 ratios in Hefei (1.16) and Qianyanzhou (0.75). We found the ratios ranging from 0.5 to 2.0 in  
587 Alaskan aerosols (ave. 1.0), indicating that  $\alpha$ -pinene mainly contributes to monoterpene-SOA  
588 tracers. 3-HGA and 3-MBTCA displayed somewhat similar temporal variations although the  
589 patterns are different from PA and PNA (Fig. 11h-k), which showed very similar variations in  
590 Alaskan aerosols.

591 Sesquiterpenes are BVOCs with high reactivity and relatively low vapor pressure  
592 (Duhl et al., 2008).  $\beta$ -Caryophyllene is dominant sesquiterpene. The ozonolysis or  
593 photooxidation of  $\beta$ -caryophyllene produces  $\beta$ -caryophyllinic acid in the atmosphere  
594 (Jaoui et al., 2007). Concentrations of  $\beta$ -caryophyllinic acid in Alaskan aerosols ranged from  
595  $0.1$  to  $3.4 \text{ ng m}^{-3}$  (ave.  $0.9 \text{ ng m}^{-3}$ ), which are higher than those from the Canadian High Arctic  
596 (ave.  $0.12 \text{ ng m}^{-3}$ ) and Arctic Ocean (ave.  $0.017 \text{ ng m}^{-3}$ ) (Fu et al., 2009; Fu et al., 2013) but  
597 lower than those reported in several sites in China ( $0.17$  to  $17.4 \text{ ng m}^{-3}$ ) (Ding et al., 2014)  
598 and Research Triangle Park in USA ( $5.9$  to  $25 \text{ ng m}^{-3}$ ) (Lewandowski et al., 2007). The  
599 temporal variation of  $\beta$ -caryophyllinic acid is very different than those of isoprene and  
600 monoterpene-SOA tracers detected in Alaskan aerosols (Fig. 11l). Akagi et al. (2011)  
601 reported that biogenic VOCs could also be emitted from biomass burning. Our result showed  
602 a high level of  $\beta$ -caryophyllinic acid in the samples that were affected by BB in central  
603 Alaska. Ciccioli et al. (2014) proposed that sesquiterpenes could be accumulated in leaves and

604 wood because of low volatility and then abundantly emitted upon heating. The temporal trend  
605 variation of  $\beta$ -caryophyllinic acid is similar to those of anhydrosugars (Fig. 6a-c and 11l).  
606 Interestingly, we found a strong correlation ( $r = 0.98$ ) of  $\beta$ -caryophyllinic acid with  
607 levoglucosan (Fig. 8j), again indicating that forest fire largely contributes to the formation of  
608  $\beta$ -caryophyllinic acid in central Alaska.

### 609 **3.7 Aromatic and polyacids: tracers of SOA**

610 We detected benzoic acid in the Alaskan aerosol with the concentration range of 0.1 to 0.9  
611 (ave.  $0.3 \text{ ng m}^{-3}$ ). Benzoic acid is produced from several anthropogenic sources. It is a  
612 primary pollutant in the automobile emission and smokes derived from burning of biomass  
613 and biofuels (Rogge et al., 1993; Kawamura et al., 2002). It is also a secondary product of  
614 photochemical degradation of toluene emitted from anthropogenic sources (Suh et al., 2003).  
615 It can play an important role to enhance the new particle formation in the atmosphere  
616 (Zhang et al., 2004). The temporal variation of benzoic acid is similar to anhydrosugars  
617 detected in Alaskan samples (Fig. 6a-c and 11m). We also found a strong positive correlation  
618 ( $r = 0.95$ ) of benzoic acid with levoglucosan (Fig. 8k), demonstrating that BB is the source of  
619 benzoic acid in central Alaska.

620 Polyacids are also the secondary photooxidation products of atmospheric organic  
621 precursors (Wang et al., 2007; Fu et al., 2012). Concentrations of total polyacids ranged from  
622  $1.2$  to  $10 \text{ ng m}^{-3}$  (ave.  $3.3 \text{ ng m}^{-3}$ ), among which glyceric acid (ave.  $1.6 \text{ ng m}^{-3}$ ) was dominant  
623 (Fig. 13). Significant positive correlations were found among all polyacids ( $r = 0.67$ - $0.87$ ) in  
624 Alaskan aerosols (Table 2). These results imply that polyacids may have similar sources or  
625 formation pathways in central Alaska. We found that polyacids showed no significant  
626 correlations with benzoic acid ( $r = 0.17$ - $0.53$ ), which is mostly of BB origin in Alaskan  
627 samples as discussed above (Table 2). These correlations and different temporal trends of  
628 benzoic acid and polyacids suggest that forest fires are not the main source of polyacids in the  
629 Alaskan samples (Fig. 11m-p). This remark is further supported by the insignificant  
630 correlations of polyacids with levoglucosan ( $r = 0.29$ - $0.47$ ) (Fig. 8l-n). Claeys et al. (2004)  
631 suggested that SOA tracer such as tartaric acid is produced by the photochemical oxidation of  
632 isoprene. Interestingly, significant positive correlations ( $r = 0.67$ - $0.78$ ) of polyacids were  
633 found with total isoprene-SOA tracers detected in Alaskan samples (Table 2), suggesting that  
634 they may be produced by photooxidation of isoprene in the Alaskan atmosphere.

### 635 **3.8 Contributions of compound classes to aerosol organic carbon**

636 The contributions of each compound class to organic carbon (OC) in the Alaskan aerosols are  
637 given in Table 3. BB tracers accounted for 1.35 to 8.35 % (ave. 4.40 %) of OC. The  
638 contribution of anhydrosugars to OC was substantially high (ave. 4.26 %) than that of lignin  
639 and resin acids (ave. 0.14 %). This value from Fairbanks is notably higher than those reported  
640 in aerosol samples collected from a round-the-world cruise (ave. 0.15 %) (Fu et al., 2011),  
641 Gosan Jeju Island in Korea (ave. 0.29 %), Sapporo (ave. 0.44 %) and Chichijima (ave. 0.06  
642 %) in Japan (Simoneit et al., 2004a), and Chennai in India (ave. 0.59 %) (Fu et al., 2010). The  
643 lipid compound classes in Fairbanks samples accounted for 1.16 to 45.8 % (ave. 12.4 %) of  
644 OC. *n*-Alkanoic acids contributed on average 7.48 % (0.67 to 15.9 %), which is much higher  
645 than those estimated in samples of round-the-world cruise (ave. 0.82 %), Sapporo (ave. 0.62  
646 %) and Chichijima (ave. 0.78 %) (Simoneit et al., 2004a; Fu et al., 2011). The tracers of  
647 primary biological aerosol particles accounted for on average 0.85 % (0.17 to 1.50 %), among  
648 which comparable contributions of primary sugars (ave. 0.39 %) and sugar alcohols (ave. 0.46  
649 %) to OC were found in Alaskan aerosols. Plastic burning tracer accounted for 0.02 to 1.07 %  
650 of OC (ave. 0.14 %), which is lower than those from Sapporo (ave. 1.1 %) and Chichijima  
651 samples (ave. 1.2 %) (Simoneit et al., 2004a) and tropical samples from India (ave. 4.50 %)  
652 (Fu et al., 2010). Biogenic SOA tracers contributed 0.18 to 3.99 % of OC (ave. 1.66 %),  
653 among which the contribution of isoprene-derived SOA tracers was high (ave. 1.28 %)  
654 followed by monoterpene (ave. 0.34 %) and sesquiterpene (ave. 0.03 %) SOA tracers. Other  
655 SOA tracers with minor contribution to OC include polyacids (ave. 0.08 %) and aromatic  
656 acids (ave. 0.02 %).

