Authors' Responses to Referees' Comments

Anonymous Referee #1

The manuscript "Fungal spores overwhelm biogenic organic aerosols in a mid- latitudinal forest" describes biomarkers of PBAP and secondary organic aerosols (SOA) for their diurnal variability in a temperate coniferous forest in Wakayama, Japan. This paper, present for the first time highly time-resolved results that fungal spores overwhelmed BVOC oxidation products in contributing to OA especially in nighttime. In general, this manuscript is well organized and the discussion is reasonable. Thus, I believe it can be accepted after a minor revision.

Response: We are grateful to the referee for the positive evaluation on our work. We have adopted most of the comments to improve the manuscript substantially.

Major comments:

(1) Updating the references used in this manuscript to more current state is suggested.

Response: We have checked and updated the references to the up-to-date versions as suggested.

(2) Experimental section should include detailed information about the statistical analysis conducted in the manuscript.

Response: We added the following paragraph describing statistical analysis methods in L143-148 in the revision:

"Statistical significances of daytime and nighttime organic tracers were evaluated based on Student's t-test at $p < 0.05$ and $p < 0.01$ level, respectively. To explore the effects of anthropogenic pollutant inputs on BSOA formation, linear correlations (Pearson) between SOA tracers and NO_3^- and SO_4^{2-} where investigated. The contributions from various sources to OC were estimated using tracer-based methods using conversion factors according to the preceding studies".

(3) Line 105: A stability study for molecules should be added, for how kept the quartz samples and how long and where kept the liquid samples before analysis?

Response: Each of the quartz samples were kept in a sealed glass jar at < –20 °C during transport (see the following photo of sample storage in the field, the actually temperature was –27.3°C). The quartz filters were then stored at ~ –20 °C in the laboratory prior to chemical analysis. We consider that the chemical losses were not large under the low temperature and sealed condition. The extracted liquids were kept at ~ –20 °C for within 24 h prior to GC/MS determination. These points were added in the revised manuscript. Please see lines 102-105 and 122-123.

(3) Line 226: A deep discussion about Table 1 should be added. Why isoprene-SOA tracers and monoterpene-SOA tracers showed positive relationship with SO42- and no relationship with NO3-. Moreover, a deep discussion of the relevant mechanism of SO42- and SOA tracers should be added.

Response: We consider that aerosol SO42- was mainly derived from anthropogenic sources. The positive relations between SOA tracers and SO42- could be caused by (1) the parallel transport of regional BSOA and anthropogenic pollutants such as SO42-, (2) gas-to-particle partition of SOA promoted by SO42- and (3) formation of SOA tracers. These possible reasons were discussed in details in L246-262.

On the other hand, although there are several possibilities for the "absence" of correlations between NO_3^- and SOA tracers, we would not discuss the issue in details, as aerosol NO_3^- is not our focus in this study. Taking the referee's comments, we revised from "…is not clear in Wakayama aerosols" to "is not clear in Wakayama aerosols, which deserve further investigations" in L265-266.

(4) Line 155: A large part of section 3.1 and 3.2 refers to supplemental material information making it hard for this reviewer/reader to follow.

Response: Taking the comment, we moved Figure S1, which is referred in section 3.1 and 3.2, to the manuscript.

(5) The authors claimed that fungal spores overwhelmed BVOC oxidation products in contributing to OA, which is opposite to previous studies. However, there was not any reference and no data from other literature compared. More discussion or explanation should be added to support this conclusion.

Response: Given the complicated nature of OA/OC sources, there are few studies so far on the quantification of OA/OC fraction from different sources. As far as the literatures of the same nature we reviewed, we compared our results with two relevant studies, of which one is from a forest site in the Amazonia (Pöschl et al., Science, 2010) and the other one is from an urban site (Zhao et al., JGR, 2013). Our results are in accordance with those in the Amazon rainforest, where primary biological aerosol and SOA accounted for 68.5% and 18.8% of total particle masses, but differs from those in the urban site. These discussions were shown in L305-311. We believe that our results are informative enough to compare with other studies in the same nature, which is still lacking in the atmospheric chemistry community.

