# 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 contribute very little to global average ice

nucleation rates (Hoose et al., 2010; Spracklen and Heald, 2014). Unveiling PBAP mass concentrations is necessary to provide benchmarks for simulating its nucleation potentials and the effect on the climate.

The most widely studied BVOCs are isoprene ($C_5H_8$), monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$). Global emission of isoprene (309–706 Tg C $yr^{-1}$) accounts for ~50% of total BVOC (Acosta Navarro et al., 2014; Guenther et al., 2006). Monoterpenes (~10% of total VOCs) and sesquiterpenes are other important SOA precursors (Ziemann and Atkinson, 2012). Atmospheric oxidation of these BVOCs depends on oxidant levels ($NO_x$ and $O_3$), humidity, light and temperature. Recent studies indicated that biogenic SOA production could be enhanced under the input of anthropogenic oxidants (Carlton et al., 2010). Under pristine conditions, BVOC oxidation and SOA formation are often accompanied by new particle formation, involving in precipitation through increasing CCN and IN numbers (Pöschl et al., 2010). The formation of SOA is often in the fine particle size (Pöschl et al., 2010), however, the relative importance of PBAPs and SOA in contributing to OA is still ambiguous.

Various observational methods have been applied to explore PBAPs and SOA in natural environment both qualitatively and quantitatively. Applications of ultraviolet aerodynamic particle sizers and wideband integrated bioaerosol sensor based on fluorescence provided much information on the abundances and size distributions of PBAP (Huffman et al., 2010; Pöhlker et al., 2012). In situ observations of SOA are frequently conducted using aerosol mass spectrometer (AMS) (Zhang et al., 2007). BVOC could also be monitored on real time using Proton Transfer Reaction – Mass Spectrometry (PTR–MS) technology (Blake et al., 2009). Detections of organic tracer compounds using gas chromatography combined with mass spectrometry (GC/MS) make it possible to compare both PBAP and SOA sources

simultaneously (Graham et al., 2003). Progresses are achieved in boreal forest (Kourtchev et al., 2008) and the Amazon (Graham et al., 2003). However, few studies focused on the mid-latitudinal forest with high time resolution (Miyazaki et al., 2012; Mochizuki et al., 2015).

In this study, we collected daytime and nighttime samples in a mid-latitude forest in Wakayama, Japan and analyzed the organic samples for various PBAP and SOA tracers using GC/MS. We report for the first time that fungal spores overwhelm BSOA in contributing to aerosol organic carbon (OC). We also report diurnal variations of PBAP tracers that reflect the natural rhythm of the forest.

## 2. Experimental

### 2.1 Site and sampling

Aerosol sampling was conducted in August 20–30, 2010 during a field campaign at Wakayama Forest Research Station, Kyoto University, in the Kii Peninsula, Japan (34.07 °N, 135.52 °E, ca. 750 m above sea level) (Han et al., 2013; Han et al., 2014). The dominant species of the forest vegetation are coniferous trees of *Cryptomeria japonica* (Japanese cedar), *Chamaecyparis obtuse* (Japanese cypress) and *Pinus densiflora* (Japanese red pine). Previous studies indicated that monoterpenes are abundantly emitted from these tree species (Matsunaga et al., 2011; Mochizuki et al., 2011). Total suspended particulate (TSP) samples were collected on pre-combusted (450 °C, 6 h) quartz filters (Pallflex 2500QAT-UP, 20 cm × 25 cm) using a high–volume air sampler (Kimoto AS-810B) at a flow rate of ~60 $m^3$ $h^{-1}$ at the ground level. Each of the quartz samples were kept in a sealed glass jar at < –20 °C during transport. The quartz filters were then stored at ~ –20 °C in the laboratory prior to chemical analysis. We believe that the chemical losses were not large under the low temperature and sealed condition