657 With the consideration of water-soluble dicarboxylic acids and related polar  
658 compounds measured in the same sample sets as reported in Deshmukh et al. (2018), the total  
659 organic compounds identified in the Alaskan aerosols accounted for 6.37 to 59.2 % with a  
660 mean of 21.4 % of OC. This result indicates that a substantial fraction of OAs studied in the  
661 Alaskan site can be identified at a molecular level.

#### 662 **4 Conclusions and implications**

663 We identified 96 organic compounds in PM<sub>2.5</sub> samples collected at Fairbanks in central  
664 Alaska during the summer campaign in 2009. Concentrations of total organic compounds  
665 ranged from 113 to 1664 (ave. 535 ng m<sup>-3</sup>). The most abundant compound classes in the  
666 Alaskan aerosol are anhydrosugars (ave. 186 ng m<sup>-3</sup>) and *n*-alkanoic acids (ave. 185 ng m<sup>-3</sup>).  
667 The temporal variations of anhydrosugars dramatically changed during the campaign,  
668 showing peaks during BB events. The similar temporal trends of lipids and strong correlations  
669 with levoglucosan demonstrated that local forest fires likely control the atmospheric levels of

670 OAs in central Alaska. The concentration ratios of levoglucosan to mannosan (2.2 to 6.8) and  
671 syringic to vanillic acid (0.02 to 0.5) suggest that **burning of softwood is common source** of  
672 OAs. The higher levels of HMW *n*-alkanoic acids and *n*-alkanols than their LMW  
673 homologues together with high CPI values of *n*-alkanes (5.2 to 9.9), *n*-alkanols (3.0 to 10) and  
674 *n*-alkanoic acids (5.6 to 9.8) further suggest that they were emitted by the thermal ablation of  
675 plant waxes during forest fire in central Alaska. The temporal patterns of mannitol and  
676 arabitol suggested that the rainfall play an important role to enhance their levels in central  
677 Alaska. The molecular compositions of phthalate esters displayed that diethyl phthalate is  
678 commonly used plasticizer in central Alaska. The molecular composition of biogenic SOA  
679 tracers with a predominance of isoprene-SOA tracers (ave. 41 ng m<sup>-3</sup>) suggested that isoprene  
680 is a crucial precursor of SOA over central Alaska. Our results provide valuable information to  
681 better understand the compositions of OAs and their sources and formation pathways in the  
682 subarctic atmosphere.

683         The Arctic is a critical region on the Earth with a significant warming and high  
684 sensitivity to climate forcing due to a strong effect on an albedo-sea ice feedback system. Our  
685 results substantiated that forest fires and plant emissions are important factors controlling the  
686 organic chemical composition of fine aerosol particles in central Alaska. It is worth therefore  
687 to note from the above discussion that the Fairbanks exemplifies many of the problems of  
688 pollution in the Arctic regions. The local and regional BB episodes in warmer season  
689 enhanced the atmospheric levels of OAs in central Alaska. Because residence time of fine  
690 particles is relatively long in the atmosphere, we propose that OAs of PM<sub>2.5</sub> at Fairbanks can  
691 be subjected to long-range transport to the Arctic causing a significant influence on the air  
692 quality and climate in the Arctic region. Although we studied the aerosol samples collected in  
693 2009, further research is needed to characterize the seasonal and interannual trends of OAs  
694 using more recent aerosol samples to better evaluate their current impact in the Arctic  
695 atmosphere.

696 *Data availability.* The data set of this paper is given in Table S1 in the supplement file.

697 *Author contributions.* KK designed the research. YK collected the aerosol samples. DKD and  
698 MMH analyzed the samples for organic tracer compounds. DKD evaluated the data and wrote  
699 the paper under the supervision of KK. All authors contributed to discussing results and  
700 commenting on the paper.

701 *Competing interests.* The authors declare that they have no conflict of interest.

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1165 **Table 1.** Concentrations (ng m<sup>-3</sup>) of organic tracer compound classes detected in PM<sub>2.5</sub>  
 1166 aerosols from central Alaska.

Compound classes	Minimum	Maximum	Mean	Median	S.D. <sup>a</sup>
Anhydrosugars	31	749	186	69	217
Lignin acids	0.5	15	3.8	2.2	4.2
Resin acid	0.9	19	6.1	5.1	4.7
<i>n</i> -Alkanes	0.5	77	24	21	23
<i>n</i> -Alkanols	5.3	119	46	29	38
<i>n</i> -Alkanoic acids	9.2	562	185	82	209
Primary sugars	0.3	44	13	12	11
Sugar alcohols	1.0	24	14	18	7.4
Phthalate esters	0.4	6.6	1.7	0.9	1.8
Aromatic acid	0.1	0.9	0.3	0.2	0.2
Polyacids	1.2	10	3.3	2.6	2.5
Isoprene oxidation products	2.0	142	41	20	43
Monoterpene oxidation products	1.0	36	9.2	7.0	8.7
Sesquiterpene oxidation products	0.1	3.4	0.9	0.3	1.0
Sum of all	113	1664	535	251	517

<sup>a</sup>Standard deviation

1167

1168 **Table 2.** Statistical summary for the linear regression among the organic tracers in PM<sub>2.5</sub>  
 1169 aerosols from central Alaska.

Linear regression	Correlation coefficient	Significance of correlation at P value < 0.05
Levogluconan vs. Mannosan	0.97	Significant
Levogluconan vs. Galactosan	0.94	Significant
Mannosan vs. Galactosan	0.95	Significant
Glucose vs. Fructose	0.91	Significant
Glucose vs. Sucrose	0.82	Significant
Fructose vs. Sucrose	0.94	Significant
Arabitol vs. Mannitol	0.95	Significant
Trehalose vs. Arabitol	0.85	Significant
Trehalose vs. Mannitol	0.74	Significant
DEP <sup>a</sup> vs. DBP <sup>b</sup>	0.85	Significant
DEP <sup>a</sup> vs. DiBP <sup>c</sup>	0.87	Significant
DEP <sup>a</sup> vs. DEHP <sup>d</sup>	0.71	Significant
DBP <sup>b</sup> vs. DiBP <sup>c</sup>	0.81	Significant
DBP <sup>b</sup> vs. DEHP <sup>d</sup>	0.88	Significant
DiBP <sup>c</sup> vs. DEHP <sup>d</sup>	0.75	Significant
C <sub>5</sub> -Alkene triols vs. 2-Methyltetrols	0.97	Significant
Glyceric acid vs. Tartaric acid	0.84	Significant
Glyceric acid vs. Citric acid	0.67	Significant
Tartaric acid vs. Citric acid	0.87	Significant
Benzoic acid vs. Glyceric acid	0.53	Not significant
Benzoic acid vs. Tartaric acid	0.39	Not significant
Benzoic acid vs. Citric acid	0.17	Not significant
Glyceric acid vs. isoprene SOA tracer	0.78	Significant
Tartaric acid vs. isoprene SOA tracer	0.75	Significant
Citric acid vs. isoprene SOA tracer	0.67	Significant