Anonymous Referee #2

Zhu et al report on biological aerosol particles contribution to organic aerosol (OA) at a fine temporal scale. Their main finding is that fungal spores overwhelm BVOC oxidation products

in terms of % contribution to OA, especially at night time due to sporulation and absence of photochemistry (45% vs 15%), but also at daytime (22% vs 19%). The paper is well written and presents novel data, and is worth to be published after revisions as detailed below. While I find that the sampling methodology, the analytical and chemical sections and discussions are sound and consistent, the interpretations the authors give of observed patterns in light of atmospheric dynamic are often weak and sometimes wrong in my opinion. Overall they are not supported by any atmospheric data, nor local meteorological or micrometeorological data, nor trajectory analysis. This lack of analysis makes all the atmospheric arguments rather speculative. I strongly encourage to make use of the data that are available to support the discussion, especially a back-trajectory analysis would be informative, coupled at least to local wind-rose analysis. Mesoscale model runs (WRF etc) would be also very helpful if feasible. The discussion needs to be refocused based on the available data.

Response: We thank Referee #2 for the positive evaluation of our work. We are grateful for the invaluable comments that allow us to improve the manuscript mainly from the viewpoint of atmospheric transport. As a matter of fact, the development and discussion through the manuscript was indeed on a basis of the atmospheric transport.

Major comments:

L97 - 104: the authors divide the study period (10 days) into two 5 days sub-periods: "During August 20–25, air masses originated from the Asian continent or passed over the Japanese islands brought pollutants from anthropogenic sources, while during August 26–30 air masses originated from the western North Pacific, which create an environment close to the pristine forest"

This is a superficial assumption not supported by any atmospheric circulation-back trajectory analysis. I did some very basic back-trajectory with Hysplit (see figure), showing that while the backward oceanic circulation (on the sampling day Aug 28) is indeed very clear (red trajectory), the terrestrial land influence (sampling day on Aug 23) is not (green). Winds are very weak, making the assessment of the air mass origin quite difficult, and the time scales involved very long. On a 72 hrs scale (see figure), if there is any land influence it appears more

from Japan than from asian continent. Then saying that continental air masses carry anthropogenic pollution signatures is also not supported, since this will depend again on the airmass trajectory (pollution sources concentrate in cities that are a minor fraction of land cover).

Response: We appreciate for the referee's validation on the backward trajectories of August 28 and August 23. The results, as was shown in the figure of the comment letter, provided accordance with our manuscript starting from August 28, but a shorter transport distance for a duration of 72 hours starting from August 23. It is noteworthy that HYSPLIT backward trajectory varied depending on start time of the day and the start height. Therefore, other than one single calculation, the statistical results of backward trajectory calculations of all hours of a day, and attempt to start from several heights are supposed to provide more reliable results. To this point, Han et al. (JGR, 2014) calculated 24 hours (namely 24 starting time points) for each day over the sampling period (Figure 4 in the original paper). The results clearly show that during 20–25 August 2010, the sampling site was mainly affected by the continental outflow. On the other hand, Han et al. (Atmos. Environ., 2013) also obtained consistent results when examining backward trajectories starting at different height (500 m, 1000 m and 1500 m above the ground level) (Figure 1 in the original paper) and at 9:00 am local time on each day. Therefore, we believe that it is reasonable to divided the sampling period into those two sub-periods on a basis of the backward trajectories. We addressed this point more explicitly by revising the manuscript. Please see L108-115 in the revised manuscript as follows: "Of the whole sampling period, the backward trajectories were calculated using HYSPLIT dispersion model starting at every hour of the day and for different starting height (500m, 1000m and 1500m above ground level) (Han et al., 2013, 2014). It can be seen that the air masses were mainly originated from the Asian continent or passed over the Japanese islands during August 20–25, which were expected to deliver pollutants from anthropogenic sources. On the other hand, air masses were mainly originated from the western North Pacific during August 26–30, which create an environment close to the pristine forest."

L168-170: "Insignificant diurnal variations of these two compounds imply that they were emitted ubiquitously in the forest possibly from plants and microorganisms".

I do not agree here: absence of diurnal variation of a compound is likely because it is not emitted at all, and the measured signal moslty advected. If there's an ubiquotuous emission, we should more see a diurnal trend, driven by PBL growth during the day and collapsing at night.

Response: As glucose and fructose are dominantly originated from plant debris and other biogenic sources as discussed in L184-186, it is reasonable to say that the local vegetation is a dominant source of these compounds. We agree with the referee's comment that the diurnal variation of planetary boundary layer height could contribute to the variation of glucose and fructose. Taking the comment, we rephrased the sentences to "Insignificant diurnal variations of these two compounds imply that they were emitted both in the daytime and the nighttime in the forest possibly from plants and microorganisms (Figure 1a–b, 3a). The diurnal variation of planetary boundary layer height could also contribute to the observed variations of glucose and fructose and other PBAP tracers. In the daytime, enhanced vertical mixing might cause dilution effect to the observed PBAP tracers. While in the nighttime, the low wind speed favors the buildup of PBAP tracers in the canopy (Figure S1), resulting in the elevated levels (Figure 3a, b)." Please see lines in L187-194 in the revised manuscript.