105 (Kawamura et al., 2010). During the campaign, four field blanks were collected following the
106 sampling procedures, except for the running of pump for only 10 seconds.
107 Nighttime (from ~18:00 to next ~6:00 local time, LT) and daytime (from ~6:00 to ~18:00
108 LT) samples were collected separately each day. Of the whole sampling period, the backward
109 trajectories were calculated using HYSPLIT dispersion model starting at every hour of the day
110 and for different starting height (500m, 1000m and 1500m above ground level) (Han et al.,
111 2013, 2014). It can be seen that the air masses were mainly originated from the Asian continent
112 or passed over the Japanese islands during August 20–25, which were expected to deliver
113 pollutants from anthropogenic sources. On the other hand, air masses were mainly originated
114 from the western North Pacific during August 26–30, which create an environment close to the
115 pristine forest. On August 23 and 28, samples were collected every 3 hours (namely, 6:00–9:00,
116 9:00–12:00, 12:00–15:00, 15:00–18:00, 18:00–21:00, 21:00–24:00, 24:00–3:00, and 3:00–6:00
117 LT). A total of 36 samples were collected during the campaign.
118 **2.2 Chemical analysis**
119 For the determination of organic molecular tracers in aerosols, filter samples were first
120 extracted with dichloromethane/methanol and derivatized by N,O-bis-
121 (trimethylsilyl)trifluoroacetamide (BSTFA) mixed with pyridine to convert OH groups to
122 trimethylsilyl (TMS) ethers and COOH groups to TMS esters (Simoneit et al., 2004). The
123 extracts were kept at ~ –20 °C and then organic compounds were quantified within 24 h by
124 GC/MS using an Agilent 7890A GC equipped with HP-5ms capillary column (30 m × 0.25 mm
125 × 0.25 μm) coupled to Agilent 5975C mass-selective detector (MSD). Individual compounds
126 were identified by comparing the mass spectra with those of authentic standards or literature
127 data and quantified by comparing the peak areas with the internal standard ($C_{13}$ n-alkane) (Zhu

et al., 2015b). Recoveries for the authentic standards or surrogates were generally better than 80%, except for pinonic acid of ~60%, as obtained by spiking standards to pre-combusted quartz filters following extraction and derivatization. No peak was found for the target compounds in the field and laboratory blanks. The analytical errors by duplicate analyses were less than 15%. The detection limits of the reported compounds were 105–557 pg $\mu l^{-1}$, which correspond to ambient concentrations of 12–64 pg $m^{-3}$ under a typical sampling volume of 700 $m^3$ and usage of 10 $cm^2$ filter section.

Aerosol OC was determined using a thermal/optical carbon analyzer (Sunset Laboratory Inc., USA) following the Interagency Monitoring Protected Visual Environments (IMPROVE) thermal evolution protocol (Birch and Cary, 1996). The analytical error in replicate analyses was within 8%. Samples were corrected for field blanks, in which OC level was < 5% of the samples. Inorganic ions were measured using an ion chromatograph (761 Compact IC, Metrohm, Switzerland). $SO_4^{2-}$ and $NO_3^-$ were discussed in the study. The detection limits were ~0.1 ng $m^{-3}$. The laboratory analytical error was within 5%. Samples were corrected for field blanks.

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. Results and discussion

151 **3.1 PBAP tracers reflecting diurnal rhythm of fungal spores and pollen**

152 **3.1.1 Fungal spore tracers**

153 Four primary saccharides (trehalose, glucose, fructose and sucrose) and four sugar alcohols
154 (arabitol, mannitol, inositol and erythritol) were detected in the forest aerosols as PBAP tracers.
155 Trehalose, arabitol and mannitol were the major species of fungus and have been used as
156 tracers for fungal spores (Jia and Fraser, 2011). These compounds showed significantly higher
157 levels in nighttime (262 ± 168, 156 ± 102 and 349 ± 243 ng $m^{-3}$ for trehalose, arabitol and
158 mannitol, respectively) than in daytime (128 ± 90.2, 76.0 ± 54.9 and 183 ± 139 ng $m^{-3}$,
159 respectively) (T-test, $p < 0.05$, Figure 1d–f). High abundances of these fungal spore tracers
160 were resulting from the nocturnal sporulation under near saturated relative humidity (Figure 2).
161 In nighttime, the mean relative humidity was 96% in the sampling period. Nevertheless, the
162 mean daytime relative humidity was still as high as 88%. Such a moist environment caused
163 enrichment of fungal spores and their discharges, resulting high abundances of their tracer in
164 aerosols. The sum of trehalose, arabitol and mannitol contributed to 70% of total PBAP tracer
165 mass, demonstrating an important role of fungi in regulating the land-atmosphere exchange in
166 the forest region.

167 Diurnal profiles of fungal spore tracers showed similar pattern on August 23 and August 28,
168 two typical days representing regional and local phenomenon, respectively. Minima of
169 trehalose, arabitol and mannitol appeared around the noontime and increased dramatically in
170 the evening on both days (Figure 3). On August 23, fungal spore tracers peaked at 21:00–24:00
171 LT and decreased slowly thereafter. In comparison, these compounds peaked slightly earlier at
172 18:00–21:00 LT on August 28. The maxima of these compounds on August 23 were higher by
173 a factor of ~1.5 than those on August 28. This phenomenon was likely related to the

precipitation that occurred at 13:00–17:00, August 23 (Figure 2), which favors the growth and release of fungal spores.

