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

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

1. Introduction

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

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

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

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

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

2. Experimental Data and Methods

2.1. Measurement site

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

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

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

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

Fifteen aerosol samples were extracted with ultrapure water followed by being filtered through a 0.22−μm pore syringe filter. The extracts were then measured for each chemical parameter. The extracts have been analyzed in terms of their water-soluble organic carbon (WSOC) concentrations (Miyazaki et al., 2014, 2012), which were converted to water-soluble organic matter (WSOM) concentrations using a conversion factor of 1.8 (Finessi et al., 2012; Yttri et al., 2007). Furthermore, the concentrations of major inorganic ions (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, NH_4^+, K^+) were obtained by injecting the extracts into an ion chromatograph (Model 761 compact IC; Metrohm) (Miyazaki et al., 2009). Thus, the fraction of non-sea-salt sulfate was calculated based on the concentrations of sulfate and sodium. Further details about the chemical analysis are given in Müller et al. (2017). In this study, the

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

2.3. Aerosol optical properties

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

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

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

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

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

where

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

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

Wavelengths of λ_1 = 400 nm and λ_2 = 675 nm used in this study are similar or the same as those used in previous studies (e.g., Bahadur et al., 2012; Cazorla et al., 2013; Russell et al., 2010).

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

3. Results and Discussion

3.1. Seasonal trends of the aerosol chemical composition and AOD

Fig. 2a presents the temporal variations of the WSA mass concentration and the daily averaged AOD at a wavelength of 500 nm from June to December 2015. The mass concentrations of WSA ranged from 0.31 to 10.65 μg m^{-3} with an average of 4.46 ± 2.31 μg m^{-3}. Significant increases in the concentrations of the WSA were observed in three periods:

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

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

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

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

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

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

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

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

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

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

2012; Moise et al., 2015). Müller et al. (2017) suggested that the increase in the WSOM mass in autumn was attributable to the emissions of α-pinene from the forest floor and the subsequent formation of SOA. Light-absorbing characteristics of α-pinene SOA have been reported by laboratory experiments (Lambe et al., 2013; Song et al., 2013; Zhong and Jang, 2011). Song et al. (2013) found significant light absorption at 355 nm and 405 nm by SOA formed from ozonolysis and NO_3 oxidation of α-pinene in the presence of highly acidic sulfate seed aerosols under dry conditions. Our results in the current study imply that biogenic emissions of organic matter from the forest floor and subsequent formation of SOA might increase the absorption characteristics of the particles in autumn.

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

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

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

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

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

Conclusions

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

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

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Table 1. Average or individual values of the optical and chemical parameters for the three periods in 2015: summer (Jul. 20–Aug. 22), a transition period (Sept. 21–Oct. 1), and autumn (Oct. 17–Nov. 5). The number of data points for the optical parameters (ND_{opt}) and the filter-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 λ = 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 λ = 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-} (μg m^{-3})	2.15, 3.40	1.67, 0.43	1.04 ± 0.50
WSOM (μgm^{-3})	0.59, 1.37	0.74, 0.69	4.02 ± 2.51
WSA (μg m^{-3})	3.45, 5.89	2.93, 1.31	5.79 ± 3.50