L185-187: "The diurnal variation of levoglucosan with daytime maxima in the Wakayama aerosols indicates that the Asian outflow of biomass burning emissions approached to the sampling site."

Again this is not adequately supported with trajectory analysis, see also comment above. If there's any (and it appears not) influence of asian continet, this will act on a multi-day scale (distance > 1000 km!), so linking this hypothetical difference to the daytime-nighttime difference makes no sense.

L182 . . . " sea-breeze circulations at day and drainage flows at night". Again not supported. Here the authors are going on a finer scale interpretation (local sea breeze developments) that is mixed with the long range transport interpretation (the asian outflow..). Is at least wind speed and direction supporting the sea breeze regime? No wind data is reported in the study.

Response: Taking the comments with respect to L185-187 and L182 in the previous version manuscript, we newly analyzed the local wind direction/speed and put it in the supporting information (Figure r1 in this response letter). Regarding the long-distant transport, the backward analysis as described above indicated that the sampling site was most likely affected by the regional aerosols from Asian continent and Japan. While the low wind speed in the nighttime favors deposition, causing low levoglucosan level. Taking the next comment on L182 together, we revised the content as follows: "). In the nighttime, levoglucosan may have been deposited to the canopy as a result of dampened vertical mixing and relatively low wind speed (Figure S1)". Please see L204-206 in the revised manuscript.
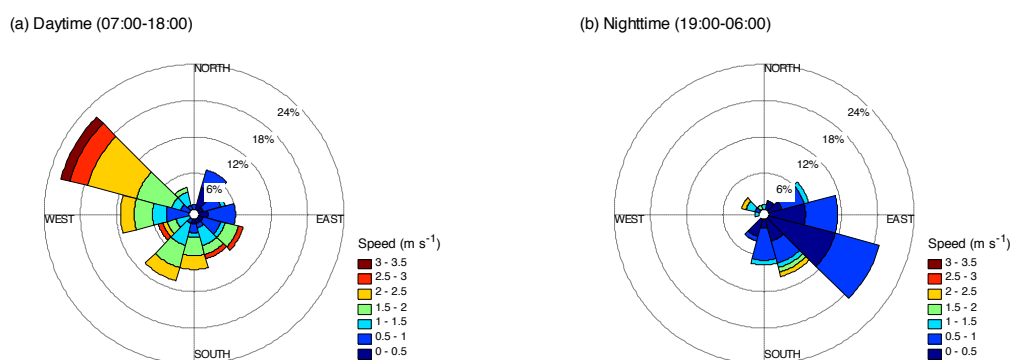

Figure r1. Frequency distributions of wind direction and wind speed over August 20–30, 2010 at Wakayama forest in (a) the daytime and (b) the nighttime. The wind direction and wind speed data were obtained at Shimizu observation site from Japan Meteorological Agency.

Fig 2 (hourly patterns) reveals interesting patterns: while BVOC patterns are more clear and consistent (panels c and d) with photochemical activity, some other are less (a, b). Some more interpretation in the light of night accumulation and turbulent mixing built up in the morning could improve the analysis, again depending on wind-turbulence data availability.

Response: Taking the comment, we newly analyzed the diurnal pattern of PBAP tracers together with meteorological information on wind speed and wind direction. We added the following sentences in the revised manuscript: "The diurnal variation of planetary boundary

layer height could also contribute to the observed variations of glucose and fructose and other PBAP tracers. In the daytime, enhanced vertical mixing might cause dilution effect to the observed PBAP tracers. While in the nighttime, the low wind speed favors the buildup of PBAP tracers in the canopy (Figure S1), resulting in the elevated levels (Figure 3a, b)." in L189-194.

Minor:

L71-73: also PTR-MS technology to measure BVOC continuously in field.

Response: We did not find relevant content in L71-73. The referee should be talking on the research background with respect to the measurement methods. Taking the comment, we added "BVOC could also be monitored on real time using Proton Transfer Reaction – Mass Spectrometry (PTR–MS) technology (Blake et al., 2009)." Please see L78-79 in the revised manuscript.

