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1 **Impact of biogenic emissions of organic matter from a**
2 **cool-temperate forest on aerosol optical properties**

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28

29 **Abstract:** Terrestrial biogenic emissions of organic matter can affect the optical properties of
30 atmospheric aerosols and thus impact the radiation budget. To investigate this, the chemical
31 parameters of submicrometer water-soluble aerosols (WSA) collected on filters were
32 compared to optical properties measured by a sky radiometer at a cool-temperate forest site in
33 northern Japan. From June to December, 2015, the WSA samples were collected within the
34 forest canopy, while aerosol optical depth (AOD), single scattering albedo (SSA), absorption
35 Ångström exponent (AAE), and scattering Ångström exponent (SAE) were retrieved above
36 the canopy. The optical properties were compared with the filter-based chemical parameters
37 only when the vertical transport of aerosol particles from the forest canopy to the air above it
38 was significant. The result showed that the AOD and the mass concentrations of WSA
39 exhibited similar and distinct seasonal variations with peaks in summer and autumn. In
40 summer, sulfate accounted for 60% of the mass of WSA, which was linked to a high SSA ($>$
41 0.95), low AAE (1.15 ± 0.84), and low SAE (1.25 ± 0.22). In contrast, water-soluble organic
42 matter (WSOM) accounted for 70% of the mass of WSA in autumn. This large fraction of
43 WSOM was associated with a decrease in SSA ($0.90\text{--}0.95$) and an increase in AAE ($2.45 \pm$
44 0.91) and SAE (1.46 ± 0.15). The results suggest that in summer, aerosol particles with a
45 greater size range corresponded to aerosol chemical compositions dominated by sulfate. In
46 contrast, smaller particles with a strong light absorption at shorter wavelengths, were likely
47 important in autumn and associated with a composition dominated by WSOM. The majority
48 of WSOM in autumn has previously been associated with emissions of α -pinene from the
49 forest floor and the subsequent formation of biogenic secondary organic aerosols (BSOA).
50 This study indicates that α -pinene-derived SOAs, mostly originating from the forest floor,
51 were associated with a summer to autumn decrease in SSA. This process can modulate the
52 radiative effect on a regional scale.

53

54 **1. Introduction**

55 Atmospheric aerosol particles affect the Earth's radiative forcing directly by absorbing
56 and scattering solar radiation (Ångström, 1964). Light absorption by aerosols is caused
57 mainly by black carbon (BC) and mineral dust (Jacobson, 2001; Ramanathan and Carmichael,
58 2008). In addition, some fractions of organic carbon (OC) also show light-absorbing
59 properties; these are referred to as brown carbon (BrC) (Andreae and Gelencsér, 2006;
60 Bahadur et al., 2012; Kirchstetter et al., 2004; Moise et al., 2015). Climate models have
61 typically assumed that BC is the only light-absorbing component of aerosols (Kirchstetter et
62 al., 2004) and the effect of light-absorbing OC was generally not considered (Koch et al.,
63 2007). The former assumption may be valid for regions where aerosol particles are dominated
64 by BC (Cazorla et al., 2013). Recent climate models better represent absorbing characteristics
65 of dust and BrC (e.g. Balkanski et al., 2007; Chen et al., 2018; Wang et al., 2014). However,
66 over regions where light absorbing aerosols are dominant, the direct radiative effect (DRE) of
67 OC remains highly uncertain.

68 Although organic matter accounts for significant fractions of submicrometer aerosols by
69 mass (up to ~90%) (Kanakidou et al., 2005), there are high uncertainties regarding the DRE
70 of biogenic secondary organic aerosols (BSOAs) (Myhre et al., 2013). These include whether
71 or not the effect of BSOAs on the DRE is negative or positive on a regional scale (Andrews
72 et al., 2017). BSOAs in the size of the visible solar spectrum ($\lambda = 380\text{--}750$ nm) can have an
73 important effect on the DRE (Scott et al., 2014). Scott et al. (2014) estimated that the global
74 annual mean DRE of BSOAs ranged between -0.78 Wm^{-2} and -0.08 Wm^{-2} . Lihavainen et al.
75 (2009) estimated that the regional DRE over a boreal forest in northern Finland ranged from
76 -0.74 Wm^{-2} and -0.37 Wm^{-2} in summer.

77 The wide range of the estimated DREs is largely due to the complex chemical and
78 physical properties, which include the absorbing and scattering, of BSOAs. A negative DRE
79 of BSOAs has been attributed to the latter (Lihavainen et al., 2009; Kim and Paulson, 2013;
80 Scott et al., 2014; Moise et al., 2015, and references therein). The efficiency of light
81 scattering depends on chemical compositions of biogenic volatile organic compounds
82 (BVOCs), their oxidation pathways that lead to the production of BSOAs, the mixing state of
83 BSOA particles, and the time scale of their atmospheric reactions (e.g., Flores et al., 2014;
84 Moise et al., 2015; Nakayama et al., 2010). Most previous studies observed no absorption of
85 solar radiation by BSOAs (Moise et al., 2015, and references therein; Nakayama et al., 2010),
86 or assumed that BSOAs have non-absorbing characteristics (Kim et al., 2010; Kim and
87 Paulson, 2013; Moise et al., 2015). In contrast, other previous studies reported light
88 absorption by organic matter at wavelengths between 350 nm and 470 nm (Andreae and
89 Gelencsér, 2006; Kirchstetter et al., 2004; Lambe et al., 2013; Song et al., 2013; Yang et al.,
90 2009). The gap in current knowledge requires a study to investigate the impact of BSOAs on
91 the DRE in the ambient atmosphere.

92 The strength and types of BVOC emissions depend on vegetation type, phenology, and
93 various meteorological conditions (e.g., Mielonen et al., 2018). Boreal and cool-temperate
94 forests cover the second largest forest area in the world (FAO, 2001). α -pinene is one of the
95 most abundant BVOC in boreal and cool-temperate forests (Guenther et al., 1995; Rinne et
96 al., 2009). Light absorbing properties of BSOA produced from α -pinene have been
97 documented in laboratory experiments (Lambe et al., 2013; Song et al., 2013; Zhong and
98 Jang, 2011). Filter-based off-line measurements of submicrometer water-soluble aerosols
99 (WSA) were made within a canopy of a cool-temperate forest site in northern Japan from
100 June to December 2015. During the same period, ground-based measurements of aerosol
101 optical properties above the forest canopy were simultaneously conducted at the same forest

102 site. In this study, chemical properties of WSA and the retrieved optical properties were
103 compared to elucidate the effect of the observed BSOA on DRE on a regional scale.