Figure Captions

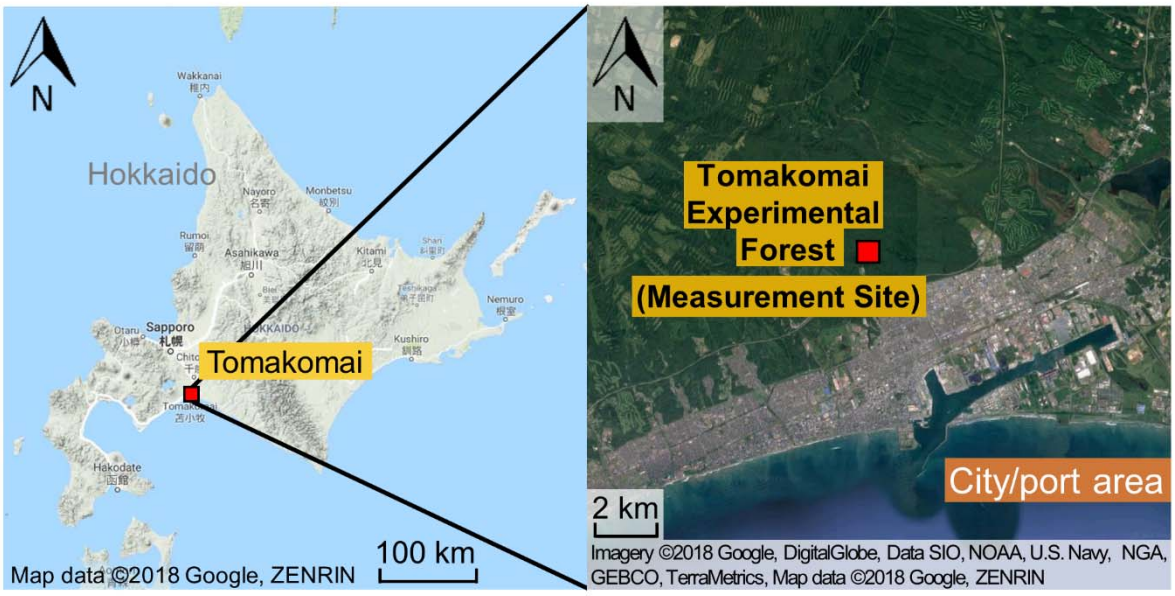
Fig. 1. Location of the sampling site: Tomakomai Experimental Forest of Hokkaido university, Hokkaido, northern Japan. Map data ©2018 Google, ZENRIN; Imagery ©2018 Google, DigitalGlobe, Data SIO, NOAA, U.S. Navy, NGA, GEBCO, TerraMetrics (https://maps.google.com/). Maps are modified with Microsoft PowerPoint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

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

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

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

Fig. 1


N
Hokkaido
Wakkanai
Nayoro
Monbetsu
Rumoi
Asahikawa
Kitami
Nemuro
Sapporo
Tomakomai
Kushiro
Hakodate
100 km
Map data ©2018 Google, ZENRIN
N
Tomakomai
Experimental
Forest
(Measurement Site)
City/port area
2 km
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GEBCO, TerraMetrics, Map data ©2018 Google, ZENRIN