L136: it appears text is confounding fungus with tracers? Please clarify this section, also better supporting the use of those sugar alcohols as PBAP tracers. How consolidates is this asumption? what limitations? waht accuracy in estimating PBAP indirectly.

Response: We checked over the context and clarified the usage of fungal spore tracers from fungal spore. We clearly described that we used sugar alcohols to investigate fungal spore and other organic compounds for other PBAPs with headlines of 3.1 "PBAP tracers reflecting diurnal rhythm of fungal spores and pollen" (please see L151), 3.1.1 "Fungal spore tracers" and 3.1.2 "Other PBAP tracers and levoglucosan". The same kind of description was also shown as "Trehalose, arabitol and mannitol were the major species of fungus and have been used as tracers for fungal spores (Jia and Fraser, 2011)" in L155-156.

The tracer-based methods for the estimation of PBAPs had been widely applied in the community. Given the complicated nature of PBAPs, it is not applicable to estimate the uncertainty for the moment. We described this precaution as "It is noteworthy that, although each tracer method gave a reasonable estimate in the original studies, uncertainties would be introduced in the current study considering the site differences. Still, the estimations are

inferable for the contributions from each source to OC in the forest aerosols." Please see L275-278 in the revised manuscript.

L162-164: can this be better supported? pollen sampling?

Response: We did not find relevant content in L162-164 in the previous version of manuscript. The referee should be talking about the source of sucrose and pollen in L180-183. For the moment we did not conduct a pollen sampling experiment. The information about the local vegetation and the blossom season is based on the biogeography of the site, which was obtained from filed surveys.

Other changes:

1. We updated the authors' information in L4-9.

2. We corrected the flow rate during sampling to ~60 m^3 h^{-1} in L101.

3. We corrected from "are the some of" to "are the sum of" in L516.

4. We added "appreciate … technical support of W. Zhang" in the Acknowledgement.

References

Han, Y., Iwamoto, Y., Nakayama, T., Kawamura, K., Hussein, T., and Mochida, M.: Observation of new particle formation over a mid–latitude forest facing the North Pacific, Atmos. Environ., 64, 77–84, 2013.

Han, Y., Iwamoto, Y., Nakayama, T., Kawamura, K., and Mochida, M.: Formation and evolution of biogenic secondary organic aerosol over a forest site in Japan, J. Geophys. Res., 119, 259–273, 2014.

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

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21   **Abstract**

22   Both primary biological aerosol particles (PBAP) and oxidation products of biogenic

23   volatile organic compounds (BVOC) contribute significantly to organic aerosols (OA) in

24   forested regions. However, little is known on their relative importance in diurnal time scales.

25   Here, we report biomarkers of PBAP and secondary organic aerosols (SOA) for their diurnal

26   variability in a temperate coniferous forest in Wakayama, Japan. Tracers of fungal spores,

27   trehalose, arabitol and mannitol, showed significantly higher levels in nighttime than daytime

28   ($p < 0.05$), resulting from the nocturnal sporulation under near saturated relative humidity. On

29   the contrary, BVOC oxidation products showed higher levels in daytime than nighttime,

30   indicating substantial photochemical SOA formation. Using tracer-based methods, we

31   estimated that fungal spores account for 45% of organic carbon (OC) in nighttime and 22% in

32   daytime, whereas BVOC oxidation products account for 15% and 19%, respectively. To our

33   knowledge, we present for the first time highly time-resolved results that fungal spores

34   overwhelmed BVOC oxidation products in contributing to OA especially in nighttime. This

35   study emphasizes the importance of both PBAPs and SOAs in forming forest organic aerosols.

36

37   **Keywords:** primary biological aerosol particles; fungal spores; biological volatile organic

38   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

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

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

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

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

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

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

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

69   2012). Atmospheric oxidation of these BVOCs depends on oxidant levels (NO_x and O_3),

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

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

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

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

74   2010). The formation of SOA is often in the fine particle size (Pöschl et al., 2010), however,

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

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

77   environment both qualitatively and quantitatively. Applications of ultraviolet aerodynamic

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

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

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

81   spectrometer (AMS) (Zhang et al., 2007). BVOC could also be monitored on real time using

82   Proton Transfer Reaction – Mass Spectrometry (PTR–MS) technology (Blake et al., 2009).

83   Detections of organic tracer compounds using gas chromatography combined with mass

84   spectrometry (GC/MS) make it possible to compare both PBAP and SOA sources

85 simultaneously (Graham et al., 2003). Progresses are achieved in boreal forest (Kourtchev et

86 al., 2008) and the Amazon (Graham et al., 2003). However, few studies focused on the mid-

87 latitudinal forest with high time resolution (Miyazaki et al., 2012; Mochizuki et al., 2015).