104 **2. Experimental Data and Methods**

105 **2.1. Measurement site**

106 **Fig. 1** shows the location and surroundings of the observation site in a cool-temperate
107 zone where ambient submicrometer aerosol samples and data on the optical properties of
108 aerosols were obtained simultaneously. The site is Hokkaido University's Tomakomai
109 Experimental Forest (TOEF) (42°43'N, 141°36'E) (Hiura, 2005) located in the southwestern
110 part of Hokkaido, northern Japan. The area of the TOEF is 2715 ha. It is located to the north
111 of urban industrial and port area of Tomakomai city, which faces the Pacific Ocean. The
112 TOEF is classified as a mixed cool-temperate forest consisting of mature and secondary
113 deciduous and planted coniferous trees. Typical naturally occurring species include
114 Mongolian oak (*Quercus crispula*), mono maple (*Acer mono*), Korean whitebeam (*Sorbus*
115 *alnifolia*), Japanese lime (*Tilia japonica*); planted species include Japanese larch (*Larix*
116 *leptolepis*), Sakhalin fir (*Abies sachalinensis*), and Sakhalin spruce (*Picea glehnii*) (Hiura,
117 2005). Also characteristic of this site are various types of forest floor covers (Takafumi and
118 Hiura, 2009) and shallow and less weathered volcanogenic regosols (Shibata et al., 1998).

119 The meteorological data used in this study were obtained by the Japan Meteorological
120 Agency (<http://www.jma.go.jp/jma/indexe.html>). In autumn and winter, northerly local wind
121 with local horizontal wind speeds of $3.3 \pm 1.4 \text{ m s}^{-1}$ were dominant and came from the
122 forested area (**Fig. 1** and **Fig. 2d**). In contrast, the prevailing southerly wind with speeds of
123 $2.7 \pm 0.8 \text{ m s}^{-1}$ came from the urban and coastal area were observed in summer. The monthly
124 average temperature from June to December 2015 ranged from $0.9 \pm 1.8 \text{ }^{\circ}\text{C}$ (December) to
125 $20.8 \pm 1.0 \text{ }^{\circ}\text{C}$ (August).

126

127 **2.2. Aerosol sampling and off-line measurements of the chemical parameters**

128 Submicrometer aerosol samples were continuously collected using a high-volume air
129 sampler (HVAS; Model 120SL, Kimoto Electric, Osaka, Japan), deployed at an altitude of
130 ~18 m above the forest floor (Müller et al., 2017). A cascade impactor (CI; Model TE-234,
131 Tisch Environmental, Cleves, OH, USA) attached to the HVAS is used to collect size-
132 segregated particles (Miyazaki et al., 2012) at a flow rate of 1130 L min⁻¹. The filter samples
133 obtained at the bottom stage of the impactor were analyzed, which collects particles with
134 aerodynamic diameter smaller than 0.95 µm. The samples were collected on quartz fiber
135 filters (25 cm × 20 cm) from June to December 2015, with a sampling duration of each
136 aerosol sample being approximately 1 week. To remove contaminants, quartz fiber filters
137 were pre-combusted at 410 °C for 6 hours. The collected filters were stored individually in
138 glass jars with a Teflon-lined screwed cap and were kept frozen at -20 °C until the analysis.

139 Fifteen aerosol samples were extracted with ultrapure water followed by being filtered
140 through a 0.22-µm pore syringe filter. The extracts were then measured for each chemical
141 parameter. The extracts have been analyzed in terms of their water-soluble organic carbon
142 (WSOC) concentrations (Miyazaki et al., 2014, 2012), which were converted to water-soluble
143 organic matter (WSOM) concentrations using a conversion factor of 1.8 (Finessi et al., 2012;
144 Yttri et al., 2007). Furthermore, the concentrations of major inorganic ions (Cl⁻, NO₂⁻, NO₃⁻,
145 SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺, NH₄⁺, K⁺) were obtained by injecting the extracts into an ion
146 chromatograph (Model 761 compact IC; Metrohm) (Miyazaki et al., 2009). Thus, the fraction
147 of non-sea-salt sulfate was calculated based on the concentrations of sulfate and sodium.
148 Further details about the chemical analysis are given in Müller et al. (2017). In this study, the

149 sum of the mass concentrations of WSOM and inorganic ions measured is defined as water-
150 soluble aerosols (WSA).

151

152 **2.3. Aerosol optical properties**

153 The optical properties of aerosols above the forest canopy were measured using a sky
154 radiometer (POM-02; Prede Co., Ltd., Tokyo, Japan). It was deployed at an altitude of ~30 m
155 above the ground at TOEF as part of the sky radiometer network (Aoki et al., 2008). It
156 measures the direct solar irradiance and diffuse sky radiance at 11 wavelengths every ~10
157 min. Aerosol optical properties were retrieved using 5 wavelengths (0.4, 0.5, 0.675, 0.87, and
158 1.02 μm) (Aoki et al., 2013; Aoki and Fujiyoshi, 2003) by using SKYRAD.pack version 4.2
159 algorithms (Nakajima et al., 1996). The spectral extinction of the solar irradiance at each
160 wavelength by aerosol particle is defined as aerosol optical depth (AOD), which is a measure
161 of aerosol loading in the atmospheric column. Because the maximum radiation intensity of
162 the solar spectrum occurs at wavelength of about 500 nm, AOD at that wavelength is
163 presented in this study as in other previous studies. AOD below 0.2 typically indicates a clear
164 atmosphere, whereas $\text{AOD} > 0.4$ indicates high aerosol loadings such as polluted air (e.g.,
165 Salinas et al., 2013). The Ångström exponent (AE) is a parameter that describes the
166 dependence of AOD on the wavelength of the light (Ångström, 1964), which is a measure of
167 the particle size. With the use of AE, the particle size can be classified into coarse and fine
168 modes (Salinas et al., 2009). For example, $\text{AE} < 1$ indicates that a volume fraction of fine-
169 mode particles is less than 0.5, while larger AE values indicates a larger fractions of fine
170 mode aerosols (Schuster et al., 2006).