<sup>a</sup>Diethyl phthalate

<sup>b</sup>Dibutyl phthalate

<sup>c</sup>Diisobutyl phthalate

<sup>d</sup>Diethylhexyl phthalate

1170

1171 **Table 3.** Contributions (%) of individual organic compound classes to organic carbon (OC) in  
 1172 PM<sub>2.5</sub> aerosols from central Alaska.<sup>a</sup>

Compound classes	Minimum	Maximum	Mean	Median	Standard deviation
<b>Biomass burning tracers</b>					
Anhydrosugars	1.32	8.12	4.26	3.64	2.13
Lignin and resin acids <sup>b</sup>	0.03	0.51	0.14	0.11	0.13
Subtotal	1.35	8.35	4.40	3.71	2.24
<b>Lipid compounds</b>					
<i>n</i> -Alkanes	0.05	8.53	1.55	0.98	2.19
<i>n</i> -Alkanols	0.40	21.3	3.32	1.82	5.47
<i>n</i> -Alkanoic acids	0.67	15.9	7.48	6.71	4.80
Subtotal	1.16	45.8	12.4	9.20	11.3
<b>Primary biological aerosols</b>					
Primary sugars	0.05	0.85	0.39	0.50	0.26
Sugar alcohols	0.07	0.95	0.46	0.33	0.33
Subtotal	0.17	1.50	0.85	0.74	0.56
<b>Phthalate esters</b>					
Phthalate esters	0.02	1.07	0.14	0.05	0.28
Aromatic acid	0.01	0.09	0.02	0.01	0.02
Polyacids	0.02	0.25	0.08	0.09	0.06
<b>Biogenic SOA tracers</b>					
Isoprene oxidation products	0.07	3.20	1.28	0.83	1.12
Monoterpene oxidation products	0.07	0.75	0.34	0.34	0.20
Sesquiterpene oxidation products	0.02	0.04	0.03	0.03	0.01
Subtotal	0.18	3.99	1.66	1.22	1.29
Dicarboxylic acids and related compounds <sup>c</sup>	1.15	2.97	1.90	1.87	0.58
Total detected organic compounds	6.37	59.2	21.4	16.9	13.8

<sup>a</sup>All the organic compounds quantified were converted to carbon contents and then divided by OC. See Deshmukh et al. (2018) for OC and dicarboxylic acids and related compounds. <sup>b</sup>The results of lignin and resin acids were combined due to the very low contribution of resin acid to OC.

1173

1174 **Figure captions**

1175 **Figure 1.** The location of the sampling site at Fairbanks in central Alaska (64.51°N and  
1176 147.51°W) and its surrounding regions.

1177 **Figure 2.** The daily average variations of meteorological parameters from 5 June to 21  
1178 September 2009 at observation site in central Alaska.

1179 **Figure 3.** The air mass backward trajectories over the observation site during the collection of  
1180 aerosol samples. The color scale shows the height of the air parcel.

1181 **Figure 4.** Chemical compositions of organic compounds in PM<sub>2.5</sub> aerosols from central  
1182 Alaska. The sample collection periods are June 5-12 (Alaska 01), June 12-25 (Alaska 02),  
1183 June 25-July 04 (Alaska 03), July 04-06 (Alaska 04), July 06-14 (Alaska 05), July 14-23  
1184 (Alaska 06), July 23-30 (Alaska 07), July 30-August 04 (Alaska 08), August 04-08 (Alaska  
1185 09), August 08-25 (Alaska 10), August 25-31 (Alaska 11), August 31-September 10 (Alaska  
1186 12) and September 10-21 (Alaska 13) in 2009.

1187 **Figure 5.** Molecular distributions of anhydrosugars and lignin and resin acids in PM<sub>2.5</sub>  
1188 aerosols collected in central Alaska.

1189 **Figure 6.** Temporal changes in the concentrations of biomass burning tracers and other  
1190 organic compounds in the Alaskan aerosols.

1191 **Figure 7.** Molecular distributions of lipid compounds in PM<sub>2.5</sub> aerosols collected in central  
1192 Alaska. See Figure 5 for the description of the box-and-whisker diagram.

1193 **Figure 8.** Correlations of organic compounds with a biomass burning tracer levoglucosan in  
1194 the Alaskan aerosol samples.

1195 **Figure 9.** Molecular distributions of primary sugars and sugar alcohols in PM<sub>2.5</sub> aerosols  
1196 collected in central Alaska. See Figure 5 for the description of the box-and-whisker diagram.

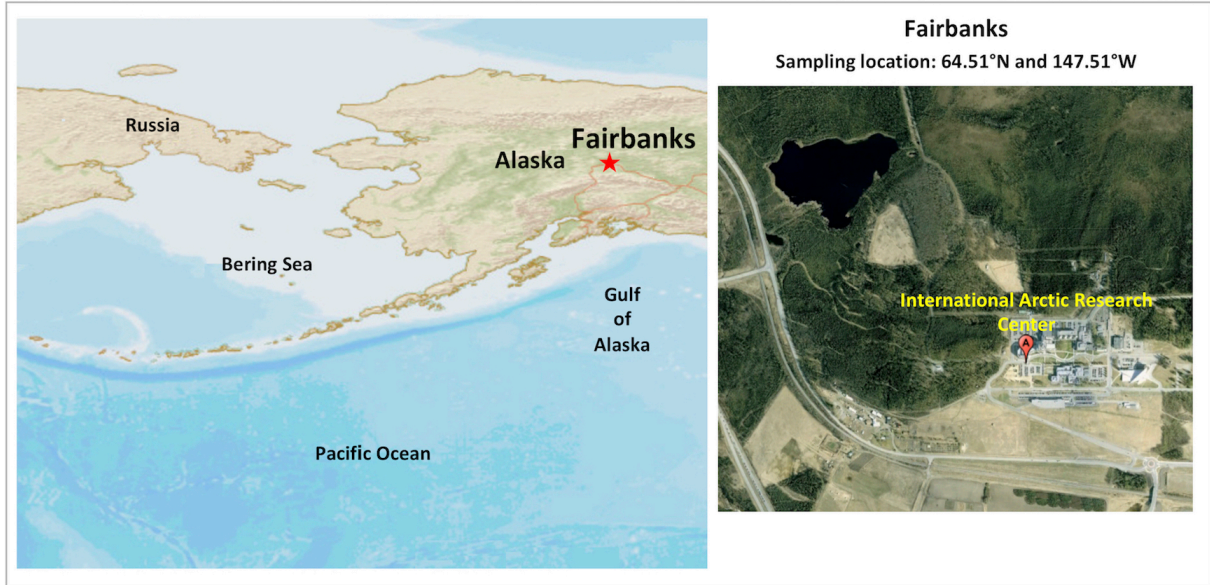
1197 **Figure 10.** Molecular distributions of phthalate esters in PM<sub>2.5</sub> aerosols collected in central  
1198 Alaska. See Figure 5 for the description of the box-and-whisker diagram.