Fig. 2

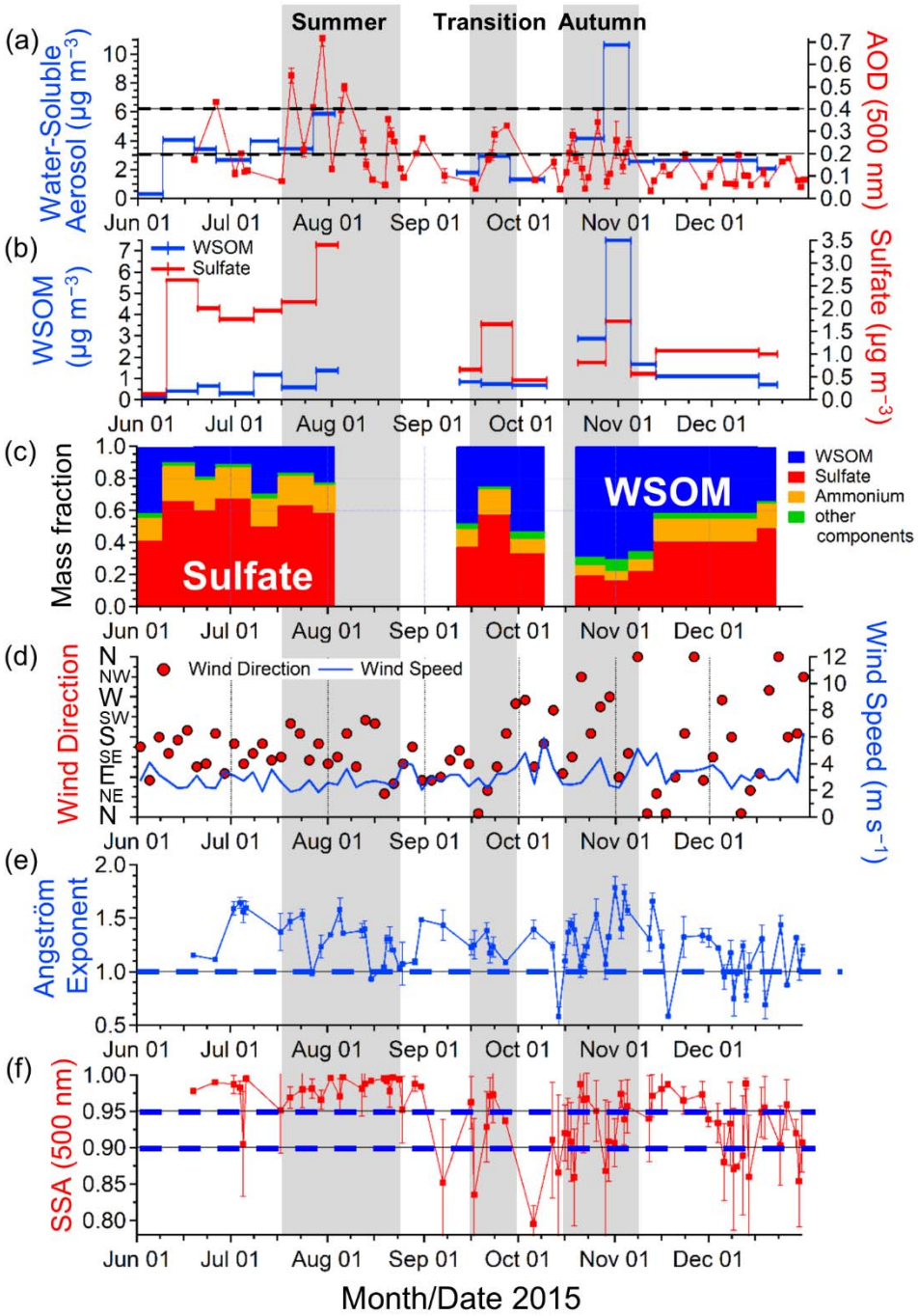

Summer
Transition
Autumn
(a)
Water-Soluble Aerosol (μg m⁻³)
AOD (500 nm)
(b)
WSOM (μg m⁻³)
Sulfate (μg m⁻³)
WSOM
Sulfate
(c)
Mass fraction
Sulfate
WSOM
Ammonium
other components
(d)
Wind Direction
Wind Speed (m s⁻¹)
Wind Direction
Wind Speed
(e)
Angström Exponent
(f)
SSA (500 nm)
Jun 01
Jul 01
Aug 01
Sep 01
Oct 01
Nov 01
Dec 01
Month/Date 2015