171 The single scattering albedo (SSA) is defined as the ratio of scattering to extinction
172 (absorption + scattering) (e.g., Hansen et al., 1997). SSA indicates whether aerosol particles

173 have radiative warming, or cooling effects which includes effects of surface reflectance
 174 (Myhre et al., 2013). $SSA > 0.95$ represents scattering/reflective aerosols (Lee et al., 2010;
 175 Levy et al., 2007), whereas $SSA < 0.90$ indicates more absorbing aerosols. The mixture of
 176 scattering and absorbing aerosols gives SSA values typically between 0.90 and 0.95. The
 177 absorption Ångström exponent (AAE) expresses the wavelength dependence of the aerosol
 178 light absorption. AAE indicates the dominant chemical composition of light-absorbing
 179 aerosols. The size range of these aerosols depends primarily on the scattering Ångström
 180 exponent (SAE). AAE and SAE are defined in the spectral dependence of the absorption
 181 aerosol optical depth (AAOD) and scattering aerosol optical depth (SAOD), respectively, as
 182 follows (Bahadur et al., 2012; Cazorla et al., 2013; Giles et al., 2012; Russell et al., 2010):

$$AAE = - \frac{\ln(AAOD(\lambda_1)/AAOD(\lambda_2))}{\ln(\lambda_1/\lambda_2)} \quad (1)$$

$$SAE = - \frac{\ln(SAOD(\lambda_1)/SAOD(\lambda_2))}{\ln(\lambda_1/\lambda_2)} \quad (2)$$

183 where

$$AAOD(\lambda) = AOD(\lambda) \times (1 - SSA(\lambda)) \quad (3)$$

$$SAOD(\lambda) = AOD(\lambda) \times SSA(\lambda) \quad (4)$$

184 Wavelengths of $\lambda_1 = 400$ nm and $\lambda_2 = 675$ nm used in this study are similar or the same as
 185 those used in previous studies (e.g., Bahadur et al., 2012; Cazorla et al., 2013; Russell et al.,
 186 2010).

187 Black carbon (BC) has an AAE value around 1.0 (e.g., Bergstrom et al., 2007; Giles et
 188 al., 2012; Russell et al., 2010). Higher AAE values, of 1.5–3.0, indicate a significant
 189 contribution from mineral dust (e.g., Bergstrom et al., 2007; Giles et al., 2012; Russell et al.,

2010). AAEs greater or less than 1.0 indicate light-absorbing aerosols coated with either light
absorbing or non-absorbing components (Lack and Cappa, 2010). SAEs represent aerosol
size ranges and typically have values between 0.0 to 4.0. Higher SAE values (e.g., > 2.0)
indicates relatively smaller particles, such as BC or anthropogenic sulfate, while smaller SAE
values (e.g., < 2.0) indicates larger particles such as dust, sea salt, or photochemically aged
aerosols (Cappa et al., 2016; Cazorla et al., 2013; Schmeisser et al., 2017, and references
therein). In this study, the SSA and AAE data are used to discuss the systematic difference in
those values among the different seasons, rather than to discuss their absolute values
quantitatively. To minimize the effect of horizontal transport of air above the canopy on the
linkage between the filter-based data and the optical parameters, we selected the data that
showed significant vertical transport of aerosols from the forest canopy to the air above.
Significant vertical transport was defined by the local horizontal and vertical wind speeds
measured at the forest canopy crane with a vertical height of 25 m at the forest site.
Specifically, the data with the horizontal wind speeds $< 3.5 \text{ m s}^{-1}$ were selected first which
are assumed to be less influenced by horizontal transport. Then the data with the positive
vertical winds (i.e., from the canopy to the above atmosphere) were further selected to be
defined as the significant vertical transport.

207

208 **3. Results and Discussion**

209 **3.1. Seasonal trends of the aerosol chemical composition and AOD**

210 **Fig. 2a** presents the temporal variations of the WSA mass concentration and the daily
211 averaged AOD at a wavelength of 500 nm from June to December 2015. The mass
212 concentrations of WSA ranged from 0.31 to 10.65 $\mu\text{g m}^{-3}$ with an average of $4.46 \pm 2.31 \mu\text{g}$
213 m^{-3} . Significant increases in the concentrations of the WSA were observed in three periods:

214 July 20-August 22, October 17-November 5, and September 21-October 1 which are referred
215 to as summer, autumn, and transition period, respectively. The AOD ranged from 0.03 to 0.72
216 with an average of 0.18 ± 0.13 . This average value is similar to that reported by Eck et al.
217 (2009), who showed that monthly averaged AOD at the wavelength of 500 nm was less than
218 0.10 at a boreal background site in Central Alaska. As stated in section 2.3, an increase in
219 AOD (>0.4) observed in summer indicates high aerosol loadings in this season. Indeed, the
220 concentrations of WSA and the AOD show a significant positive correlation ($R^2 = 0.76$).
221 Although the number of the WSA samples is limited ($n = 15$), the positive correlation
222 suggests a close linkage between the two parameters.

223 **Fig. 2b** shows the seasonal variation in the mass concentrations of WSOM and sulfate,
224 whereas **Fig. 2c** presents the chemical mass fractions in WSA. During the first half of
225 summer, $\sim 60\%$ of the WSA mass was sulfate (up to $3.40 \mu\text{g m}^{-3}$). In contrast, WSOM
226 accounted for $\sim 70\%$ of the WSA mass in autumn, the concentration reaching as large as 7.50
227 $\mu\text{g m}^{-3}$. Müller et al. (2017) reported similar temporal trends of the fractions and
228 concentrations for WSOM, and sulfate for the data in 2013 at the same forest site. They made
229 positive matrix factorization (PMF) for the source apportionment of the observed aerosols by
230 using various molecular tracers of biogenic sources as well as anthropogenic sources. The
231 PMF analysis distinguished the contributions of biogenic and anthropogenic sources to the
232 observed aerosols. Müller et al. (2017) indicated that the increased concentrations and
233 fractions of sulfate in summer were attributable to the inflow of anthropogenic aerosols from
234 the urban area, whereas those of WSOM in autumn were mostly attributed to BSOA from the
235 forest floor.

236 To examine the dominant sources of the observed aerosols for each season in this study,
237 **Fig. 2d** shows the local wind direction and wind speeds at the forest site. In summer,
238 southerly winds were predominant, indicating that the observed aerosols were mainly

239 transported from the coastal industrial area of Tomakomai city (**Fig. 1**). Moreover, the
240 contribution of sea-salt sulfate to the total sulfate mass was negligible ($< 2\%$). These result
241 suggests that the increased concentration of sulfate in summer was attributable to the
242 anthropogenic sources, the result of which is similar to that obtained in 2013 (Müller et al.,
243 2017). On the other hand, northerly wind was predominant in autumn (**Fig. 2d**), indicating
244 that the observed increase in the WSOM concentrations was mainly associated with the
245 influence from the forest area in this season (**Fig. 1**). This result is also similar to that
246 obtained by Müller et al. (2017). In summary, the overall result suggests that anthropogenic
247 sulfate and biogenic WSOM dominated the WSA in the forest canopy in summer and autumn,
248 respectively.