### 3.1.2 Other PBAP tracers and levoglucosan

Sucrose, a key component of pollen grain (Yttri et al., 2007), showed significantly higher levels ($p < 0.01$) in daytime ($31.9 \pm 17.7$ ng $m^{-3}$) than nighttime ($14.6 \pm 14.2$ ng $m^{-3}$) (Figure 1c). The diurnal profile of sucrose showed peaks in the afternoon (Figure 3a), indicating the flowering time of the vegetation. As the blossom season of the dominant coniferous trees is March–April in the region, the source of sucrose is likely from the pollen of the widely distributed floor vegetation, *Ambrosia artemisiifolia*, *Artemisia indica*, and plants of *Poaceae* family, which are flowering during the sampling period.

Glucose and fructose are originated dominantly from plant debris (Medeiros et al., 2006; Zhu et al., 2015a), and sometimes from microorganisms and soil dust (Rogge et al., 2007;Simoneit et al., 2004). There was no serious continental outflow of Asian dust over the sampling period (based on observations by Japan Meteorological Agency). 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). Interestingly, the mass concentrations of glucose were one order of magnitude higher than those of fructose. This might be related to the higher abundance of glucose in trees. For

example, tissues of a wide range of subtropical plants were found to contain more glucose than fructose (Baker et al., 1998).

Being exclusively produced by the thermal depolymerization and dehydration of cellulose and hemicellulose, levoglucosan has been used as a specific tracer for biomass burning (Simoneit et al., 1999; Zhu et al., 2015b). Levoglucosan showed significantly higher levels ($p < 0.05$) in daytime (2.52 ± 2.08 ng $m^{-3}$) than nighttime (1.14 ± 0.94 ng $m^{-3}$). Moreover, we found higher levels of levoglucosan in August 20–25 (2.97 ± 1.64 ng $m^{-3}$) than August 26–30 (0.53 ± 0.44 ng $m^{-3}$); those concentrations in the latter period are close to the regional background level from Okinawa Island (Zhu et al., 2015b). 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). In addition, local burning activities could also contribute to the daytime elevation of levoglucosan although they might be insignificant.

**3.1.3 Daytime abundances of SOA tracers**

A total of 11 compounds were detected as SOA tracers. Six isoprene-tracers, including 2-methylglyceric acid (MGA), two 2-methyltetrols (2-methylthreitol and 2-methylerythritol, MTLs), and three C5-alkene triols (3-methyl-2,3,4-trihydroxy-1-butene, cis-2-methyl-1,3,4-trihydroxy-1-butene and trans-2-methyl-1,3,4-trihydroxy-1-butene, MTHBs), showed higher levels in daytime (Figure 1j–l). Similar daytime abundances were also found for 4 monoterpene-tracers; pinonic acid (PNA), pinic acid (PA) ($p < 0.05$), 3-hydroxyglutaric acid (HGA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (Figure 1m–p). Total isoprene-SOA tracers (281 ± 274 and 199 ± 207 ng $m^{-3}$ in daytime and nighttime, respectively) were more abundant by a factor of ~5 than total monoterpene-SOA tracers (54.6 ± 50.2 and 36.3 ± 33.6 ng $m^{-3}$, respectively). Isoprene is more abundantly emitted than monoterpenes from this

219 coniferous forest. This is consistent with the observations at a mountain site in central Japan
220 (Fu et al., 2014). Sesquiterpene-tracer, caryophylinic acid, showed consistently low levels in
221 both daytime (1.22 ± 1.23 ng $m^{-3}$) and nighttime (0.94 ± 0.83 ng $m^{-3}$) (Figure 1q). The daytime
222 abundances of isoprene- and monoterpene-tracers reflected the production of SOA by the
223 photooxidation of BVOC in the forest.

224 **3.2 Influence of anthropogenic oxidant on SOA formation**

225 The diurnal profile of SOA tracers showed a clear single peak pattern in the afternoon on
226 August 28–29. Total isoprene-tracers peaked at 15:00–18:00 (28.4 ng $m^{-3}$), while total
227 monoterpene-tracers peaked slightly earlier at 12:00–15:00 (12.7 ng $m^{-3}$) (Figure 3c–d). Their
228 afternoon peaks are consistent with the maxima of ambient temperature and solar radiation
229 (Figure 2). These results indicate that SOA is formed by photooxidation of isoprene and
230 monoterpenes emitted from local vegetation under natural conditions. Our results are consistent
231 with the afternoon peaks of semi-volatile oxygenated organic aerosol (SVOOA) component
232 determined by the positive matrix factorization of the AMS spectra collected during the same
233 campaign (Han et al., 2014), which were produced by photooxidation of freshly emitted BVOC
234 from the local forest.