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

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

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

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

92 natural rhythm of the forest.

93

94 **2. Experimental**

95 **2.1 Site and sampling**

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

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

98 135.52 °E, ca. 750 m above sea level) (Han et al., 2013; Han et al., 2014). The dominant

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

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

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

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

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

104 25 cm) using a high–volume air sampler (Kimoto AS-810B) at a flow rate of ~60 m^3 h^{-1} at the

105 ground level. Each of the quartz samples were kept in a sealed glass jar at < −20 °C during

106 transport. The quartz filters were then stored at ~ −20 °C in the laboratory prior to chemical

107 analysis. We believe that the chemical losses were not large under the low temperature and

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110 sealed condition (Kawamura et al., 2010). During the campaign, four field blanks were

111 collected following the sampling procedures, except for the running of pump for only 10

112 seconds.

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

114 LT) samples were collected separately each day. Of the whole sampling period, the backward

115 trajectories were calculated using HYSPLIT dispersion model starting at every hour of the day

116 and for different starting height (500m, 1000m and 1500m above ground level) (Han et al.,

117 2013, 2014). It can be seen that the air masses were mainly originated from the Asian

118 continent or passed over the Japanese islands during August 20–25, which were expected to

119 deliver pollutants from anthropogenic sources. On the other hand, air masses were mainly

120 originated from the western North Pacific during August 26–30, which create an environment

121 close to the pristine forest. On August 23 and 28, samples were collected every 3 hours

122 (namely, 6:00–9:00, 9:00–12:00, 12:00–15:00, 15:00–18:00, 18:00–21:00, 21:00–24:00,

123 24:00–3:00, and 3:00–6:00 LT). A total of 36 samples were collected during the campaign.

124 **2.2 Chemical analysis**

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

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

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

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

129 extracts were kept at ~ –20 °C and then organic compounds were quantified within 24 h by

130 GC/MS using an Agilent 7890A GC equipped with HP-5ms capillary column (30 m × 0.25

131 mm × 0.25 μm) coupled to Agilent 5975C mass-selective detector (MSD). Individual

132 compounds were identified by comparing the mass spectra with those of authentic standards or

143 literature data and quantified by comparing the peak areas with the internal standard (C_{13} n-

144 alkane) (Zhu et al., 2015b). Recoveries for the authentic standards or surrogates were

145 generally better than 80%, except for pinonic acid of ~60%, as obtained by spiking standards

146 to pre-combusted quartz filters following extraction and derivatization. No peak was found for

147 the target compounds in the field and laboratory blanks. The analytical errors by duplicate

148 analyses were less than 15%. The detection limits of the reported compounds were 105–557

149 pg μl^{-1}, which correspond to ambient concentrations of 12–64 pg m^{-3} under a typical sampling

150 volume of 700 m^3 and usage of 10 cm^2 filter section.

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

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

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

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

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

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

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

158 field blanks.

159 Statistical significances of daytime and nighttime organic tracers were evaluated based on

160 Student's t-test at $p < 0.05$ and $p < 0.01$ level, respectively. To explore the effects of

161 anthropogenic pollutant inputs on BSOA formation, linear correlations (Pearson) between

162 SOA tracers and NO_3^- and SO_4^{2-} where investigated. The contributions from various sources

163 to OC were estimated using tracer-based methods using conversion factors according to the

164 preceding studies.

165

166 **3. Results and discussion**

167 **3.1 PBAP tracers reflecting diurnal rhythm of fungal spores and pollen**

168 **3.1.1 Fungal spore tracers**

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

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

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

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

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

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

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

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

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

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

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

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

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

182 the forest region.

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

184 28, two typical days representing regional and local phenomenon, respectively. Minima of

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

186 the evening on both days (Figure 3). On August 23, fungal spore tracers peaked at 21:00–

187 24:00 LT and decreased slowly thereafter. In comparison, these compounds peaked slightly

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

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

192 precipitation that occurred at 13:00–17:00, August 23 (Figure 2), which favors the growth and

193 release of fungal spores.

3.1.2 Other PBAP tracers and levoglucosan

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

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

197 1c). The diurnal profile of sucrose showed peaks in the afternoon (Figure 3a), indicating the

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

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

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

201 family, which are flowering during the sampling period.