249

250 **3.2. Ångström exponent, AOD, and water-soluble aerosols (WSA)**

251 **Fig. 2e** shows the seasonal variation of the daily averaged AE. The average AE value
252 was 1.19 ± 0.28 , most of which exceeded 1.00 during the study period (**Table 1**). As
253 described in section 2.3, the AE with mostly >1.00 indicates the dominance of submicrometer
254 aerosols. The result suggests that the variation in AOD was associated with the chemical
255 composition of submicrometer aerosols. In previous studies, the dependence of satellite-
256 derived AOD on the characteristics of aerosol particles were reported in central and suburban
257 Helsinki and over the United States, including the coastal regions (Natunen et al., 2010; Toth
258 et al., 2014). Using ground- and satellite-based AOD retrievals at urban and suburban sites in
259 Singapore, Chew et al. (2016) found a significant positive correlation between AOD and
260 $PM_{2.5}$ (particulate matter with a diameter less than $2.5 \mu\text{m}$), when the aerosol layer existed
261 near the surface or the planetary boundary layer (PBL) was well-mixed.

262 In addition, other previous studies showed that AOD can be affected by emissions of
263 BVOCs and chemical compositions of WSA (Goldstein et al., 2009; Mielonen et al., 2018;
264 Nguyen et al., 2016). Nguyen et al. (2016) attributed the increase in AOD to the increase of
265 hygroscopic sulfate particles over the southeast United States during summer. Goldstein et al.
266 (2009) and Mielonen et al. (2018) found a relation between increased AOD and increased
267 emissions of BVOC from forests in southeastern USA. In our study, the local wind data
268 indicates the significance of vertical transport of air masses, indicating that the AOD during
269 the study period was largely influenced by the increased mass concentrations of
270 submicrometer WSA in the forest canopy.

271

272 **3.3. Impact of the biogenic emissions of organic matter on light-scattering and** 273 **absorbing characteristics of aerosols**

274 To investigate the influence of biogenic emissions of organic matter on light-scattering
275 and light-absorbing characteristics of aerosols above the forest canopy, **Fig. 2f** shows the
276 temporal variation of the daily averaged SSA at a wavelength of 500 nm. In summer, the
277 average SSA was 0.98 ± 0.01 , most of which were larger than 0.95, indicating that the
278 observed aerosols had mainly scattering characteristics. In contrast, most of the SSA in
279 autumn ranged 0.90–0.95 (with an average of 0.93 ± 0.02); this was generally lower than the
280 SSA in summer (an average of 0.98 ± 0.01) and the transition period (an average of $0.95 \pm$
281 0.02) by 5% and 2%, respectively (**Table 1**). The difference in the SSA in each season
282 suggests that the aerosols above the forest canopy in autumn have more light-absorbing
283 characteristics.

284 It has been demonstrated that some types of organic carbon (OC) in aerosols show
285 strong light absorption at visible and UV wavelengths (e.g., Bahadur et al., 2012; Giles et al.,

286 2012; Moise et al., 2015). Müller et al. (2017) suggested that the increase in the WSOM mass
287 in autumn was attributable to the emissions of α -pinene from the forest floor and the
288 subsequent formation of SOA. Light-absorbing characteristics of α -pinene SOA have been
289 reported by laboratory experiments (Lambe et al., 2013; Song et al., 2013; Zhong and Jang,
290 2011). Song et al. (2013) found significant light absorption at 355 nm and 405 nm by SOA
291 formed from ozonolysis and NO₃ oxidation of α -pinene in the presence of highly acidic
292 sulfate seed aerosols under dry conditions. Our results in the current study imply that
293 biogenic emissions of organic matter from the forest floor and subsequent formation of SOA
294 might increase the absorption characteristics of the particles in autumn.

295 **Fig. 3** shows the dependence of SSA on wavelength during the summer and autumn
296 periods for the data of AOD larger than 0.2. The data with AOD < 0.2 was excluded for the
297 following analysis to focus on possible sources of aerosols with these high AOD. Generally,
298 no spectral dependence of SSA was observed during summer (**Fig. 3a**). In contrast, the SSA
299 in autumn showed a strong dependence on wavelength, which were lower at shorter
300 wavelength (<600 nm) in that season (**Fig. 3b**). Previous studies found that hygroscopic
301 aerosol particles such as sulfate have near neutral spectral dependence on SSA (e.g., Giles et
302 al., 2012); however, the SSA of BC, urban-industrial aerosols, and biomass burning aerosols
303 decreased as the wavelength increased (e.g., Dubovik et al., 2002; Giles et al., 2012; Li et al.,
304 2015; Russell et al., 2010). Yet the SSA of aerosol particles dominated by OC have been
305 characterized as increasing with increases in wavelength (Bahadur et al., 2012; Cazorla et al.,
306 2013; Giles et al., 2012; Russell et al., 2010), which has been explained by the strong light
307 absorption in the wavelength range between 350 nm 470 nm. Indeed, many types of organic
308 species show light-absorbing characteristics at this wavelength range (e.g., Andreae and
309 Gelencsér, 2006; Kirchstetter et al., 2004; Lambe et al., 2013; Song et al., 2013; Yang et al.,
310 2009). Russell et al. (2010) showed that for urban aerosols in Mexico City, the spectral

311 dependence of SSA on wavelength changed from negative to positive with increasing
312 fractions of organic mass in aerosol particles. In this study, the difference in the spectral
313 dependence on the wavelength between summer and autumn suggests that hygroscopic
314 aerosol particles contributed to less light-absorbing characteristics in summer, whereas
315 particles dominated by organic matter contributed to more light-absorbing characteristics in
316 autumn. This is supported by the dominant chemical component in summer (sulfate) and
317 autumn (WSOM) as discussed above (**Fig. 2b** and **Fig. 2c**).

318 **Fig. 4** shows a scatterplot of AAE and SAE, for the data of AOD >0.2 in summer and
319 autumn. In autumn, the AAE and SAE showed relatively larger values with averages of 2.45
320 ± 0.91 and 1.46 ± 0.15 , respectively. On the other hand, in summer, the majority (85%) of the
321 data have relatively smaller values less than 2.5 and 1.5 for AAE and SAE, respectively. The
322 result indicates that small particles with strong light absorption at shorter wavelength were
323 dominant in autumn, whereas larger particles with less light-absorbing properties were more
324 evident in summer. Previous studies showed that light-absorbing OC aerosols in smaller size
325 ranges are indicated by AAE > 1.5 and SAE > 1.5. Using ground-based remote sensing
326 techniques, Russell et al. (2010) found that the increased mass fraction of organic matter in
327 submicrometer aerosols corresponded to an AAE of 1.5 in boreal forests in the USA and
328 Canada. Bahadur et al. (2012) investigated the AAE of OC aerosols at various urban
329 industrial and background sites and reported the global average to be 4.55 ± 2.01 . Therefore,
330 the higher AAE values in autumn from this study imply a significant influence of OC on
331 light-absorbing properties; this is consistent with the results of previous works.