235 Interestingly, on August 23–24, days with regional anthropogenic oxidant input, isoprene-
236 and monoterpene-tracers showed not only afternoon peaks at 12:00–15:00, but also nighttime
237 peaks (Figure 3c–d) following the intensive precipitation during 13:00–17:00 (Figure 2). These
238 results suggest that SOA is continuously produced even in nighttime with sufficient oxidants.
239 AMS observation in the same campaign indicated that highly oxidized low volatility
240 oxygenated organic aerosols (LVOOA) are even more abundant than that of SVOOA on

241 August 23–24, especially in nighttime (Han et al., 2014). Nighttime production of SOA was
242 also observed in the United States (US) (Zhao et al., 2013).
243 Moreover, on days with regional input of oxidants, the SOA tracer levels were 1–2 orders of
244 magnitude higher than those under natural conditions both in daytime and nighttime.
245 Meanwhile, we found positive relations between $SO_4^{2-}$ and isoprene-SOA tracers as well as
246 monoterpene-SOA tracers (Table 1). These phenomena could be explained by the following
247 reasons. Firstly, regional BSOA could be transported along with anthropogenic oxidants.
248 Observations at Okinawa island, southern Japan indicated that the variations of monoterpene-
249 SOA tracers and caryophylinic acid are related to the continental outflow of BVOC oxidation
250 products (Zhu et al., 2016). Secondly, the earlier generation products of BVOC oxidation tend
251 to shift to the particle phase during gas/particle partitioning given their semivolatility nature
252 (Cahill et al., 2006), such a shift might be more prominent on days with aged regional aerosols
253 accompanied by a daytime increase of organics determined by AMS (Han et al., 2014). The
254 third possibility is that the anthropogenic oxidants might promote BSOA formation. We focus
255 on the third possibility and further testified this hypothesis.
256 We examined the degrees of BSOA tracer buildups in daytime as compared to nighttime
257 (ΔBSOA = mean daytime BSOA tracer levels – mean nighttime BSOA tracer levels) (Table 2).
258 ΔBSOA values on August 20–25 were higher by more than 1 order of magnitude than that on
259 August 26–30. These results implied that, although transported BSOA might contribute to their
260 elevation, anthropogenic oxidants substantially promoted the SOA formation in Wakayama
261 forest. A recent field study in the southeastern US suggested that the formation of methyltetrols
262 is mediated by $SO_4^{2-}$, being consistent with our results (Xu et al., 2015). They also reported that
263 $NO_3^{\bullet}$ radical was involved in the nighttime monoterpene oxidation. However, inorganic $NO_3^-$

did not correlate with monoterpene-SOA tracers during nighttime, indicating that the contribution of $NO_3^{\bullet}$ radical to nighttime monoterpene oxidation is not clear in Wakayama aerosols, which deserve further investigations.

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

The contributions of each source component to OC were estimated using tracer-based methods. OC fractions from fungal spores were estimated based on mannitol levels assuming that there were 1.7 pg mannitol and 13 pg OC per spore (Bauer et al., 2008). The secondary organic carbon (SOC) fraction resulting from VOC oxidation was estimated following Kleindienst et al. (2007) based on the chamber experiment. Contributions of plant debris to OC were estimated based on glucose following Puxbaum and Tenze-Kunit (2003). Contributions of biomass burning aerosols to OC were estimated based on levoglucosan following Zhu et al. (2015b). It is noteworthy that, although each tracer methods 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.

Fungal spores contribute a major fraction (45%) to OC in nighttime. In daytime, although the mass fraction was about half to that in nighttime (22%), fungal spores are still the largest known source of OC (Figure 4). In comparison, BVOC oxidation products (BSOC) contribute to 15% and 19% of OC in nighttime and daytime, respectively. Interestingly, the large BSOC fraction of OC mainly occurred on days with anthropogenic influences (August 20–25) (17% in daytime and 23% in nighttime). On days close to natural conditions (August 26–29), BSOC has a small contribution to OC (4.0% in nighttime and 4.7% in daytime). The larger contributions of BSOC to OC might be associated with the BSOC that are transported from the Asian

287 continent, a stimulating effect of anthropogenic oxidants on daytime BSOA formation, as well
288 as the enhanced gas to particle conversion of BVOC. These results suggest that increased fossil
289 fuel combustion and the subsequent oxidant emissions would cause a larger contribution of
290 BSOA to OA, which may in part compensate the human-caused global warming by acting as
291 CCN. Such effects are supposed to be incorporated into model simulations of the future climate
292 in the Anthropocene.