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

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

204 2007;Simoneit et al., 2004). There was no serious continental outflow of Asian dust over the

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

206 diurnal variations of these two compounds imply that they were emitted both in the daytime

207 and the nighttime in the forest possibly from plants and microorganisms (Figure 1a–b, 3a).

208 The diurnal variation of planetary boundary layer height could also contribute to the observed

209 variations of glucose and fructose and other PBAP tracers. In the daytime, enhanced vertical

210 mixing might cause dilution effect to the observed PBAP tracers. While in the nighttime, the

211 low wind speed favors the buildup of PBAP tracers in the canopy (Figure S1), resulting in the

212 elevated levels (Figure 3a, b). Interestingly, the mass concentrations of glucose were one order

213 of magnitude higher than those of fructose. This might be related to the higher abundance of

219 glucose in trees. For example, tissues of a wide range of subtropical plants were found to

220 contain more glucose than fructose (Baker et al., 1998).

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

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

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

224 < 0.05) in daytime (2.52 ± 2.08 ng m^{-3}) than nighttime (1.14 ± 0.94 ng m^{-3}). Moreover, we

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

226 (0.53 ± 0.44 ng m^{-3}); those concentrations in the latter period are close to the regional

227 background level from Okinawa Island (Zhu et al., 2015b). In the nighttime, levoglucosan

228 may have been deposited to the canopy as a result of dampened vertical mixing and relatively

229 low wind speed (Figure S1). In addition, local burning activities could also contribute to the

230 daytime elevation of levoglucosan although they might be insignificant.

231 **3.1.3 Daytime abundances of SOA tracers**

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

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

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

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

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

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

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

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

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

241 33.6 ng m^{-3}, respectively). Isoprene is more abundantly emitted than monoterpenes from this

Deleted: Given the location of Wakayama forest in the Kii Peninsular, the sea-land breeze system is very likely to deliver clean maritime air masses to the sampling site in daytime and drainage airflow from the Japanese islands in nighttime. The diurnal variation of levoglucosan with daytime maxima in the Wakayama aerosols indicates that the Asian outflow of biomass burning emissions approached to the sampling site.

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

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

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

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

254   the photooxidation of BVOC in the forest.

255   **3.2 Influence of anthropogenic oxidant on SOA formation**

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

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

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

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

260   (Figure 2). These results indicate that SOA is formed by photooxidation of isoprene and

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

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

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

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

265   freshly emitted BVOC from the local forest.

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

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

268   peaks (Figure 3c–d) following the intensive precipitation during 13:00–17:00 (Figure 2).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

290 on the third possibility and further testified this hypothesis.

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

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

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

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

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

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

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

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

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

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

301   clear in Wakayama aerosols, which deserve further investigations.

302   **3.3 OC fractions from fungal spores and BVOC oxidation**

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

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

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

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

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

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

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

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

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

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

313   from each source to OC in the forest aerosols.

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

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

316   known source of OC (Figure 4). In comparison, BVOC oxidation products (BSOC) contribute

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

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

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

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

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

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

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

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

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

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

328 simulations of the future climate in the Anthropocene.

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

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

331 based on glucose level, and could be underestimated. Nevertheless, there are still quite

332 amounts of OC not being determined (34% and 51% in nighttime and daytime, respectively).

333 Other than the uncertainties introduced by the tracer methods, a notable fraction of OC could

334 be contributed from humic-like substances that are chemically and physically similar with

335 terrestrial and aquatic humic and fulvic acids (Graber and Rudich, 2006). Mono- and di-

336 carboxylic acids, originating from a broad range of primary organic compounds, could

337 contribute 38–44% of OC (Legrand et al., 2013). Pollen could also contribute to OC because

338 of its large size. Amines are another source of OC, but not well studied (Sintermann and

339 Neftel, 2015). These sources from various sectors need to be further characterized for an

340 unambiguous understanding of the sources of forest aerosols.

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

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

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

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

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

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349 66% of OA during the daytime and the nighttime, respectively, while primary sources

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

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

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

353 sources of organic aerosols in the forest atmosphere.

354

355 **4. Conclusions**

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

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

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

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

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

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

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

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

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

365 affecting biogenic aerosols in forest ecosystem.

366

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

543 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[***]

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

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

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

548 [b] Negative values indicate negative correlations.

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

550

551

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

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

554   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

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

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

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

558   monoterpene- and sesquiterpene- (CPA) tracers.