332 In summary, the current study indicates that biogenic organic aerosols observed in the
333 forest canopy can affect the optical properties of aerosol above the canopy. Namely, the lower
334 SSA in autumn indicates that the light absorption by smaller aerosol particles was more
335 significant than in summer. As stated above, our previous study indicated that the observed

336 WSOM, which was a dominant component in autumn, was associated with emission of
337 organic matter from the forest floor (Müller et al., 2017). Therefore, the subsequent formation
338 of BSOA is closely linked with the enhanced light-absorbing properties of the aerosol
339 particles in this season. This might have important implications for the prediction of the
340 radiative effect of biogenic organic aerosols produced in forest area on a regional scale in
341 future.

342

343 **Conclusions**

344 The current study indicates that biogenic secondary organic aerosols (BSOAs) observed
345 in the canopy of a cool-temperate forest can affect the optical properties of aerosol above the
346 canopy. Namely, the lower SSA in autumn indicates that the light absorption by smaller
347 aerosol particles was more significant than in summer. As stated above, our previous study
348 indicated that the observed WSOM, which was a dominant component in autumn, was
349 associated with emission of organic matter (mostly α -pinene) from the forest floor (Müller et
350 al., 2017). Therefore, the subsequent formation of BSOAs is closely linked with the enhanced
351 light-absorbing properties of the aerosol particles in this season.

352 The study suggests the importance of BSOA from the forest for the impact on the
353 scattering/absorption characteristics of aerosols above the forest canopy. This impact should
354 be considered for the prediction of the aerosol radiative forcing on a regional scale and the
355 effect of biogenic organic aerosols on climate in future. Additional field studies at other
356 forest sites and comprehensive in-situ and remote sensing measurements are required to
357 confirm the results and to elucidate the detailed mechanism of how BSOA affect the optical
358 properties on regional and global scale.

359

360

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365

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592 **Table 1.** Average or individual values of the optical and chemical parameters for the three
 593 periods in 2015: summer (Jul. 20–Aug. 22), a transition period (Sept. 21–Oct. 1), and autumn
 594 (Oct. 17–Nov. 5). The number of data points for the optical parameters (ND_{opt}) and the filter-
 595 based chemical parameters (ND_{filter}) are shown for each season.

	Summer $ND_{opt} = 129$, $ND_{filter} = 2$ (Jul. 20— Aug. 22)	Transition period $ND_{opt} = 30$ $ND_{filter} = 2$ (Sept. 21– Oct. 1)	Autumn $ND_{opt} = 159$ $ND_{filter} = 3$ (Oct. 17– Nov. 5)
Aerosol optical depth (AOD) at $\lambda = 500$ nm	0.31 ± 0.18	0.25 ± 0.06	0.18 ± 0.09
Ångström exponent (AE)	1.29 ± 0.04	1.22 ± 0.04	1.39 ± 0.04
Single scattering albedo (SSA) at $\lambda = 500$ nm	0.98 ± 0.01	0.95 ± 0.02	0.93 ± 0.02
Absorption Ångström exponent (AAE)	1.15 ± 0.84	0.78 ± 0.47	2.45 ± 0.91
Scattering Ångström exponent (SAE)	1.25 ± 0.22	1.13 ± 0.06	1.46 ± 0.15
SO_4^{2-} ($\mu\text{g m}^{-3}$)	2.15, 3.40	1.67, 0.43	1.04 ± 0.50
WSOM ($\mu\text{g m}^{-3}$)	0.59, 1.37	0.74, 0.69	4.02 ± 2.51
WSA ($\mu\text{g m}^{-3}$)	3.45, 5.89	2.93, 1.31	5.79 ± 3.50

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598

599 Figure Captions

600 **Fig. 1.** Location of the sampling site: Tomakomai Experimental Forest of Hokkaido
601 university, Hokkaido, northern Japan. Map data ©2018 Google, ZENRIN; Imagery
602 ©2018 Google, DigitalGlobe, Data SIO, NOAA, U.S. Navy, NGA, GEBCO,
603 TerraMetrics (<https://maps.google.com/>). Maps are modified with Microsoft PowerPoint
604 2013.

605 **Fig. 2.** Time series of (a) the concentration of submicron water-soluble aerosols (WSA)
606 obtained by the filter-based measurements and the aerosol optical depth (AOD) at a
607 wavelength of 500 nm, (b) the mass concentrations of submicrometer water-soluble
608 organic matter (WSOM) and sulfate, (c) the chemical mass fraction of the submicrometer
609 WSA, (d) local wind direction and wind speeds, (e) the Ångström exponent (AE), and (f)
610 the single scattering albedo (SSA) at $\lambda = 500$ nm from June to December, 2015. The
611 temporal resolution of the filter-based chemical data is approximately 1 week. For the
612 optical properties, the temporal resolution is one day, where the daily averaged values
613 with the standard deviations are presented. Shaded areas indicate the three periods
614 defined as summer (July 20–August 22), transition period (September 21–October 1),
615 and autumn (October 17–November 5).

616 **Fig. 3.** Wavelength dependence of the single scattering albedo (SSA) during (a) the summer
617 period and (b) the autumn period with AOD > 0.2. Gray symbols indicate the daily
618 average values, whereas red symbols show the average values of those daily average
619 SSA.

620 **Fig. 4.** Scatter plot of the absorption Ångström exponent (AAE) and the scattering Ångström
621 exponent (SAE) for the summer period (blue) and the autumn period (red) with AOD >
622 0.2.