293 It is noteworthy that the contribution of plant debris to OC (5.6% in nighttime and 4.6% in
294 daytime) could not be neglected. These fractions account for only the primary OC sources
295 based on glucose level, and could be underestimated. Nevertheless, there are still quite amounts
296 of OC not being determined (34% and 51% in nighttime and daytime, respectively). Other than
297 the uncertainties introduced by the tracer methods, a notable fraction of OC could be
298 contributed from humic-like substances that are chemically and physically similar with
299 terrestrial and aquatic humic and fulvic acids (Graber and Rudich, 2006). Mono- and di-
300 carboxylic acids, originating from a broad range of primary organic compounds, could
301 contribute 38–44% of OC (Legrand et al., 2013). Pollen could also contribute to OC because of
302 its large size. Amines are another source of OC, but not well studied (Sintermann and Neftel,
303 2015). These sources from various sectors need to be further characterized for an unambiguous
304 understanding of the sources of forest aerosols.

305 Among few studies on the observation-based quantification of OC/OA sources of forest
306 aerosols, our results are in accordance with those in the Amazon rainforest, where primary
307 biological aerosol and SOA accounted for 68.5% and 18.8% of total particle masses, without
308 consideration of the diurnal variations (Pöschl et al., 2010). At an urban site with various OA
309 sources, Bakersfield, California, Zhao et al. (2013) reported that SOA accounted for 78% and

66% of OA during the daytime and the nighttime, respectively, while primary sources accounted for 15% of OA. Under a changing climate and uncertain anthropogenic emission scenario, although OA could be contributed by complicated sources in a pristine forest environment, our results demonstrate that biogenic particles and gases are rather the major sources of organic aerosols in the forest atmosphere.

## 4. Conclusions

We collected daytime and nighttime samples in a mid-latitude coniferous forest in Wakayama, central Japan. Focusing on fungal spores and BSOA, we quantified organic tracers containing information of various aerosol sources. Nighttime higher levels of trehalose and sugar alcohols were clarified under near saturated relative humidity, indicating the flourishing of fungal sporulation. BSOA tracers were more abundant in the daytime, indicating their photooxidation production among other sources. Enhanced BSOA tracer levels were observed on days with notable input of anthropogenic oxidant. Using tracer-based methods, we estimated that fungal spores contribute dominantly to OC in forest aerosols not only in the nighttime, but also in the daytime. The study emphasizes the importance of fungal spores in affecting biogenic aerosols in forest ecosystem.

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Ziemann, P. J., and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chem. Soc. Rev., 41, 6582–6605, 2012.

501 Table 1. Linear correlation coefficients (*r*) between secondary organic aerosol tracers and $NO_3^-$
502 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*** |

504 [a] Secondary organic aerosol tracer compounds are as follows: MGA, 2-methylglyceric acid; C5T, C5-alkene triols;
505 MTLs, 2-methyltetrols; PA, pinic acid; PNA, pinonic acid; 3-HGA, 3-hydroxyglutaric acid, MBTCA, 3-methyl-1,
506 2, 3-butanetricarboxylic acid.

507 [b] Negative values indicate negative correlations.

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

509

510

511 Table 2. Daytime buildups (differences between daytime and nighttime levels) of SOA tracers
512 on days with (August 20–25) and without (August 26–30) input of anthropogenic oxidants in
513 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 |

514 [a] Secondary organic aerosol tracer compounds are as follows: MGA, 2-methylglyceric acid; C5T, C5-alkene triols;
515 MTLs, 2-methyltetrols; PA, pinic acid; PNA, pinonic acid; 3-HGA, 3-hydroxyglutaric acid, MBTCA, 3-methyl-1,
516 2, 3-butanetricarboxylic acid; CPA, β-caryophyllinic acid; BSOA tracers are the sum of isoprene-, monoterpene-
517 and sesquiterpene- (CPA) tracers.
518

519 **Figure captions**

520

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

525

526 Figure 2. Meteorological parameters over August 20–30, 2010 at Wakayama forest, for (a)
527 averaged diurnal variations of temperature, relative humidity and solar radiation, and (b) hourly
528 means over the periods. Hourly precipitation was also shown in panel (b).