Fig. 3

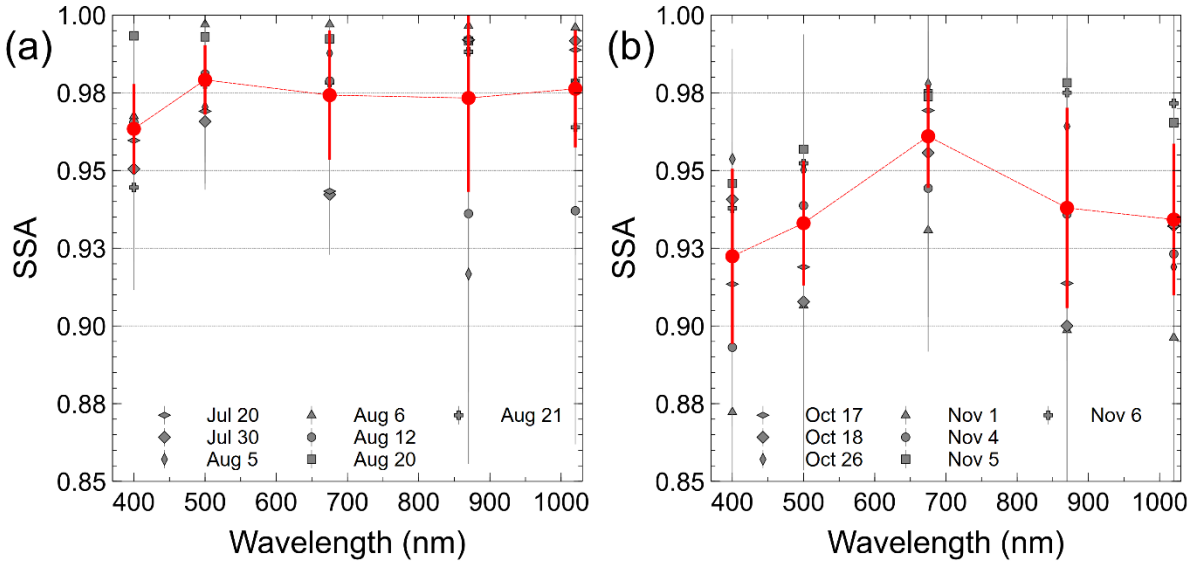
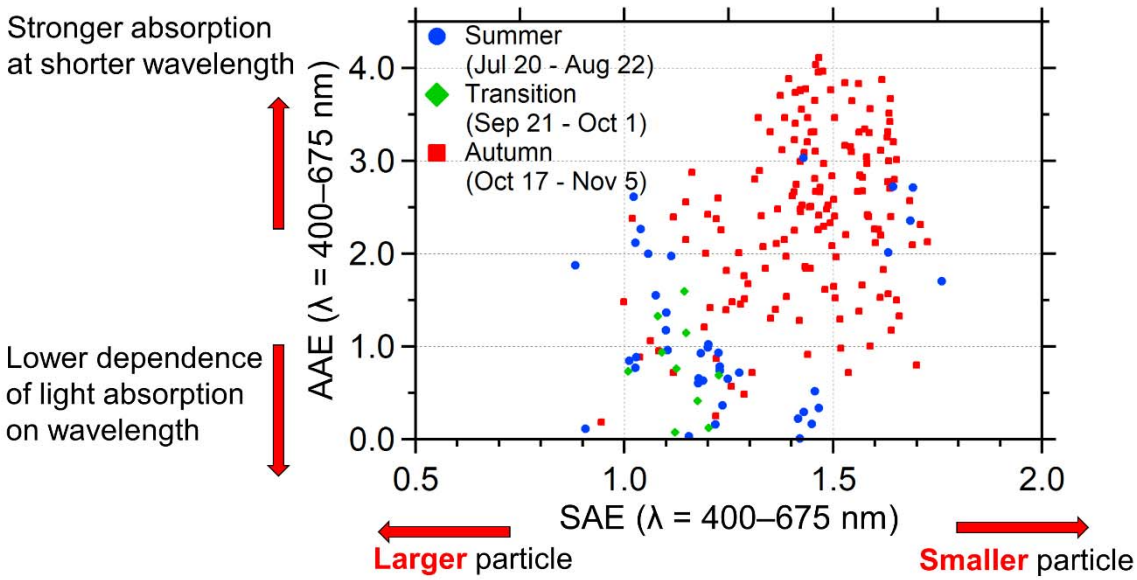

(a)
(b)
SSA
Wavelength (nm)
1.00
0.98
0.95
0.93
0.90
0.88
0.85
400
500
600
700
800
900
1000
Jul 20
Jul 30
Aug 5
Aug 6
Aug 12
Aug 20
Aug 21
Oct 17
Oct 18
Oct 26
Nov 1
Nov 4
Nov 5
Nov 6

Fig. 4


Stronger absorption
at shorter wavelength
Lower dependence
of light absorption
on wavelength
Summer
(Jul 20 - Aug 22)
Transition
(Sep 21 - Oct 1)
Autumn
(Oct 17 - Nov 5)
AAE (λ = 400–675 nm)
4.0
3.0
2.0
1.0
0.0
0.5
1.0
1.5
2.0
SAE (λ = 400–675 nm)
Larger particle
Smaller particle

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 ($\mu g\ m^{-3}$)	Sulfate ($\mu g\ m^{-3}$)	WSOM ($\mu g\ m^{-3}$)
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.

	AOD (λ = 500 nm)		**AE**		**SSA (λ = 500 nm)**	
Date (MM/DD)	**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 λ = 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.

	SSA in Summer									
Date	**λ = 400 nm**		**λ = 500 nm**		**λ = 675 nm**		**λ = 870 nm**		**λ = 1020 nm**	
(MM/DD)	**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.

	SSA in Autumn									
Date	**λ = 400 nm**		**λ = 500 nm**		**λ = 675 nm**		**λ = 870 nm**		**λ = 1020 nm**	
(MM/DD)	**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