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Fungal spores overwhelm biogenic organic aerosols in a mid-latitudinal forest

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Abstract

Both primary biological aerosol particles (PBAP) and oxidation products of biogenic volatile organic compounds (BVOC) contribute significantly to organic aerosols (OA) in forested regions. However, little is known on their relative importance in diurnal time scales. Here, we report biomarkers of PBAP and secondary organic aerosols (SOA) for their diurnal variability in a temperate coniferous forest in Wakayama, Japan. Tracers of fungal spores, trehalose, arabitol and mannitol, showed significantly higher levels in nighttime than daytime ($p < 0.05$), resulting from the nocturnal sporulation under near saturated relative humidity. On the contrary, BVOC oxidation products showed higher levels in daytime than nighttime, indicating substantial photochemical SOA formation. Using tracer-based methods, we estimated that fungal spores account for 45% of organic carbon (OC) in nighttime and 22% in daytime, whereas BVOC oxidation products account for 15% and 19%, respectively. To our knowledge, we present for the first time highly time-resolved results that fungal spores overwhelmed BVOC oxidation products in contributing to OA especially in nighttime. This study emphasizes the importance of both PBAPs and SOAs in forming forest organic aerosols.

Keywords: primary biological aerosol particles; fungal spores; biological volatile organic compounds; organic aerosols.

1. Introduction

Biogenic particles and gases emitted from various vegetation types affect earth climate, biogeochemical cycles of carbon and nitrogen, air quality and human health. Particles such as fungal and fern spores, bacteria, viruses, algae, vegetation debris and pollen are directly emitted and thus termed as primary biological aerosol particles (PBAP) (Després et al., 2012; Elbert et al., 2007). Being mostly in the size range of 0.1–100 μm, PBAPs often contribute to a large mass fraction of organic aerosols (OA) but a small fraction of total particles (Pöschl et al., 2010). On the other hand, biogenic volatile organic compounds (BVOC) are highly reactive and thus subjected to photooxidation to form fine particles of secondary organic aerosols (SOA) and gas/particle partitioning of the reaction products (Claeys et al., 2004). There are substantial progresses in understanding the source strengths, composition and atmospheric transformations of biogenic particles, however, their contributions to OA and hence forces of their effects on climate are still uncertain.

Global PBAP emission is as high as 1000 Tg y^{-1} (Jaenicke, 2005). Fungal spore is the dominant component with the emission strengths of 8 to 186 Tg y^{-1} (Després et al., 2012; Elbert et al., 2007; Heald and Spracklen, 2009). Fungal spores (1–30 μm) could account for up to 45% of coarse particulate matter (Fröhlich-Nowoisky et al., 2009). In contrast, global bacteria emissions are much smaller with abundances of 0.04–1.8 Tg y^{-1} (Burrows et al., 2009). Pollen could contribute up to 65% of total PBAP mass in the flowering season, although their number contribution is only ~1% of total PBAP (Manninen et al., 2014). Certain PBAPs showed close correlations with atmospheric cloud condensation nucleus (CCN) and ice nucleus (IN) (Hiranuma et al., 2015; Huffman et al., 2013). However, simulations indicated that PBAPs are of regional importance for IN formation as they

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24   contribute very little to global average ice nucleation rates (Hoose et al., 2010; Spracklen and

25   Heald, 2014). Unveiling PBAP mass concentrations is necessary to provide benchmarks for

26   simulating its nucleation potentials and the effect on the climate.

27   The most widely studied BVOCs are isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$) and

28   sesquiterpenes ($C_{15}H_{24}$). Global emission of isoprene (309–706 Tg C yr^{-1}) accounts for ~50%

29   of total BVOC (Acosta Navarro et al., 2014; Guenther et al., 2006). Monoterpenes (~10% of

30   total VOCs) and sesquiterpenes are other important SOA precursors (Ziemann and Atkinson,

31   2012). Atmospheric oxidation of these BVOCs depends on oxidant levels (NO_x and O_3),

32   humidity, light and temperature. Recent studies indicated that biogenic SOA production could

33   be enhanced under the input of anthropogenic oxidants (Carlton et al., 2010). Under pristine

34   conditions, BVOC oxidation and SOA formation are often accompanied by new particle

35   formation, involving in precipitation through increasing CCN and IN numbers (Pöschl et al.,

36   2010). The formation of SOA is often in the fine particle size (Pöschl et al., 2010), however,

37   the relative importance of PBAPs and SOA in contributing to OA is still ambiguous.