1199 **Figure 11.** Temporal changes in the concentrations of phthalate esters and other organic  
1200 compounds in the Alaskan aerosols.

1201 **Figure 12.** Molecular distributions of biogenic secondary organic aerosol tracers in PM<sub>2.5</sub>  
1202 aerosols collected in central Alaska. See Figure 5 for the description of the box-and-whisker  
1203 diagram.

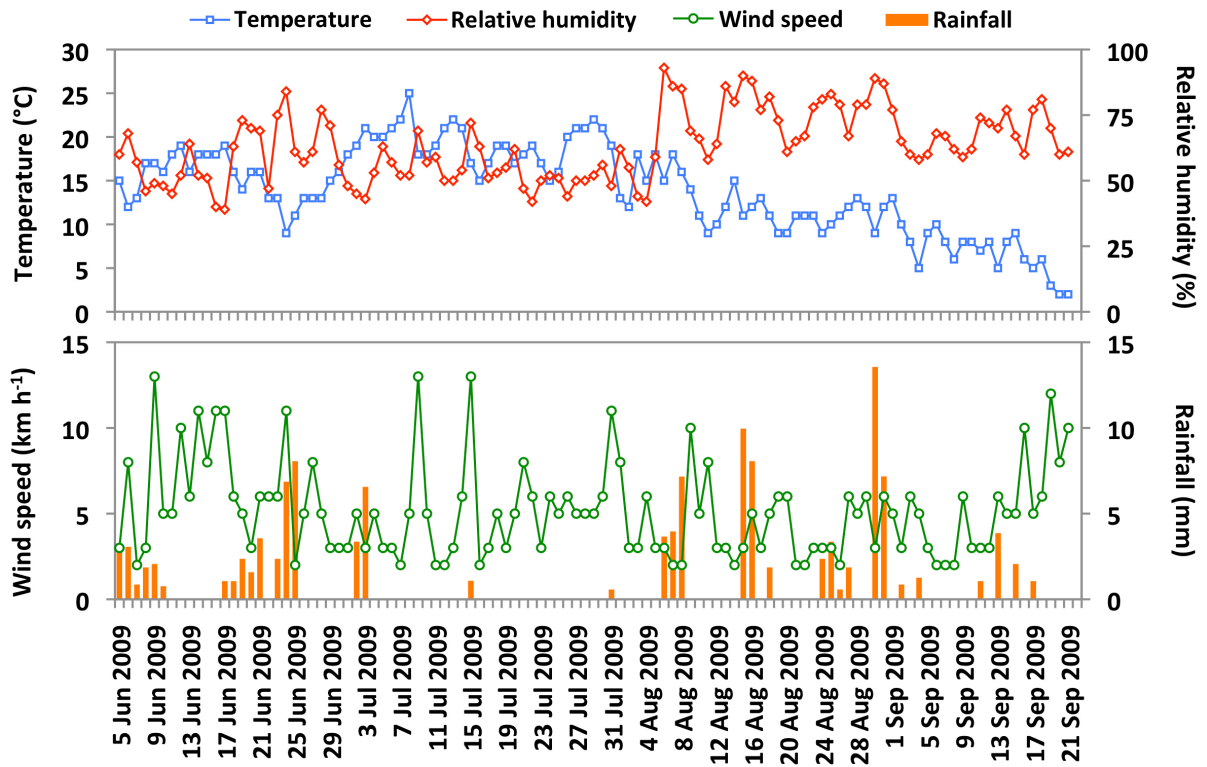
1204 **Figure 13.** Molecular distributions of aromatic and polyacids in PM<sub>2.5</sub> aerosols collected in  
1205 central Alaska. See Figure 5 for the description of the box-and-whisker diagram.