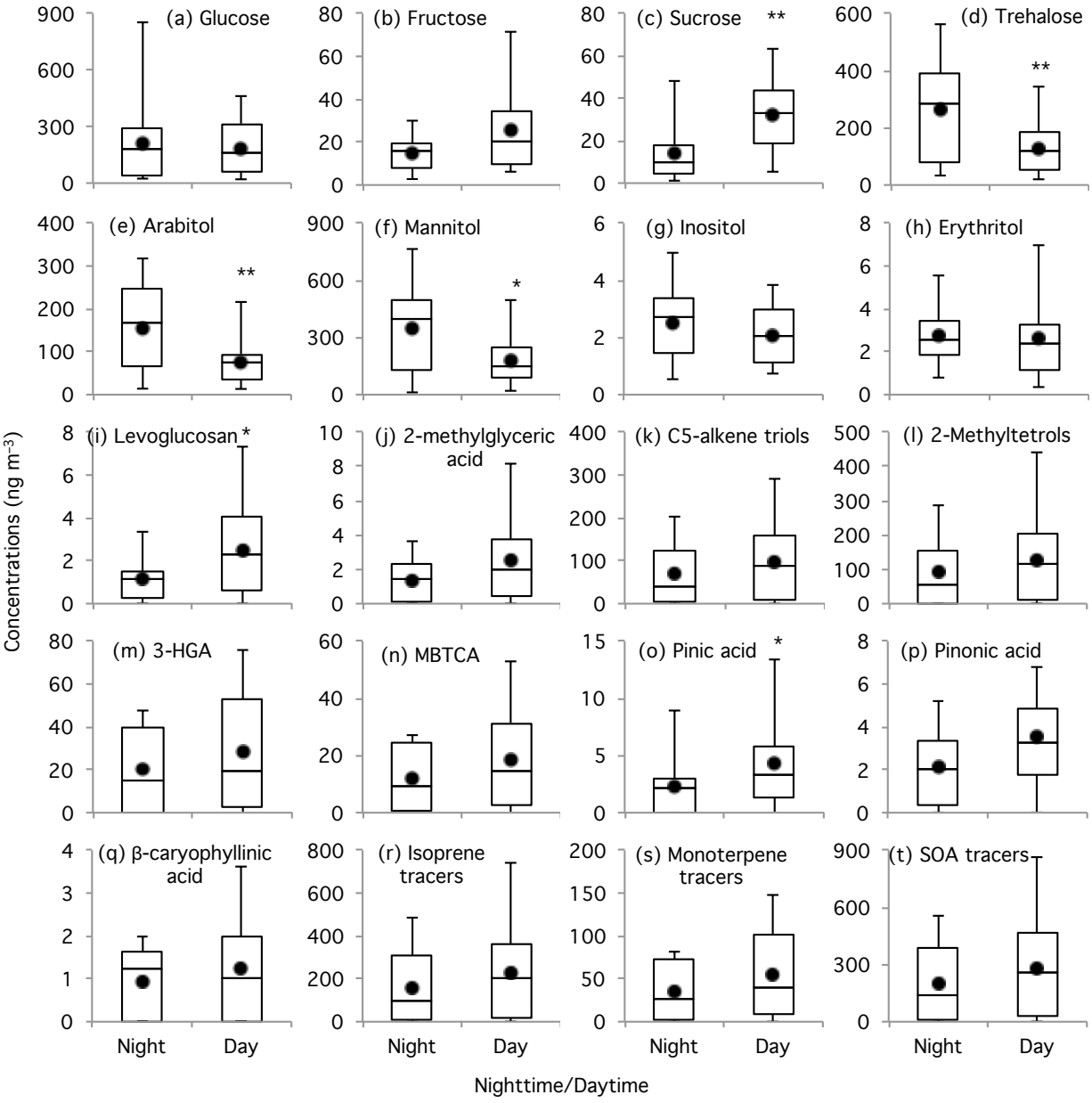
529

530 Figure 3. Diurnal profiles of organic compounds in forest aerosols in Wakayama on August 23–
531 24 (left) and August 28–29, 2010 (right).

532

533 Figure 4. Contributions from different sources to organic carbon in Wakayama forest aerosols
534 during the nighttime and the daytime.