38   Various observational methods have been applied to explore PBAPs and SOA in natural

39   environment both qualitatively and quantitatively. Applications of ultraviolet aerodynamic

40   particle sizers and wideband integrated bioaerosol sensor based on fluorescence provided

41   much information on the abundances and size distributions of PBAP (Huffman et al., 2010;

42   Pöhlker et al., 2012). In situ observations of SOA are frequently conducted using aerosol mass

43   spectrometer (AMS) (Zhang et al., 2007). Detections of organic tracer compounds using gas

44   chromatography combined with mass spectrometry (GC/MS) make it possible to compare

45   both PBAP and SOA sources simultaneously (Graham et al., 2003). Progresses are achieved in

46   boreal forest (Kourtchev et al., 2008) and the Amazon (Graham et al., 2003). However, few

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47   studies focused on the mid-latitudinal forest with high time resolution (Miyazaki et al., 2012;

48   Mochizuki et al., 2015).

49   In this study, we collected daytime and nighttime samples in a mid-latitude forest in

50   Wakayama, Japan and analyzed the organic samples for various PBAP and SOA tracers using

51   GC/MS. We report for the first time that fungal spores overwhelm BSOA in contributing to

52   aerosol organic carbon (OC). We also report diurnal variations of PBAP tracers that reflect the

53   natural rhythm of the forest.

54

55   **2. Experimental**

56   **2.1 Site and sampling**

57   Aerosol sampling was conducted in August 20–30, 2010 during a field campaign at

58   Wakayama Forest Research Station, Kyoto University, in the Kii Peninsula, Japan (34.07 °N,

59   135.52 °E, ca. 750 m above sea level) (Han et al., 2013; Han et al., 2014). The dominant

60   species of the forest vegetation are coniferous trees of *Cryptomeria japonica* (Japanese cedar),

61   *Chamaecyparis obtuse* (Japanese cypress) and *Pinus densiflora* (Japanese red pine). Previous

62   studies indicated that monoterpenes are abundantly emitted from these tree species

63   (Matsunaga et al., 2011; Mochizuki et al., 2011). Total suspended particulate (TSP) samples

64   were collected on pre-combusted (450 °C, 6 h) quartz filters (Pallflex 2500QAT-UP, 20 cm ×

65   25 cm) using a high–volume air sampler (Kimoto AS-810B) at a flow rate of ~60 L min^{-1} at

66   the ground level. During the campaign, four field blanks were collected following the

67   sampling procedures, except for the running of pump for only 10 seconds.

68   Nighttime (from ~18:00 to next ~6:00 local time, LT) and daytime (from ~6:00 to ~18:00

69   LT) samples were collected separately each day. Depending on the air mass origins, the

70   sampling period could be divided into two sub-periods. During August 20–25, air masses

71   originated from the Asian continent or passed over the Japanese islands brought pollutants

72   from anthropogenic sources, while during August 26–30 air masses originated from the

73   western North Pacific, which create an environment close to the pristine forest (Han et al.,

74   2013; Han et al., 2014). On August 23 and 28, samples were collected every 3 hours (namely,

75   6:00–9:00, 9:00–12:00, 12:00–15:00, 15:00–18:00, 18:00–21:00, 21:00–24:00, 24:00–3:00,

76   and 3:00–6:00 LT). A total of 36 samples were collected during the campaign.

77   **2.2 Chemical analysis**

78   For the determination of organic molecular tracers in aerosols, filter samples were first

79   extracted with dichloromethane/methanol and derivatized by N,O-bis-

80   (trimethylsilyl)trifluoroacetamide (BSTFA) mixed with pyridine to convert OH groups to

81   trimethylsilyl (TMS) ethers and COOH groups to TMS esters (Simoneit et al., 2004). Organic

82   compounds in the extracts were then quantified by GC/MS using an Agilent 7890A GC

83   equipped with HP-5ms capillary column (30 m × 0.25 mm × 0.25 μm) coupled to Agilent

84   5975C mass-selective detector (MSD). Individual compounds were identified by comparing

85   the mass spectra with those of authentic standards or literature data and quantified by

86   comparing the peak areas with the internal standard (C_{13} n-alkane) (Zhu et al., 2015b).

87   Recoveries for the authentic standards or surrogates were generally better than 80%, except for

88   pinonic acid of ~60%, as obtained by spiking standards to pre-combusted quartz filters

89   following extraction and derivatization. No peak was found for the target compounds in the

90   field and laboratory blanks. The analytical errors by duplicate analyses were less than 15%.

91   The detection limits of the reported compounds were 105–557 pg μl^{-1}, which correspond to

92   ambient concentrations of 12–64 pg m^{-3} under a typical sampling volume of 700 m^3 and usage

93   of 10 cm^2 filter section.