Fig. 1

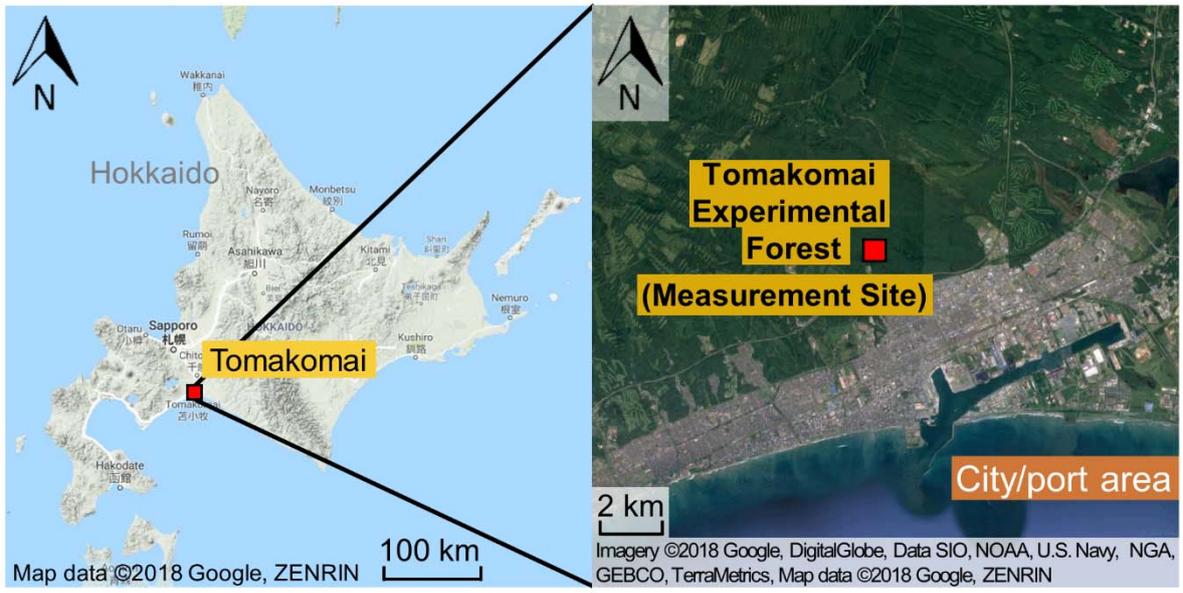


Fig. 2

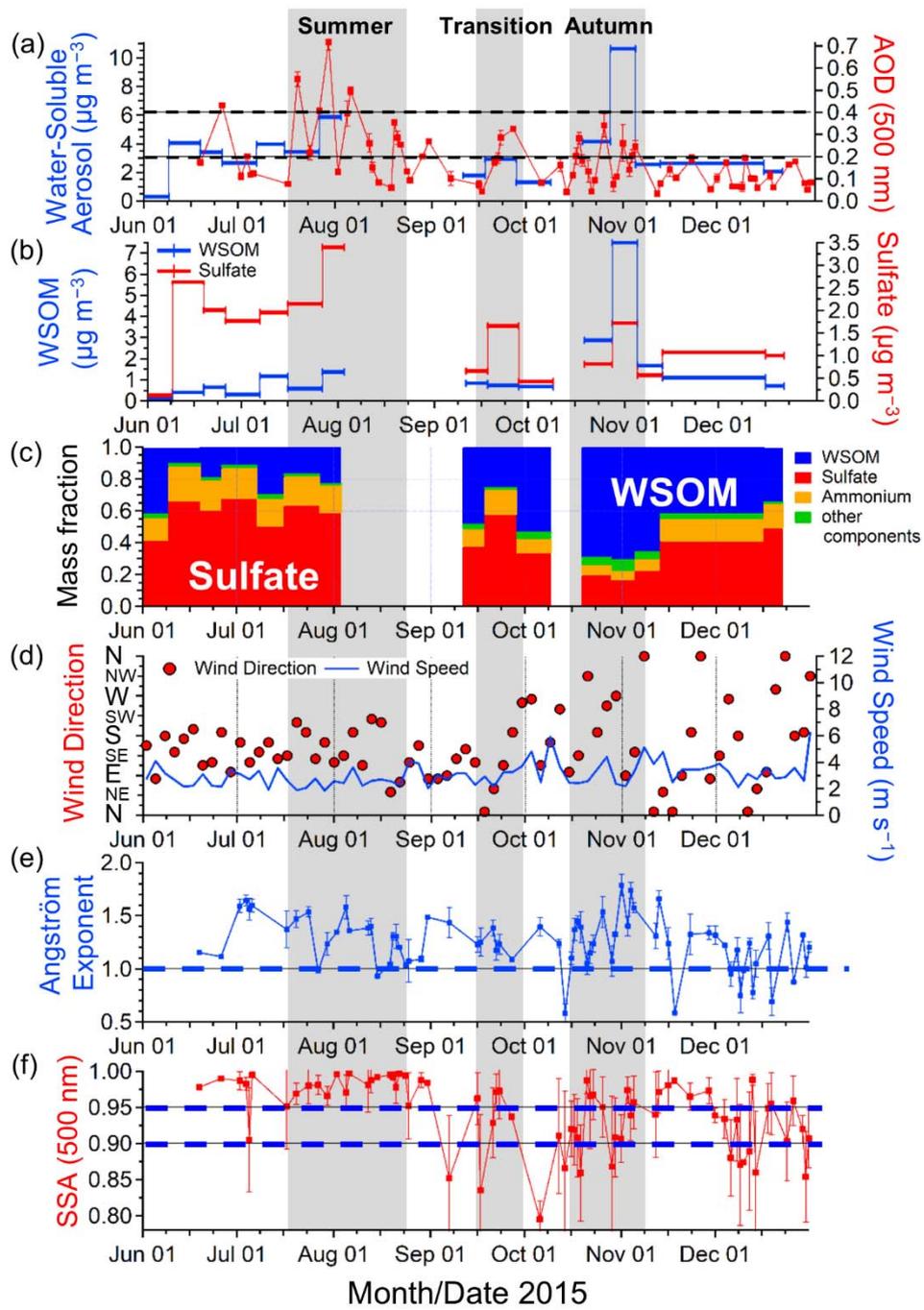


Fig. 3

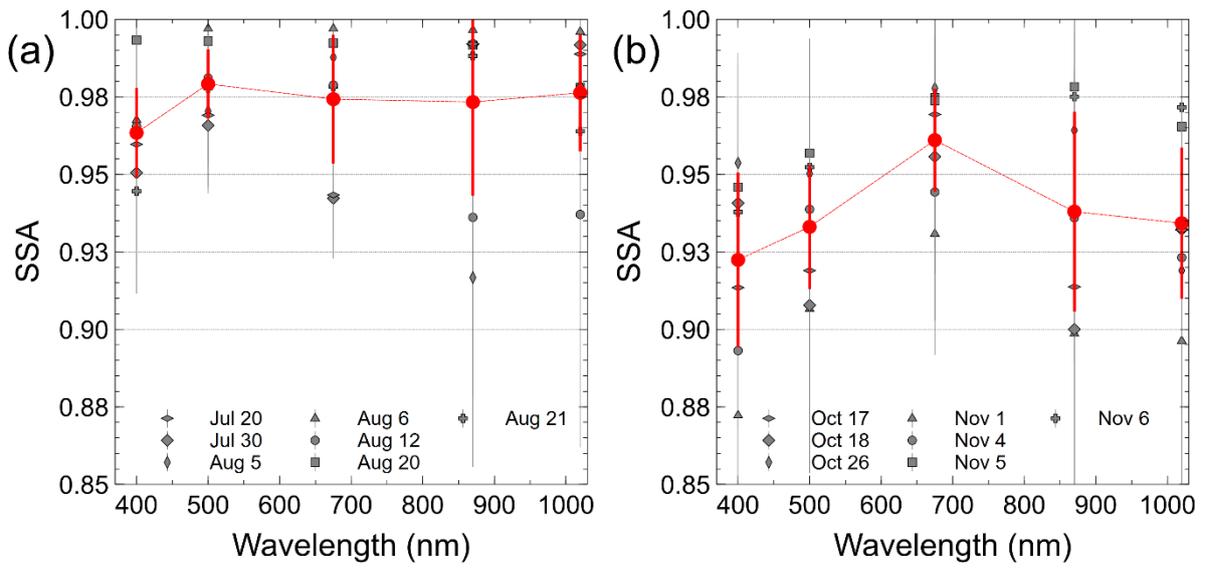
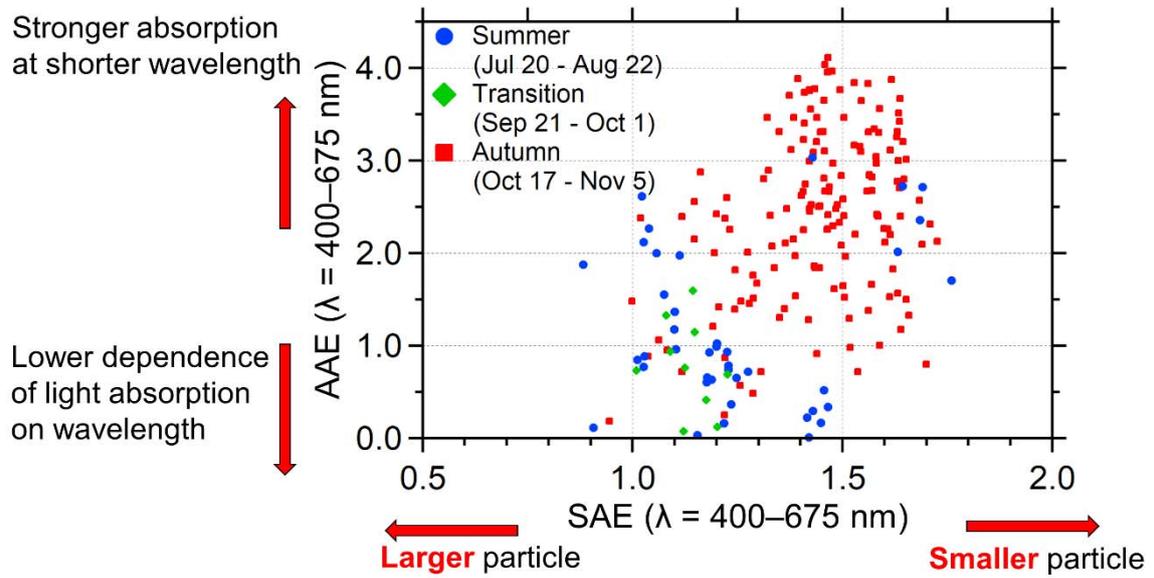


Fig. 4



Appendix A. Supplementary Data:

Impact of biogenic emissions of organic matter from a cool-temperate forest on aerosol optical properties retrieved from a Sky Radiometer

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Table S1. The mass concentrations of water-soluble aerosols (WSA), sulfate, and water-soluble organic matter (WSOM) during each sampling period in 2015.

Sampling start date (MM/DD)	Sampling end date (MM/DD)	WSA ($\mu\text{g m}^{-3}$)	Sulfate ($\mu\text{g m}^{-3}$)	WSOM ($\mu\text{g m}^{-3}$)
05/28	06/09	0.313	0.13	0.130
06/09	06/19	4.056	2.64	0.414
06/19	06/26	3.410	2.01	0.658
06/26	07/07	2.676	1.77	0.304
07/07	07/16	3.969	1.96	1.170
07/16	07/27	3.451	2.15	0.591
07/27	08/03	5.888	3.40	1.373
09/11	09/18	1.803	0.66	0.849
09/18	09/28	2.930	1.67	0.742
09/28	10/09	1.313	0.43	0.686
10/19	10/28	4.157	0.82	2.878
10/28	11/05	10.647	1.73	7.496
11/05	11/13	2.562	0.57	1.685
11/13	12/16	2.650	1.08	1.116
12/16	12/22	2.059	1.01	0.715

Table S2. The daily average (Avg.) values with the standard deviation (Std.) of the Aerosol optical depth (AOD) at a wavelength of 500 nm, Ångström exponent (AE), and single scattering albedo (SSA) at 500 nm during the study period from June 19 to December 31, 2015.