1206



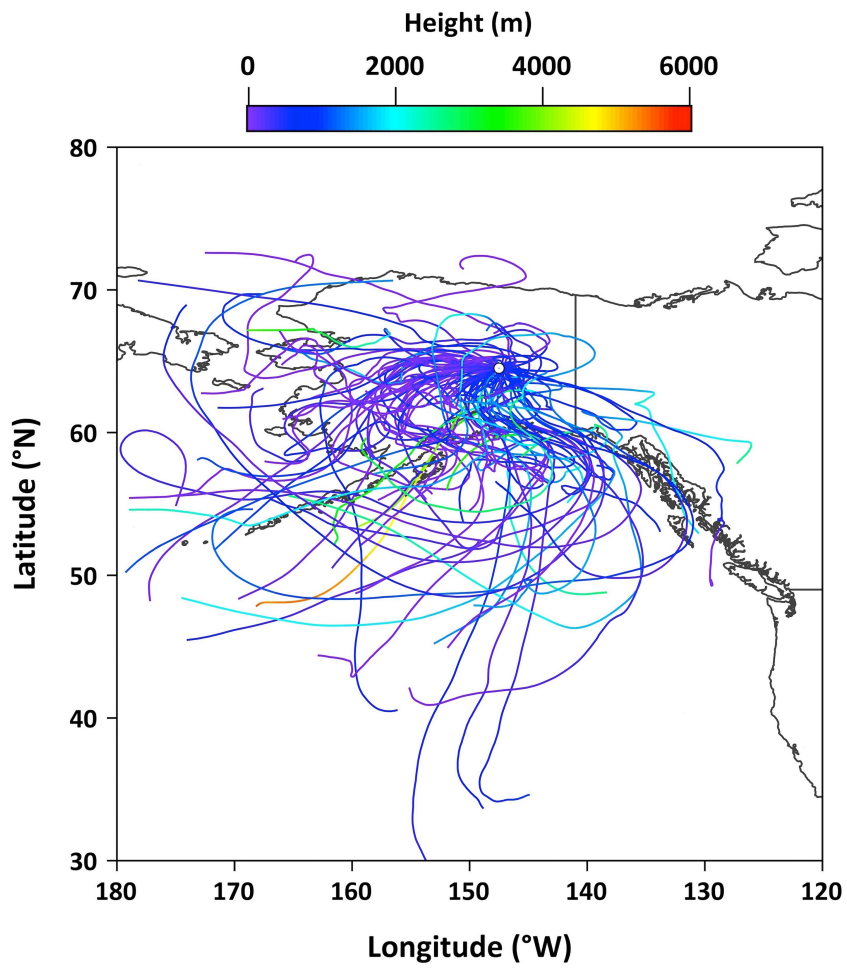
1207

1208 **Figure 1**



1209

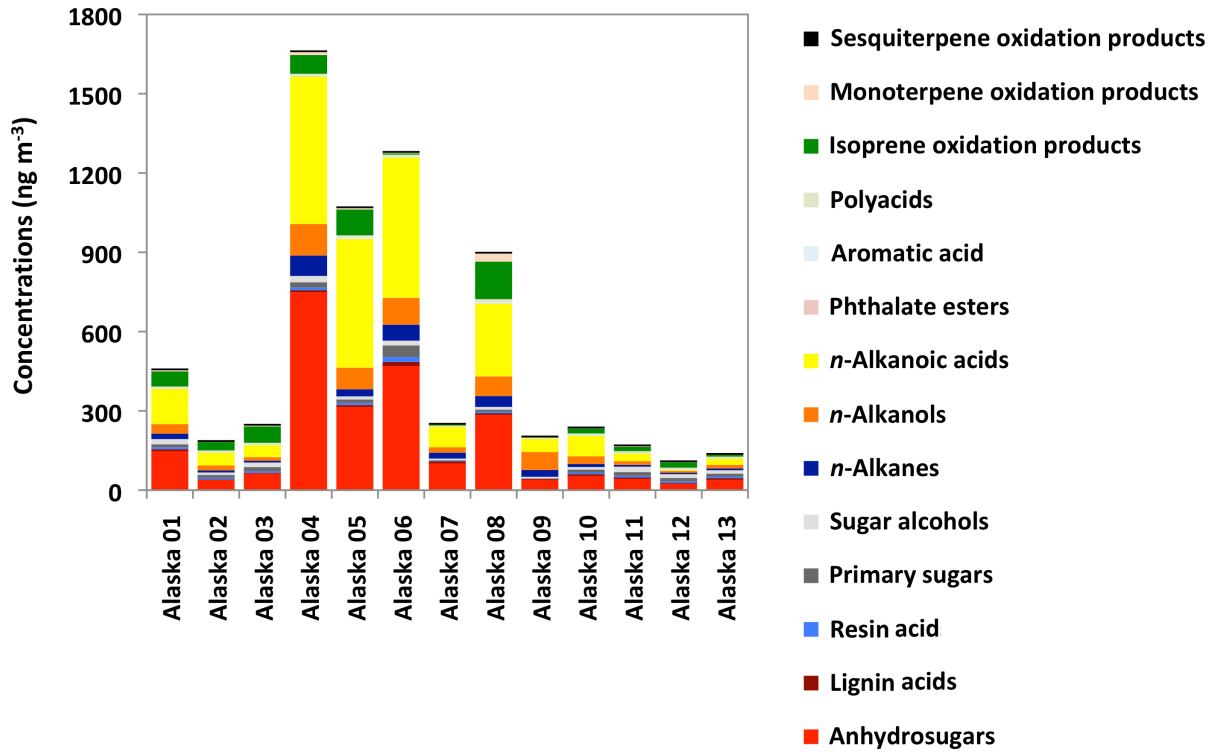
1210 **Figure 2**



1211

1212 **Figure 3**

1213

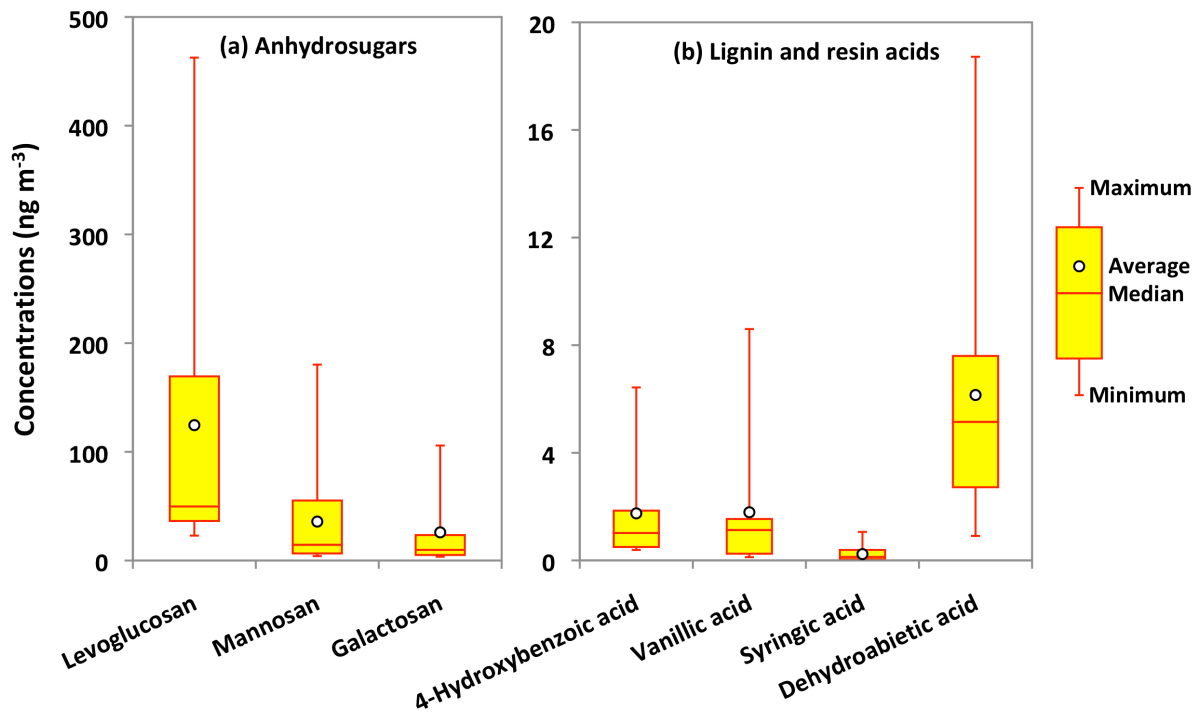