94   Aerosol OC was determined using a thermal/optical carbon analyzer (Sunset Laboratory

95   Inc., USA) following the Interagency Monitoring Protected Visual Environments (IMPROVE)

96   thermal evolution protocol (Birch and Cary, 1996). The analytical error in replicate analyses

97   was within 8%. Samples were corrected for field blanks, in which OC level was < 5% of the

98   samples. Inorganic ions were measured using an ion chromatograph (761 Compact IC,

99   Metrohm, Switzerland). SO_4^{2-} and NO_3^- were discussed in the study. The detection limits

100   were ~0.1 ng m^{-3}. The laboratory analytical error was within 5%. Samples were corrected for

101   field blanks.

102

103   **3. Results and discussion**

104   **3.1 PBAP tracers reflecting diurnal rhythm of fungal spores and pollen**

105   **3.1.1 Fungal spore tracers**

106   Four primary saccharides (trehalose, glucose, fructose and sucrose) and four sugar alcohols

107   (arabitol, mannitol, inositol and erythritol) were detected in the forest aerosols as PBAP

108   tracers. Trehalose, arabitol and mannitol were the major species of fungus and have been used

109   as tracers for fungal spores (Jia and Fraser, 2011). These compounds showed significantly

110   higher levels in nighttime (262 ± 168, 156 ± 102 and 349 ± 243 ng m^{-3} for trehalose, arabitol

111   and mannitol, respectively) than in daytime (128 ± 90.2, 76.0 ± 54.9 and 183 ± 139 ng m^{-3},

112   respectively) (T-test, $p < 0.05$, Figure 1d–f). High abundances of these fungal spore tracers

113   were resulting from the nocturnal sporulation under near saturated relative humidity (Figure

114   S1). In nighttime, the mean relative humidity was 96% in the sampling period. Nevertheless,

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115   the mean daytime relative humidity was still as high as 88%. Such a moist environment caused

116   enrichment of fungal spores and their discharges, resulting high abundances of their tracer in

117   aerosols. The sum of trehalose, arabitol and mannitol contributed to 70% of total PBAP tracer

118   mass, demonstrating an important role of fungi in regulating the land-atmosphere exchange in

119   the forest region.

120   Diurnal profiles of fungal spore tracers showed similar pattern on August 23 and August

121   28, two typical days representing regional and local phenomenon, respectively. Minima of

122   trehalose, arabitol and mannitol appeared around the noontime and increased dramatically in

123   the evening on both days (Figure 2). On August 23, fungal spore tracers peaked at 21:00–

124   24:00 LT and decreased slowly thereafter. In comparison, these compounds peaked slightly

125   earlier at 18:00–21:00 LT on August 28. The maxima of these compounds on August 23 were

126   higher by a factor of ~1.5 than those on August 28. This phenomenon was likely related to the

127   precipitation that occurred at 13:00–17:00, August 23 (Figure S1), which favors the growth

128   and release of fungal spores.

129   **3.1.2 Other PBAP tracers and levoglucosan**

130   Sucrose, a key component of pollen grain (Yttri et al., 2007), showed significantly higher

131   levels ($p < 0.01$) in daytime (31.9 ± 17.7 ng m^{-3}) than nighttime (14.6 ± 14.2 ng m^{-3}) (Figure

132   1c). The diurnal profile of sucrose showed peaks in the afternoon (Figure 2a), indicating that

133   the flowering time of the vegetation. As the blossom season of the dominant coniferous trees

134   is March–April in the region, the source of sucrose is likely from the pollen of the widely

135   distributed floor vegetation, *Ambrosia artemisiifolia*, *Artemisia indica*, and plants of *Poaceae*

136   family, which are flowering during the sampling period.

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137   Glucose and fructose are originated dominantly from plant debris (Medeiros et al., 2006;

138   Zhu et al., 2015a), and sometimes from microorganisms and soil dust (Rogge et al.,

139   2007;Simoneit et al., 2004). There was no serious continental outflow of Asian dust over the

140   sampling period (based on observations by Japan Meteorological Agency). Insignificant

141   diurnal variations of these two compounds imply that they were emitted ubiquitously in the

142   forest possibly from plants and microorganisms (Figure 1a–b, 2a). Interestingly, the mass

143   concentrations of glucose were one order of magnitude higher than those of fructose. This

144   might be related to the higher abundance of glucose in trees. For example, tissues of a wide

145   range of subtropical plants were found to contain more glucose than fructose (Baker et al.,

146   1998).