Date (MM/DD)	AOD ($\lambda = 500$ nm)		AE		SSA ($\lambda = 500$ nm)	
	Avg.	Std.	Avg.	Std.	Avg.	Std.
06/19	0.17	0.00	1.15	0.00	0.98	0.00
06/26	0.43	0.00	1.12	0.00	0.99	0.00
07/02	0.11	0.01	1.59	0.06	0.99	0.01
07/04	0.20	0.01	1.64	0.05	0.98	0.01
07/05	0.12	0.01	1.56	0.10	0.91	0.07
07/06	0.12	0.01	1.60	0.06	1.00	0.00
07/17	0.08	0.01	1.37	0.18	0.95	0.06
07/20	0.55	0.03	1.47	0.08	0.97	0.01
07/24	0.22	0.03	1.54	0.05	0.98	0.02
07/27	0.41	0.01	0.98	0.02	0.98	0.01
07/30	0.72	0.04	1.23	0.11	0.97	0.01
08/02	0.13	0.00	1.35	0.00	1.00	0.00
08/05	0.39	0.06	1.58	0.11	0.97	0.02
08/06	0.50	0.02	1.36	0.00	1.00	0.00
08/12	0.26	0.04	1.38	0.07	0.98	0.04
08/13	0.15	0.02	1.40	0.08	0.99	0.02
08/15	0.08	0.00	0.93	0.00	0.99	0.00
08/19	0.06	0.00	1.05	0.00	1.00	0.00
08/20	0.36	0.00	1.30	0.03	0.99	0.01
08/21	0.29	0.03	1.31	0.11	0.98	0.02
08/22	0.26	0.01	1.20	0.00	1.00	0.00
08/24	0.13	0.01	1.03	0.03	0.99	0.00
08/25	0.09	0.01	1.07	0.20	0.95	0.05
08/29	0.20	0.01	1.09	0.03	0.99	0.01
08/31	0.27	0.00	1.49	0.00	0.98	0.00
09/07	0.10	0.03	1.44	0.14	0.85	0.09
09/16	0.07	0.02	1.23	0.07	0.96	0.04
09/17	0.04	0.00	1.25	0.13	0.84	0.10
09/21	0.18	0.02	1.38	0.07	0.93	0.05
09/22	0.19	0.02	1.17	0.09	0.97	0.03
09/23	0.29	0.03	1.23	0.09	0.97	0.04
09/27	0.33	0.00	1.09	0.00	0.94	0.00
10/06	0.08	0.01	1.39	0.09	0.80	0.02
10/12	0.16	0.03	1.24	0.04	0.91	0.08
10/14	0.04	0.00	0.58	0.09	0.87	0.11
10/16	0.12	0.01	1.10	0.06	0.92	0.04
10/17	0.20	0.04	1.37	0.10	0.92	0.05
10/18	0.28	0.03	1.44	0.05	0.91	0.05

10/19	0.18	0.03	1.39	0.15	0.86	0.07
10/21	0.13	0.05	1.05	0.10	0.99	0.02
10/22	0.04	0.01	1.15	0.10	0.97	0.07
10/23	0.09	0.01	1.24	0.08	0.97	0.03
10/26	0.34	0.05	1.54	0.15	0.95	0.04
10/29	0.08	0.03	1.07	0.14	0.87	0.10
10/30	0.11	0.00	1.33	0.02	0.91	0.05
11/01	0.26	0.08	1.79	0.10	0.91	0.03
11/03	0.14	0.03	1.40	0.09	0.97	0.02
11/04	0.20	0.03	1.74	0.07	0.94	0.04
11/05	0.25	0.03	1.57	0.05	0.96	0.04
11/12	0.03	0.01	1.31	0.12	0.94	0.06
11/13	0.08	0.01	1.66	0.07	0.97	0.03
11/16	0.14	0.03	1.24	0.15	0.98	0.03
11/18	0.11	0.00	0.58	0.00	0.99	0.00
11/23	0.19	0.02	1.33	0.19	0.97	0.02
11/29	0.05	0.01	1.34	0.07	0.97	0.02
12/01	0.10	0.02	1.32	0.09	0.94	0.01
12/04	0.17	0.01	1.22	0.02	0.93	0.03
12/06	0.07	0.01	0.95	0.12	0.88	0.05
12/08	0.07	0.01	1.18	0.11	0.93	0.06
12/09	0.06	0.02	0.75	0.16	0.87	0.08
12/10	0.20	0.00	0.99	0.00	0.87	0.00
12/12	0.10	0.01	1.24	0.05	0.89	0.08
12/13	0.10	0.01	0.78	0.06	0.99	0.01
12/14	0.06	0.01	1.05	0.13	0.86	0.08
12/18	0.12	0.02	1.31	0.12	0.95	0.03
12/19	0.06	0.00	0.69	0.13	0.96	0.04
12/24	0.16	0.01	1.44	0.09	0.90	0.05
12/26	0.18	0.01	0.88	0.01	0.96	0.03
12/29	0.08	0.01	1.32	0.02	0.92	0.02
12/30	0.05	0.00	1.01	0.10	0.85	0.06
12/31	0.08	0.01	1.20	0.05	0.91	0.04

Table S3. The average values of Absorption Ångström exponent (AAE) and the scattering Ångström exponent (SAE) at $\lambda = 400 - 675$ nm with AOD > 0.2 during the summer, transition, and autumn period.

Summer		Transition		Autumn	
AAE	SAE	AAE	SAE	AAE	SAE
1.15 ± 0.84	1.25 ± 0.22	0.78 ± 0.47	1.13 ± 0.06	2.45 ± 0.91	1.46 ± 0.15

Table S4. The average (Avg.) values with the standard deviation (Std.) of the single scattering albedo (SSA) at each wavelength (λ) with AOD > 0.2 during the summer period.

Date (MM/DD)	SSA in Summer									
	$\lambda = 400 \text{ nm}$		$\lambda = 500 \text{ nm}$		$\lambda = 675 \text{ nm}$		$\lambda = 870 \text{ nm}$		$\lambda = 1020 \text{ nm}$	
	Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.
07/20	0.96	0.02	0.97	0.01	0.94	0.02	0.99	0.01	0.99	0.01
07/30	0.95	0.01	0.97	0.01	0.94	0.01	0.99	0.01	0.99	0.01
08/05	0.96	0.02	0.97	0.02	0.99	0.01	0.92	0.06	0.98	0.02
08/06	0.97	0.01	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00
08/12	0.97	0.04	0.98	0.04	0.98	0.05	0.94	0.06	0.94	0.08
08/20	0.99	0.01	0.99	0.01	0.99	0.01	0.99	0.01	0.98	0.02
08/21	0.94	0.03	0.98	0.02	0.98	0.02	0.99	0.01	0.96	0.04

Table S5. The average (Avg.) values with the standard deviation (Std.) of the single scattering albedo (SSA) at each wavelength (λ) with AOD > 0.2 during the autumn period.

Date (MM/DD)	SSA in Autumn									
	$\lambda = 400$ nm		$\lambda = 500$ nm		$\lambda = 675$ nm		$\lambda = 870$ nm		$\lambda = 1020$ nm	
	Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.
10/17	0.91	0.05	0.92	0.05	0.97	0.04	0.91	0.07	0.93	0.08
10/18	0.94	0.03	0.91	0.05	0.96	0.04	0.90	0.07	0.93	0.07
10/26	0.95	0.03	0.95	0.04	0.98	0.03	0.96	0.04	0.92	0.08
11/01	0.87	0.02	0.91	0.03	0.93	0.04	0.90	0.05	0.90	0.08
11/04	0.89	0.05	0.94	0.04	0.94	0.04	0.94	0.05	0.92	0.07
11/05	0.95	0.04	0.96	0.04	0.97	0.04	0.98	0.03	0.97	0.03
11/06	0.94	0.02	0.95	0.02	0.98	0.02	0.98	0.02	0.97	0.03