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1215 **Figure 4**

1216

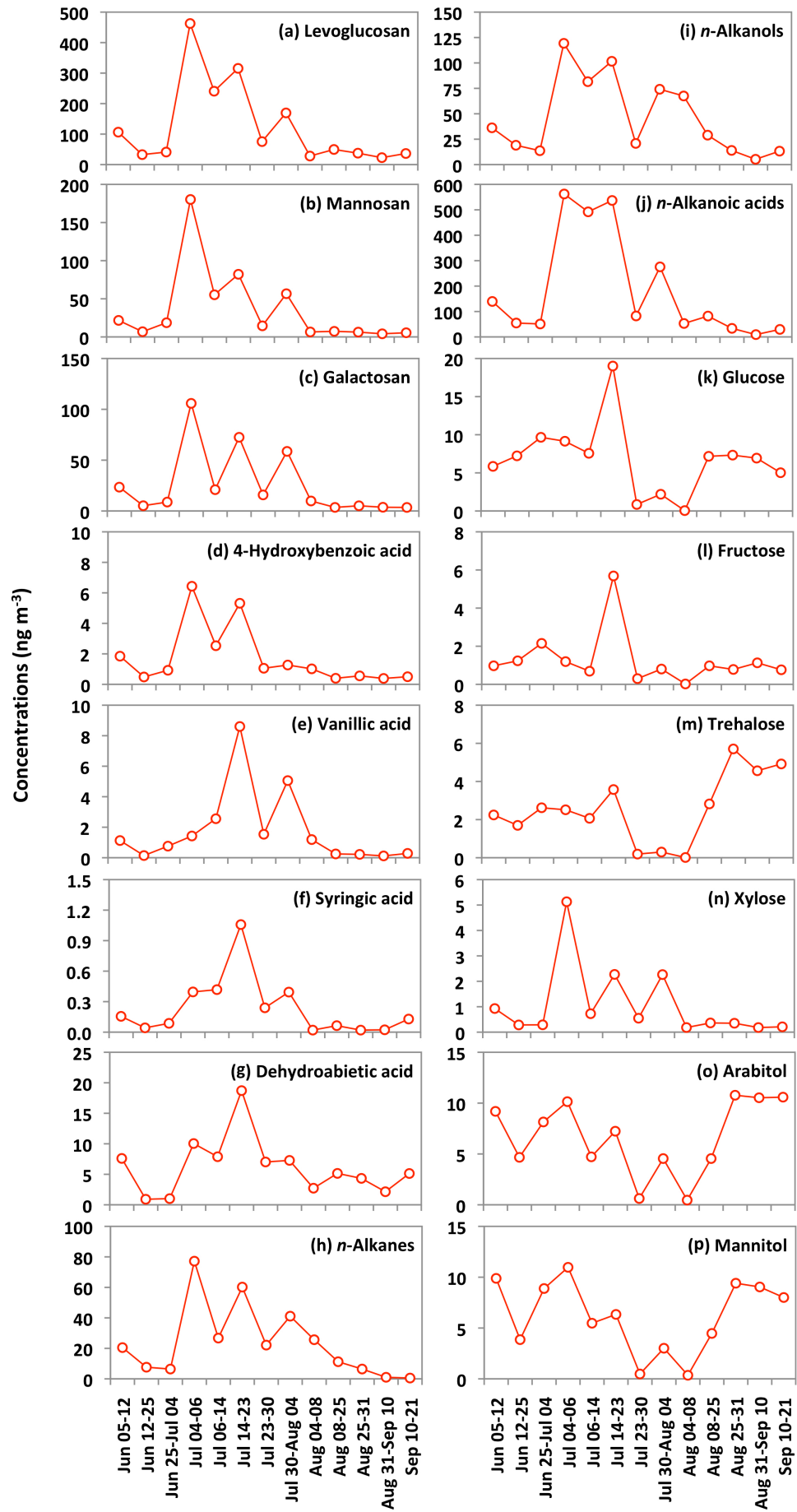
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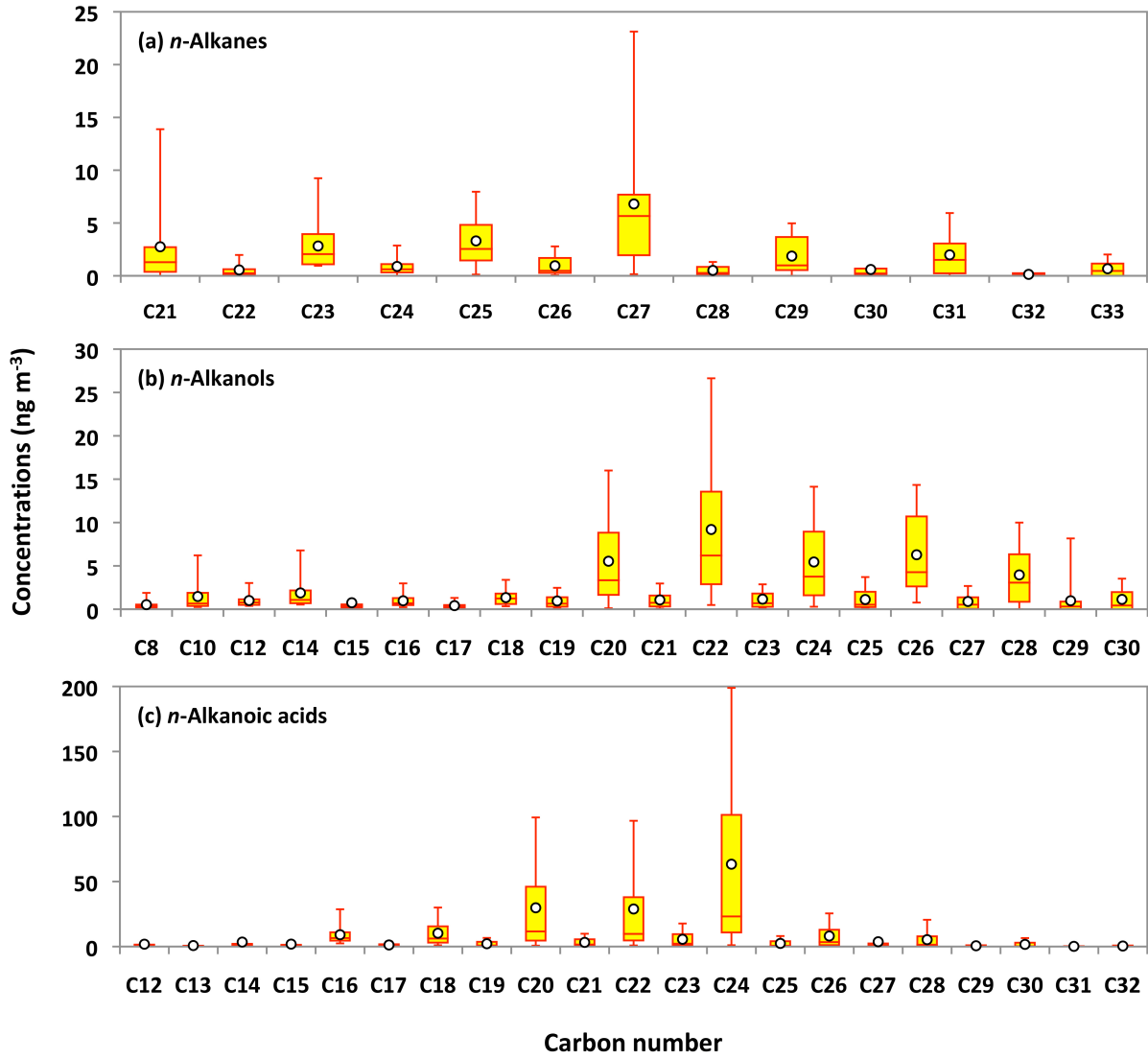
1219 **Figure 5**