147   Being exclusively produced by the thermal depolymerization and dehydration of cellulose

148   and hemicellulose, levoglucosan has been used as a specific tracer for biomass burning

149   (Simoneit et al., 1999; Zhu et al., 2015b). Levoglucosan showed significantly higher levels (p

150   < 0.05) in daytime (2.52 ± 2.08 ng m^{-3}) than nighttime (1.14 ± 0.94 ng m^{-3}). Moreover, we

151   found higher levels of levoglucosan in August 20–25 (2.97 ± 1.64 ng m^{-3}) than August 26–30

152   (0.53 ± 0.44 ng m^{-3}); those concentrations in the latter period are close to the regional

153   background level from Okinawa Island (Zhu et al., 2015b). Given the location of Wakayama

154   forest in the Kii Peninsular, the sea-land breeze system is very likely to deliver clean maritime

155   air masses to the sampling site in daytime and drainage airflow from the Japanese islands in

156   nighttime. The diurnal variation of levoglucosan with daytime maxima in the Wakayama

157   aerosols indicates that the Asian outflow of biomass burning emissions approached to the

158   sampling site. In addition, local burning activities could also contribute to the daytime

159   elevation of levoglucosan although they might be insignificant.

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160 3.1.3 Daytime abundances of SOA tracers

161 A total of 11 compounds were detected as SOA tracers. Six isoprene-tracers, including 2-

162 methylglyceric acid (MGA), two 2-methyltetrols (2-methylthreitol and 2-methylerythritol,

163 MTLs), and three C5-alkene triols (3-methyl-2,3,4-trihydroxy-1-butene, cis-2-methyl-1,3,4-

164 trihydroxy-1-butene and trans-2-methyl-1,3,4-trihydroxy-1-butene, MTHBs), showed higher

165 levels in daytime (Figure 1j–l). Similar daytime abundances were also found for 4

166 monoterpene-tracers; pinonic acid (PNA), pinic acid (PA) ($p < 0.05$), 3-hydroxyglutaric acid

167 (HGA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (Figure 1m–p). Total isoprene-

168 SOA tracers (281 ± 274 and 199 ± 207 ng m^{-3} in daytime and nighttime, respectively) were

169 more abundant by a factor of ~5 than total monoterpene-SOA tracers (54.6 ± 50.2 and $36.3 \pm$

170 33.6 ng m^{-3}, respectively). Isoprene is more abundantly emitted than monoterpenes from this

171 coniferous forest. This is consistent with the observations at a mountain site in central Japan

172 (Fu et al., 2014). Sesquiterpene-tracer, caryophylinic acid, showed consistently low levels in

173 both daytime (1.22 ± 1.23 ng m^{-3}) and nighttime (0.94 ± 0.83 ng m^{-3}) (Figure 1q). The

174 daytime abundances of isoprene- and monoterpene-tracers reflected the production of SOA by

175 the photooxidation of BVOC in the forest.

176 3.2 Influence of anthropogenic oxidant on SOA formation

177 The diurnal profile of SOA tracers showed a clear single peak pattern in the afternoon on

178 August 28–29. Total isoprene-tracers peaked at 15:00–18:00 (28.4 ng m^{-3}), while total

179 monoterpene-tracers peaked slightly earlier at 12:00–15:00 (12.7 ng m^{-3}) (Figure 2c–d). Their

180 afternoon peaks are consistent with the maxima of ambient temperature and solar radiation

181 (Figure S1). These results indicate that SOA is formed by photooxidation of isoprene and

182 monoterpenes emitted from local vegetation under natural conditions. Our results are

183   consistent with the afternoon peaks of semi-volatile oxygenated organic aerosol (SVOOA)

184   component determined by the positive matrix factorization of the AMS spectra collected

185   during the same campaign (Han et al., 2014), which were produced by photooxidation of

186   freshly emitted BVOC from the local forest.

187   Interestingly, on August 23–24, days with regional anthropogenic oxidant input, isoprene-

188   and monoterpene-tracers showed not only afternoon peaks at 12:00–15:00, but also nighttime

189   peaks (Figure 2c–d) following the intensive precipitation during 13:00–17:00 (Figure S1).

190   These results suggest that SOA is continuously produced even in nighttime with sufficient

191   oxidants. AMS observation in the same campaign indicated that highly oxidized low volatility

192   oxygenated organic aerosols (LVOOA) are even more abundant than that of SVOOA on

193   August 23–24, especially in nighttime (Han et al., 2014). Nighttime production of SOA was

194   also observed in the United States (US) (Zhao et al., 2013).

195   Moreover, on days with regional input of oxidants, the SOA tracer levels were 1–2 orders

196   of magnitude higher than those under natural conditions both in daytime and nighttime.