535

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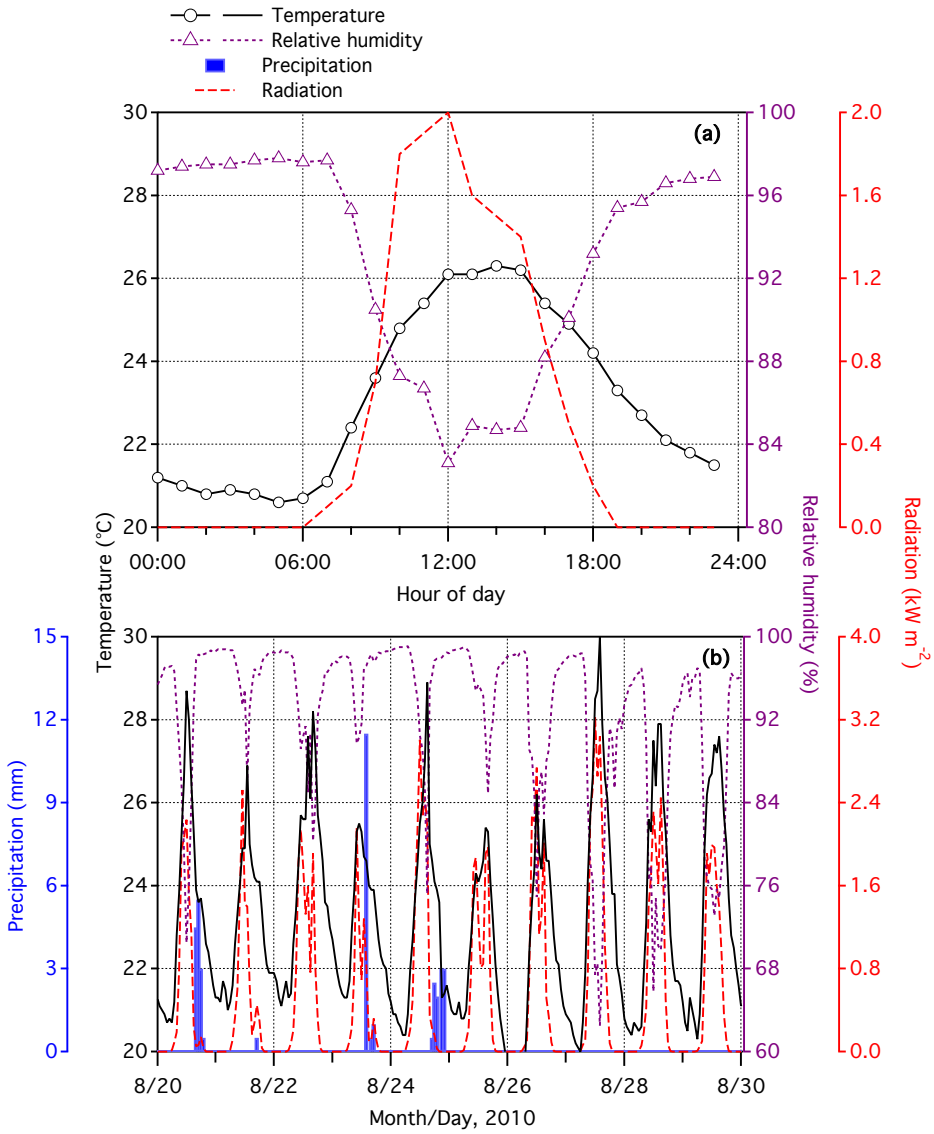