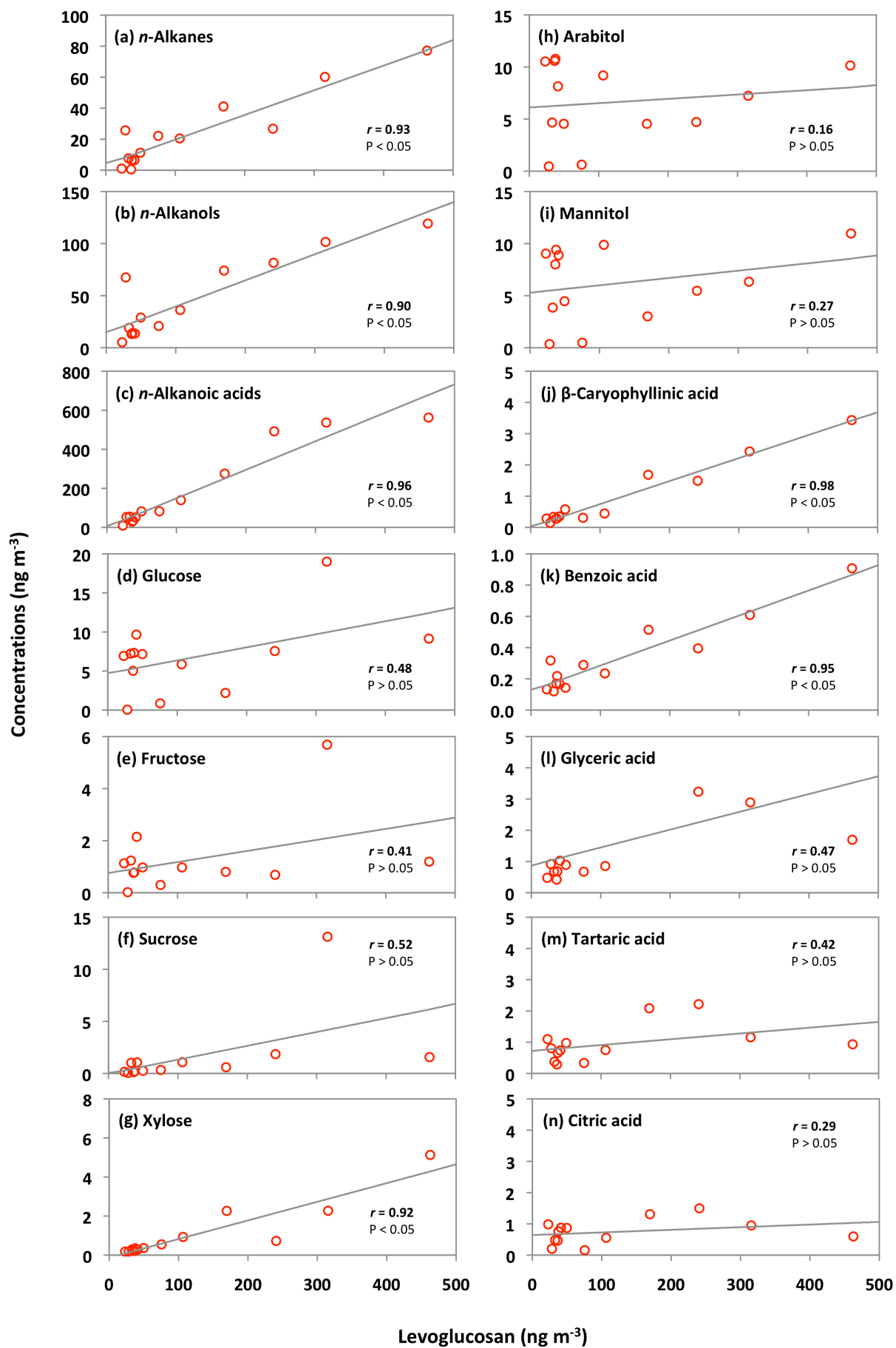




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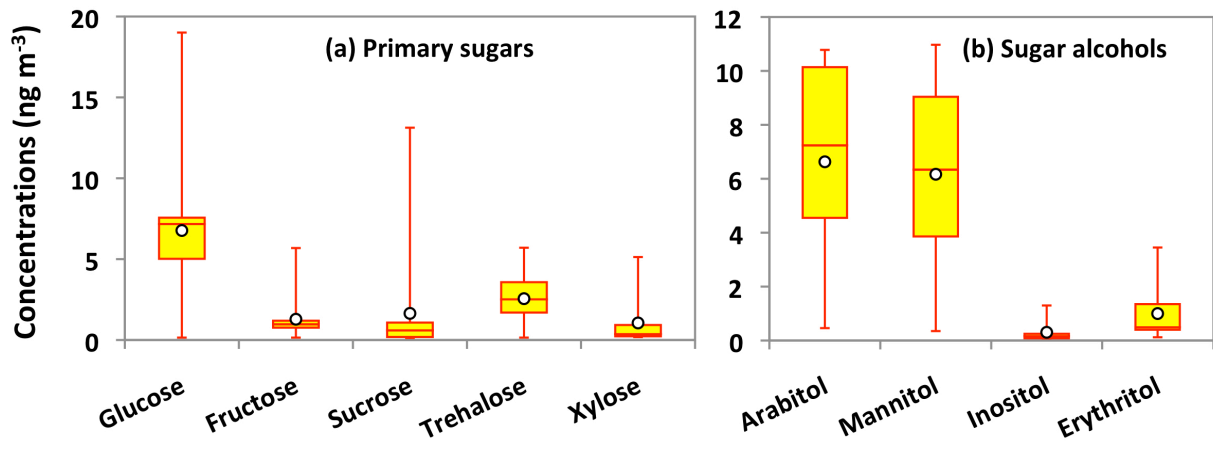
1221 **Figure 6**





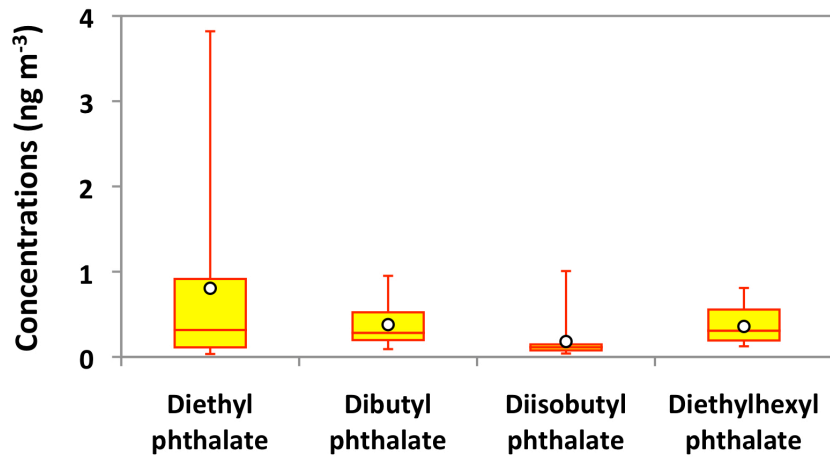
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1226 **Figure 8**