197   Meanwhile, we found positive relations between SO_4^{2-} and isoprene-SOA tracers as well as

198   monoterpene-SOA tracers (Table 1). These phenomena could be explained by the following

199   reasons. Firstly, regional BSOA could be transported along with anthropogenic oxidants.

200   Observations at Okinawa island, southern Japan indicated that the variations of monoterpene-

201   SOA tracers and caryophylinic acid are related to the continental outflow of BVOC oxidation

202   products (Zhu et al., 2016). Secondly, the earlier generation products of BVOC oxidation tend

203   to shift to the particle phase during gas/particle partitioning given their semivolatility nature

204   (Cahill et al., 2006), such a shift might be more prominent on days with aged regional aerosols

205   accompanied by a daytime increase of organics determined by AMS (Han et al., 2014). The

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206   third possibility is that the anthropogenic oxidants might promote BSOA formation. We focus

207   on the third possibility and further testified this hypothesis.

208   We examined the degrees of BSOA tracer buildups in daytime as compared to nighttime

209   (ΔBSOA = mean daytime BSOA tracer levels – mean nighttime BSOA tracer levels) (Table

210   2). ΔBSOA values on August 20–25 were higher by more than 1 order of magnitude than that

211   on August 26–30. These results implied that, although transported BSOA might contribute to

212   their elevation, anthropogenic oxidants substantially promoted the SOA formation in

213   Wakayama forest. A recent field study in the southeastern US suggested that the formation of

214   methyltetrols is mediated by SO_4^{2-}, being consistent with our results (Xu et al., 2015). They

215   also reported that $NO_3^{\bullet}$ radical was involved in the nighttime monoterpene oxidation.

216   However, inorganic NO_3^- did not correlate with monoterpene-SOA tracers during nighttime,

217   indicating that the contribution of $NO_3^{\bullet}$ radical to nighttime monoterpene oxidation is not

218   clear in Wakayama aerosols.

219   **3.3 OC fractions from fungal spores and BVOC oxidation**

220   The contributions of each source component to OC were estimated using tracer-based

221   methods. OC fractions from fungal spores were estimated based on mannitol levels assuming

222   that there were 1.7 pg mannitol and 13 pg OC per spore (Bauer et al., 2008). The secondary

223   organic carbon (SOC) fraction resulting from VOC oxidation was estimated following

224   Kleindienst et al. (2007) based on the chamber experiment. Contributions of plant debris to

225   OC were estimated based on glucose following Puxbaum and Tenze-Kunit (2003).

226   Contributions of biomass burning aerosols to OC were estimated based on levoglucosan

227   following Zhu et al. (2015b). It is noteworthy that, although each tracer methods gave a

228   reasonable estimate in the original studies, uncertainties would be introduced in the current

229 study considering the site differences. Still, the estimations are inferable for the contributions

230 from each source to OC in the forest aerosols.

231   Fungal spores contribute a major fraction (45%) to OC in nighttime. In daytime, although

232 the mass fraction was about half to that in nighttime (22%), fungal spores are still the largest

233 known source of OC (Figure 3). In comparison, BVOC oxidation products (BSOC) contribute

234 to 15% and 19% of OC in nighttime and daytime, respectively. Interestingly, the large BSOC

235 fraction of OC mainly occurred on days with anthropogenic influences (August 20–25) (17%

236 in daytime and 23% in nighttime). On days close to natural conditions (August 26–29), BSOC

237 has a small contribution to OC (4.0% in nighttime and 4.7% in daytime). The larger

238 contributions of BSOC to OC might be associated with the BSOC that are transported from

239 the Asian continent, a stimulating effect of anthropogenic oxidants on daytime BSOA

240 formation, as well as the enhanced gas to particle conversion of BVOC. These results suggest

241 that increased fossil fuel combustion and the subsequent oxidant emissions would cause a

242 larger contribution of BSOA to OA, which may in part compensate the human-caused global

243 warming by acting as CCN. Such effects are supposed to be incorporated into model

244 simulations of the future climate in the Anthropocene.

245   It is noteworthy that the contribution of plant debris to OC (5.6% in nighttime and 4.6% in

246 daytime) could not be neglected. These fractions account for only the primary OC sources

247 based on glucose level, and could be underestimated. Significant fractions of OC (34% and

248 51%) of are not determined in nighttime and daytime, respectively. Other than the

249 uncertainties introduced by the tracer methods, a notable fraction of OC could be contributed

250 from humic-like substances that are chemically and physically similar with terrestrial and

251 aquatic humic and fulvic acids (Graber and Rudich, 2006). Mono- and di-carboxylic acids,

252   originating from a broad range of primary organic compounds, could contribute 38–44% of

253   OC (Legrand et al., 2013). Pollen could also contribute to OC because of its large size.

254   Amines are another source of OC, but not well studied (Sintermann and Neftel, 2015). These

255   sources from various sectors need to be further characterized for an unambiguous

256   understanding of the sources of forest aerosols.