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561   **Figure captions**

562

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

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

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

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

567

568   Figure 2. Meteorological parameters over August 20–30, 2010 at Wakayama forest, for (a)

569   averaged diurnal variations of temperature, relative humidity and solar radiation, and (b)

570   hourly means over the periods. Hourly precipitation was also shown in panel (b).

571

572   Figure 3. Diurnal profiles of organic compounds in forest aerosols in Wakayama on August

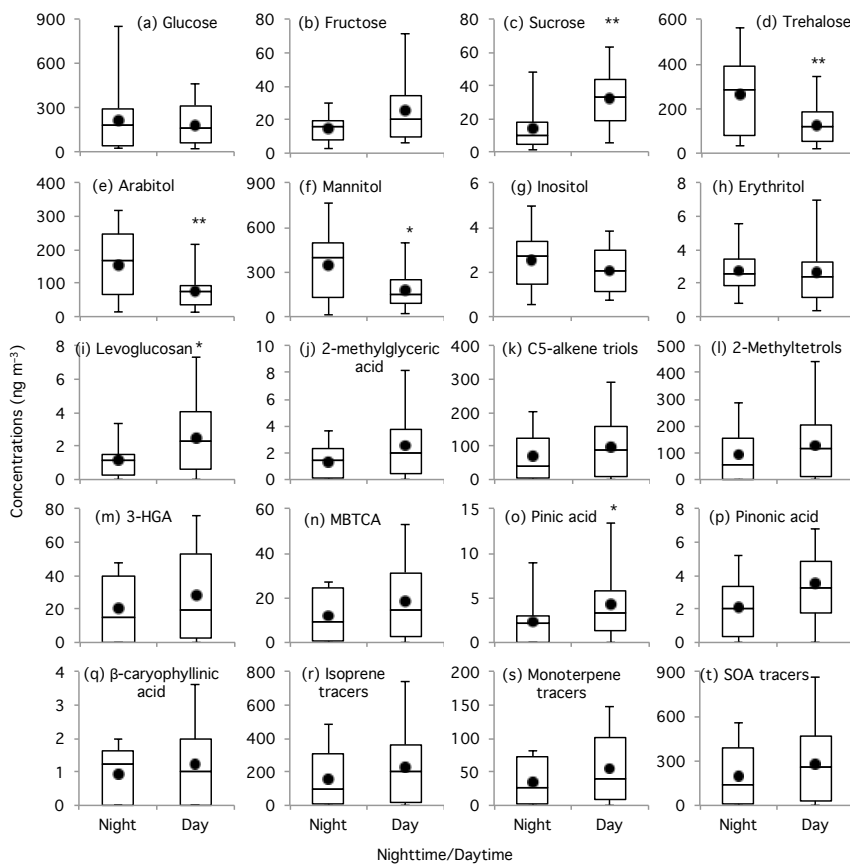573   23–24 (left) and August 28–29, 2010 (right).

574

575   Figure 4. Contributions from different sources to organic carbon in Wakayama forest aerosols

576   during the nighttime and the daytime.
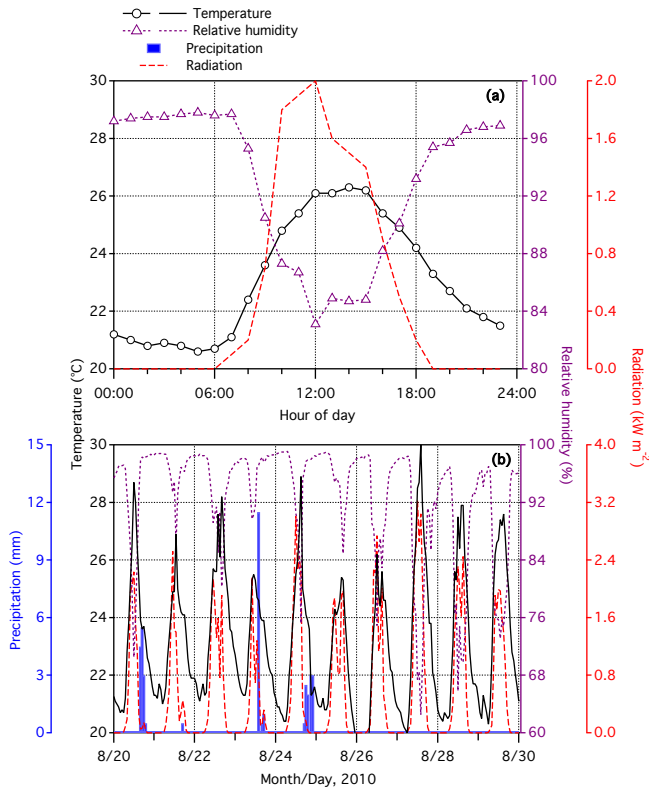
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Figure 1. Diurnal variations of organic compounds in forest aerosols in Wakayama, Japan during August 20–30, 2010. The 10th, 25th, 50th, 75th, and 90th percentiles of the nighttime and daytime samples were shown in the box-whisker plot. The means were shown in solid circles. Statistically significances were also shown (T-test, *, p < 0.05; **, p < 0.01).