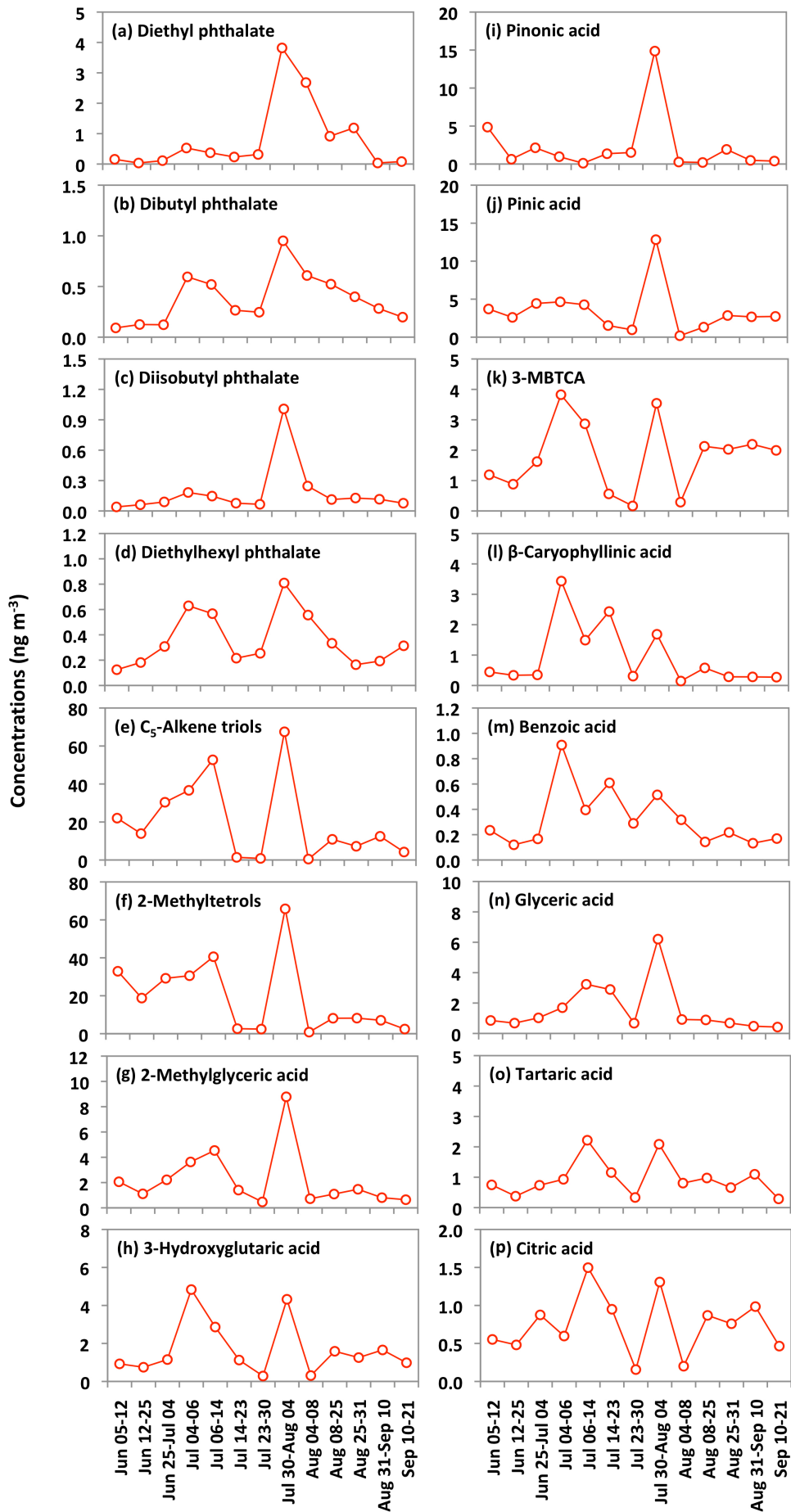
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1228 **Figure 9**



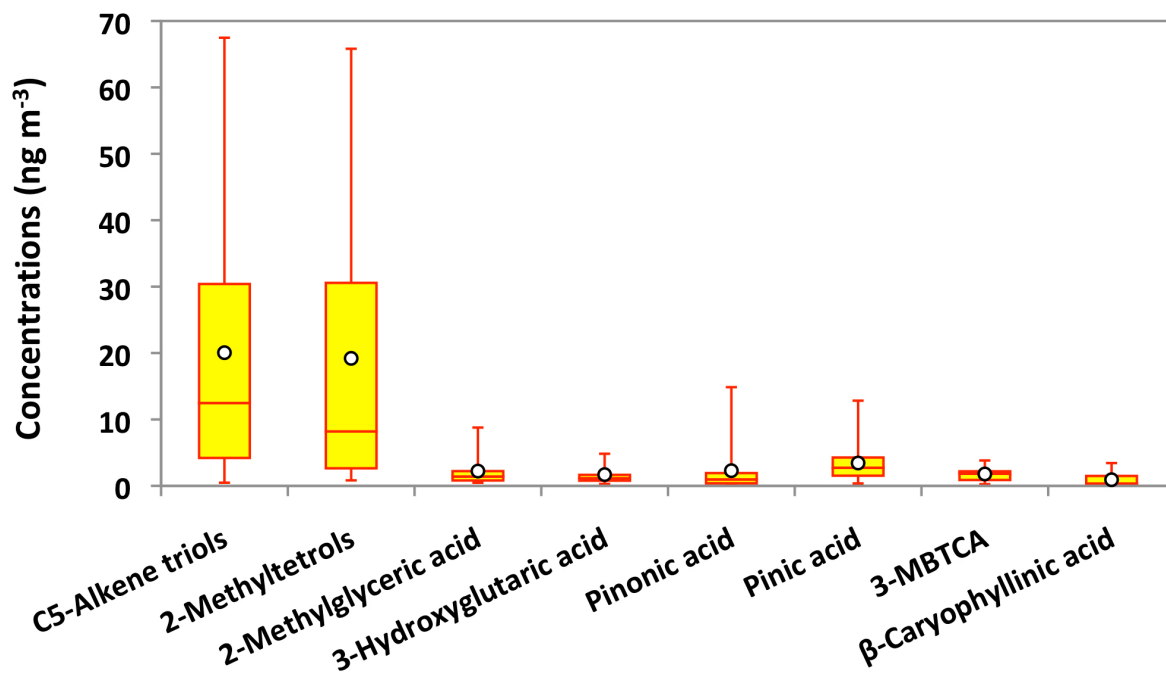
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1230 **Figure 10**

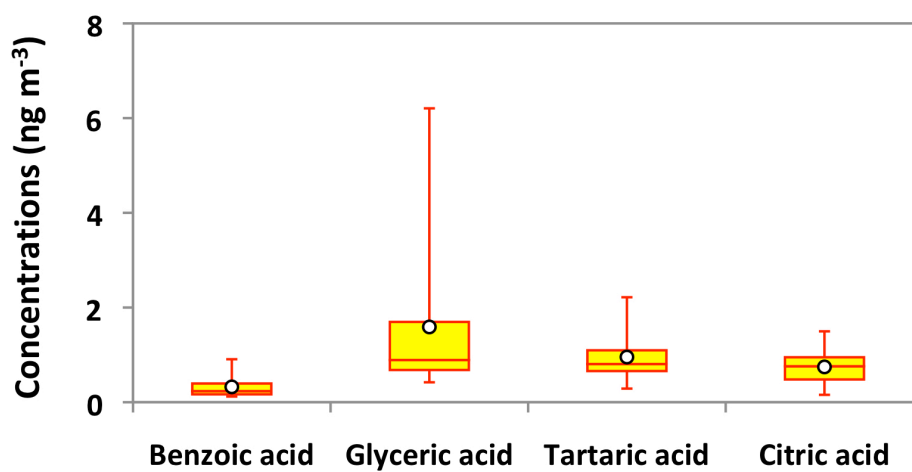


1231

1232 **Figure 11**



1233  
1234 **Figure 12**



1235  
1236 **Figure 13**