257   Among few studies on the observation-based quantification of OC/OA sources of forest

258   aerosols, our results are in accordance with those in the Amazon rainforest, where primary

259   biological aerosol and SOA accounted for 68.5% and 18.8% of total particle masses, without

260   consideration of the diurnal variations (Pöschl et al., 2010). At an urban site with various OA

261   sources, Bakersfield, California, Zhao et al. (2013) reported that SOA accounted for 78% and

262   66% of OA during the daytime and the nighttime, respectively, while primary sources

263   accounted for 15% of OA. Under a changing climate and uncertain anthropogenic emission

264   scenario, although OA could be contributed by complicated sources in a pristine forest

265   environment, our results demonstrate that biogenic particles and gases are rather the major

266   sources of organic aerosols in the forest atmosphere.

267

268   **4. Conclusions**

269   We collected daytime and nighttime samples in a mid-latitude coniferous forest in

270   Wakayama, central Japan. Focusing on fungal spores and BSOA, we quantified organic

271   tracers containing information of various aerosol sources. Nighttime higher levels of trehalose

272   and sugar alcohols were clarified under near saturated relative humidity, indicating the

273   flourishing of fungal sporulation. BSOA tracers were more abundant in the daytime, indicating

274   their photooxidation production among other sources. Enhanced BSOA tracer levels were

275   observed on days with notable input of anthropogenic oxidant. Using tracer-based methods,

276   we estimated that fungal spores contribute dominantly to OC in forest aerosols not only in the

277   nighttime, but also in the daytime. The study emphasizes the importance of fungal spores in

278   affecting biogenic aerosols in forest ecosystem.

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294   **References**

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449 Table 1. Linear correlation coefficients (r) between secondary organic aerosol tracers and

450 NO_3^- and SO_4^{2-} in forest aerosols during August 20–30, 2010, Wakayama, central Japan.

		MGA [a]	C5T	MTLs	Isoprene tracers	3-HGA	MBTCA	PA	PNA	Monoterpene tracers
NO_3^-	All dataset	0.08	-0.13 [b]	-0.06	-0.09	-0.11	-0.01	-0.02	0.18	-0.06
	Daytime	-0.07	-0.26	-0.15	-0.2	-0.27	-0.22	-0.25	0.01	-0.25
	Nighttime	-0.32	-0.36	-0.34	-0.35	-0.30	-0.18	-0.33	-0.19	-0.27
SO_4^{2-}	All dataset	0.84[***][c]	0.87[***]	0.84[***]	0.86[***]	0.91[***]	0.9[***]	0.70[***]	0.65[***]	0.91[***]
	Daytime	0.86[***]	0.89[***]	0.84[***]	0.88[***]	0.91[***]	0.92[***]	0.76[**]	0.67[**]	0.92[***]
	Nighttime	0.82[***]	0.82[***]	0.82[***]	0.83[***]	0.90[***]	0.86[***]	0.53[*]	0.58[*]	0.89[***]

452 [a] Secondary organic aerosol tracer compounds are as follows: MGA, 2-methylglyceric acid; C5T, C5-alkene

453 triols; MTLs, 2-methyltetrols; PA, pinic acid; PNA, pinonic acid; 3-HGA, 3-hydroxyglutaric acid, MBTCA, 3-

454 methyl-1, 2, 3-butanetricarboxylic acid.

455 [b] Negative values indicate negative correlations.

456 [c] [*], $p < 0.05$; [**], $p < 0.01$; [***], $p < 0.001$.

457

458

459   Table 2. Daytime buildups (differences between daytime and nighttime levels) of SOA tracers

460   on days with (August 20–25) and without (August 26–30) input of anthropogenic oxidants in

461   forest aerosols, Wakayama, central Japan.

Period	MGA [a]	C5T	MTLs	Isoprene tracers	3-HGA	MBTCA	PA	PNA	Monoterpene tracers	CPA	BSOA tracers
August, 20–25	2.06	47.1	60.9	110	14.1	12.0	3.31	1.52	30.9	0.10	141
August, 26–30	0.02	1.73	2.33	4.08	0.16	0.22	0.37	1.18	1.93	0.51	6.53
August, 20–30	1.17	27.2	35.3	63.7	7.98	6.87	2.03	1.37	18.2	0.28	82.2

462   [a] Secondary organic aerosol tracer compounds are as follows: MGA, 2-methylglyceric acid; C5T, C5-alkene

463   triols; MTLs, 2-methyltetrols; PA, pinic acid; PNA, pinonic acid; 3-HGA, 3-hydroxyglutaric acid, MBTCA, 3-

464   methyl-1, 2, 3-butanetricarboxylic acid; CPA, β-caryophyllinic acid; BSOA tracers are the some of isoprene-,

465   monoterpene- and sesquiterpene- (CPA) tracers.