543 Figure 2. Meteorological parameters over August 20–30, 2010 at Wakayama forest, for (a)

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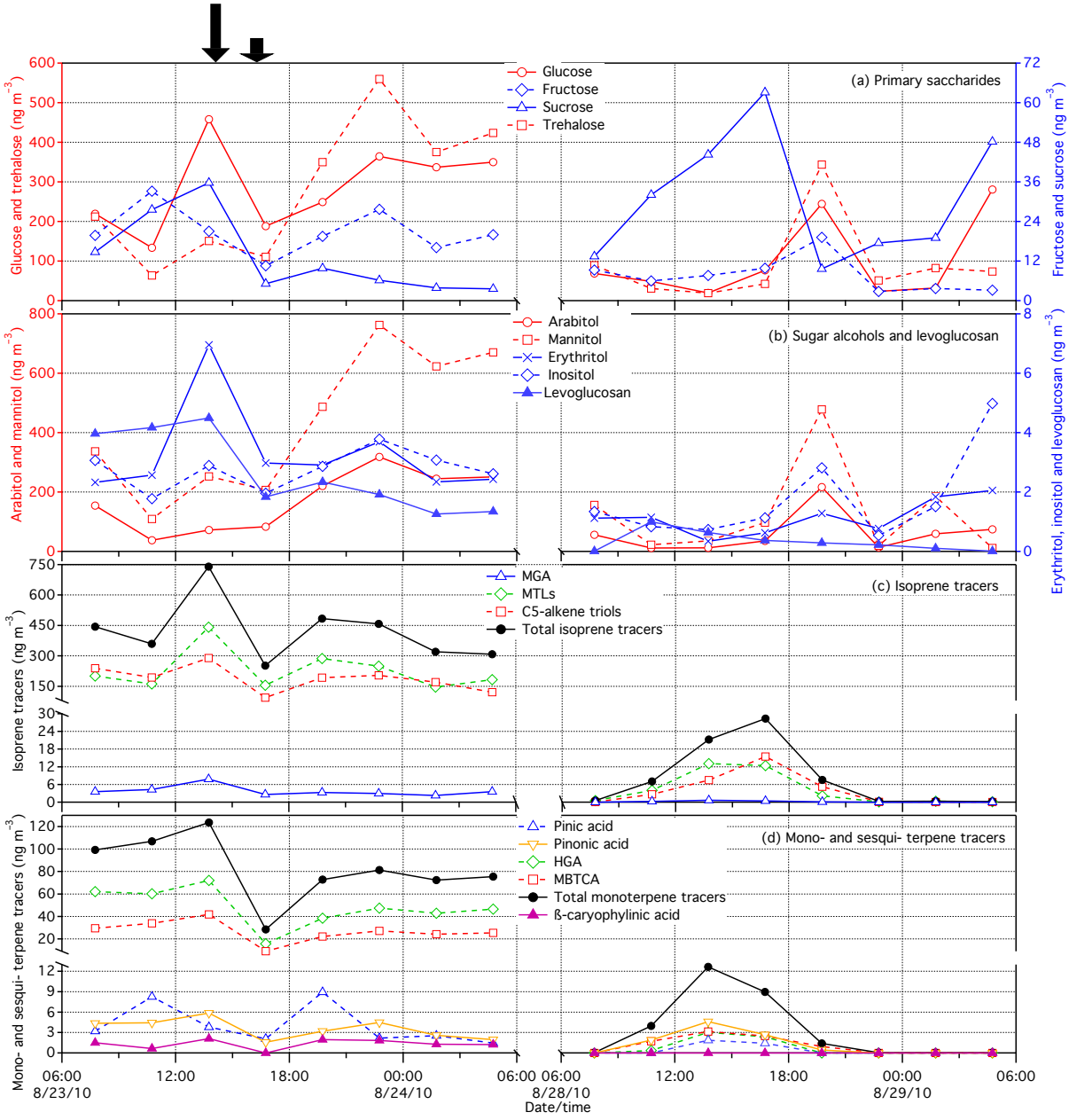
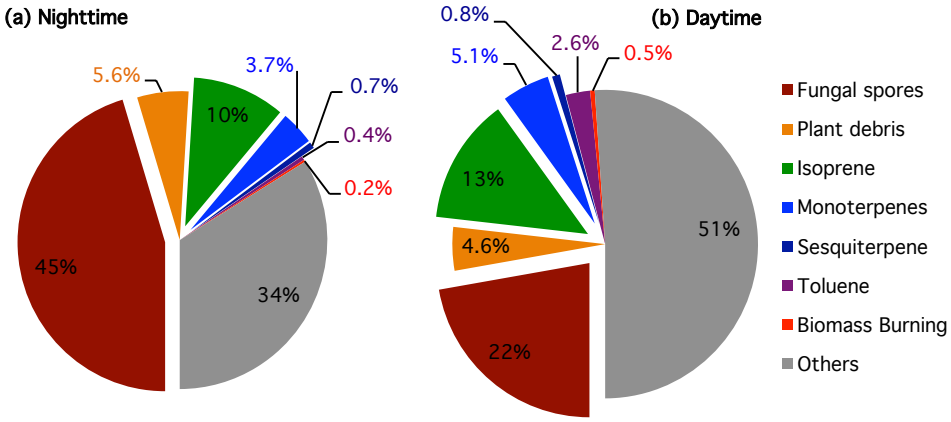



Figure 3. Diurnal profiles of organic compounds in forest aerosols in Wakayama on August 23–24 (left) and August 28–29 (right), 2010. Precipitation events occurred on 13:00–14:00 (11.2 mm) and 15:00–17:00 (1.5 mm) local time, August 23 as were marked by arrows on top of the left panels.

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