586

587 Figure 2. Meteorological parameters over August 20–30, 2010 at Wakayama forest, for (a)

588 averaged diurnal variations of temperature, relative humidity and solar radiation, and (b)

589 hourly means over the periods. Hourly precipitation was also shown in panel (b).

590
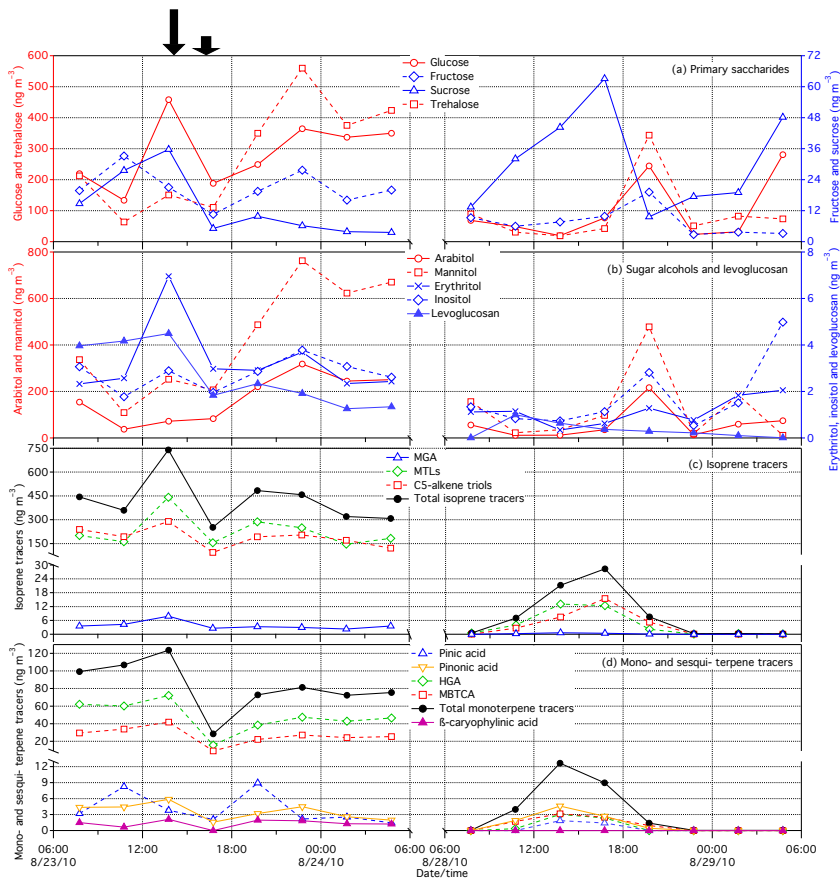
591

592 Figure 3. Diurnal profiles of organic compounds in forest aerosols in Wakayama on August

593 23–24 (left) and August 28–29 (right), 2010. Precipitation events occurred on 13:00–14:00

594 (11.2 mm) and 15:00–17:00 (1.5 mm) local time, August 23 as were marked by arrows on top

595 of the left panels.

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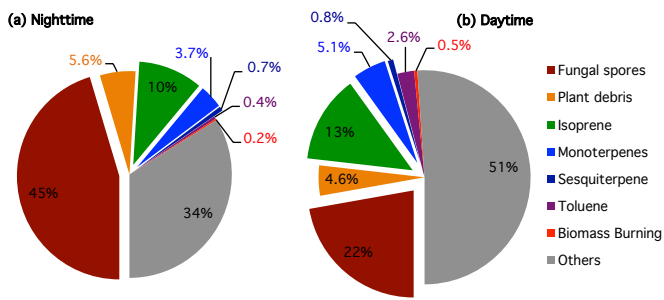
597

598 Figure 4. Contributions from different sources to organic carbon in Wakayama forest aerosols

599 during the nighttime and the daytime.

600

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