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467   **Figure captions**

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469   Figure 1. Diurnal variations of organic compounds in forest aerosols in Wakayama, Japan

470   during August 20–30, 2010. The 10th, 25th, 50th, 75th, and 90th percentiles of the nighttime

471   and daytime samples were shown in the box-whisker plot. The means were shown in solid

472   circles. Statistically significances were also shown (T-test, *, $p < 0.05$; **, $p < 0.01$).
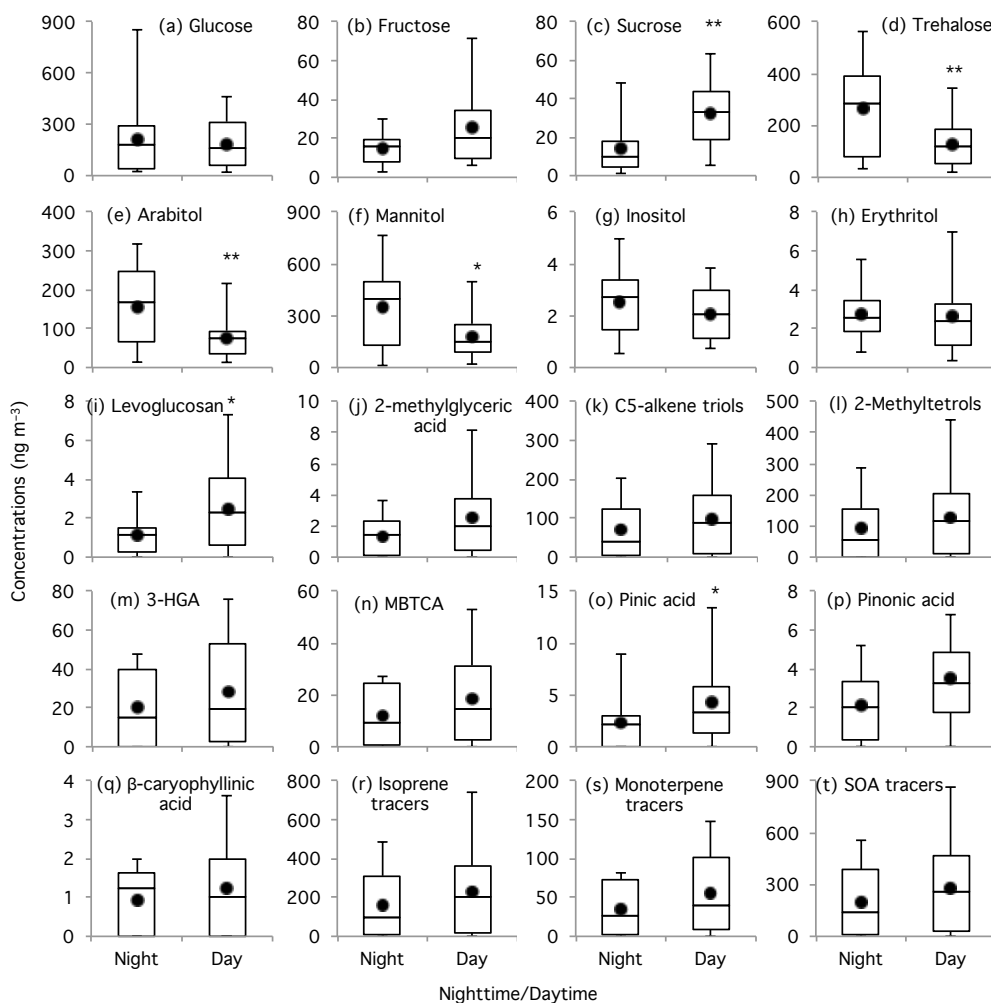
473

474   Figure 2. Diurnal profiles of organic compounds in forest aerosols in Wakayama on August

475   23–24 (left) and August 28–29, 2010 (right).

476

477   Figure 3. Contributions from different sources to organic carbon in Wakayama forest aerosols
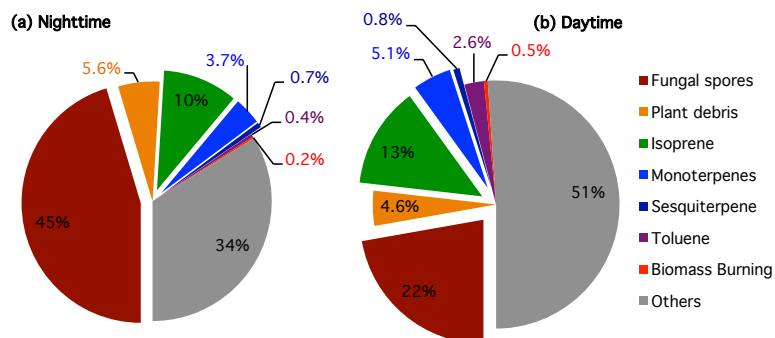
478   during the nighttime and the daytime.

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Figure 1. Diurnal variations of organic compounds in forest aerosols in Wakayama, Japan

during August 20–30, 2010. The 10th, 25th, 50th, 75th, and 90th percentiles of the nighttime

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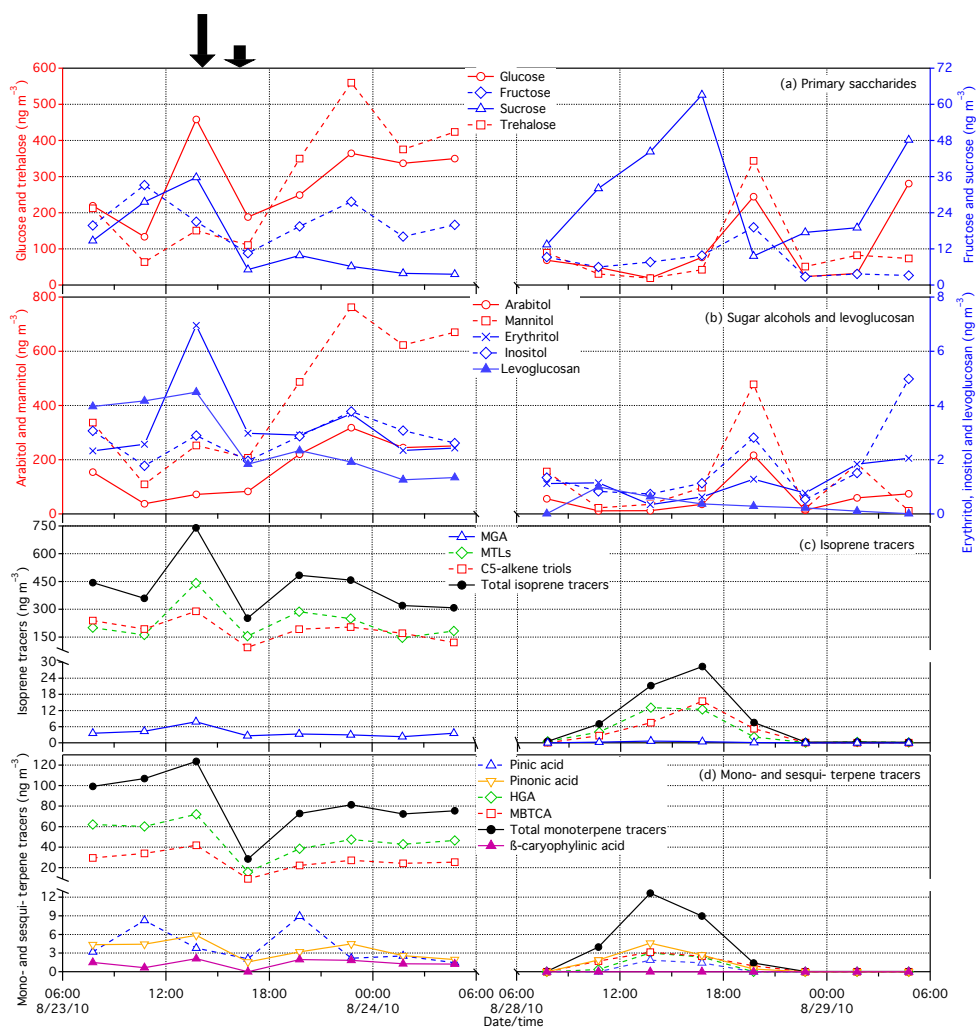
Figure 2. Diurnal profiles of organic compounds in forest aerosols in Wakayama on August

23–24 (left) and August 28–29 (right), 2010. Precipitation events occurred on 13:00–14:00

(11.2 mm) and 15:00–17:00 (1.5 mm) local time, August 23 as were marked by arrows on top

of the left panels.

491

492   Figure 3. Contributions from different sources to organic carbon in Wakayama forest aerosols

493   during the nighttime and the daytime.

494