Diurnal variation and size-dependence of the hygroscopicity of organic aerosol at a forest site in Wakayama, Japan: their relationship to CCN concentrations

Yange Deng[1], Hikari Yai[1], Hiroaki Fujinari[1], Kaori Kawana[2,3], Tomoki Nakayama[4,5], and Michihiro Mochida[1,4]

[1]Graduate School of Environmental Studies, Nagoya University, Nagoya, Japan
[2]Institute of Low Temperature Science, Hokkaido University, Hokkaido, Japan
[3]Now at Research and Development Center for Global Change, Japan Agency for Marine-Earth Science and Technology, Yokohama, Japan
[4]Institute for Space-Earth Environmental Research, Nagoya University, Nagoya, Japan
[5]Now at Graduate School of Fisheries and Environmental Sciences, Nagasaki University, Nagasaki, Japan

Correspondence to: Michihiro Mochida (mochida@isee.nagoya-u.ac.jp)

Abstract. Formation of biogenic secondary organic aerosol (BSOA) and its subsequent evolution can modify the hygroscopicity of the organic aerosol component (OA) in the forest atmosphere, and affect the concentrations of cloud condensation nuclei (CCN) there. In this study, size-resolved aerosol hygroscopic growth at 85 % relative humidity and size-resolved aerosol composition were measured using a hygroscopic tandem differential mobility analyzer and an aerosol mass spectrometer, respectively, at a forest site in Wakayama, Japan, in August and September 2015. The hygroscopicity parameter of OA (κ_{org}) presented daily minima in the afternoon hours, and it also showed increase with the increase of particle dry diameter. The magnitudes of the diurnal variations of κ_{org} for particles with dry diameters of 100 and 300 nm were on average 0.091 and 0.096, respectively, and the difference of κ_{org} between particles with dry diameters of 100 and 300 nm was on average 0.056. The relative contributions of the estimated fresh BSOA and regional OA to total OA could explain 40 % of the observed diurnal variations and size-dependence of κ_{org}. The hygroscopicity parameter of fresh BSOA was estimated to range from 0.089 to 0.12 for particles with dry diameters from 100 to 300 nm. Compared with the use of time- and size-resolved κ_{org}, the use of time- and size-averaged κ_{org} leads to under- and over-estimation of the fractional contribution of OA to CCN number concentrations in the range from −4.9 to 26 %. This indicates that the diurnal variations and size-dependence of κ_{org} strongly affect the overall contribution of OA to CCN concentrations. The fractional contribution of fresh BSOA to CCN number

concentrations could reach 0.28 during the period of intensive BSOA formation. The aging of the fresh BSOA, if it occurs, increases the estimated contribution of BSOA to CCN number concentrations by 50–84 %.

1 Introduction

The hygroscopicity (ability to absorb water) of organic aerosol (OA) components is governed by their chemical composition, and has two important roles in the atmosphere. It influences light scattering by aerosols (Titos et al., 2016) and affects the ability of aerosols to work as cloud condensation nuclei (CCN; McFiggans et al., 2006). The hygroscopicity of OA may also influence the aqueous chemistry in aerosols and cloud droplets, which provide a potentially important pathway for the formation of secondary organic aerosols (SOA; McNeill, 2015). Nevertheless, the hygroscopicity of OA is not well characterized in terms of its temporal and spatial variations, size-dependence, and its relationship with the chemical composition of OA, given that OA is a complex mixture of a number of compounds.

Studies on the hygroscopicity parameter κ of OA (κ_{org}; Petters and Kreidenweis, 2007) in different locations have presented different characteristics of temporal variation and size-dependence. Based on a year-long observation under supersaturated water vapor conditions (SUPS) at a downwind site of Manaus in central Amazonia, Thalman et al. (2017) reported that κ_{org} presented the lowest value of ~0.1 in September and the highest value of ~0.15 in December, and that the ranges of the diurnal variations of κ_{org} were 0.10 to 0.16 (night to day) and 0.08 to 0.14 (night to day) under the influence of local biomass-burning air masses during the dry season and urban-pollution air masses during the wet season, respectively. Bougiatioti et al. (2016) reported diurnal variation of κ_{org} in the range 0.09–0.18 (day to night) under SUPS for particles influenced by biomass burning in the eastern Mediterranean. Deng et al. (2018) reported diurnal variation ranges of κ_{org} of 0.09 to 0.30 (day to night) and 0.16 to 0.24 (day to night) on days with and without evident new particle formation (NPF), respectively, under SUPS (0.23 % water vapor supersaturation (SS) condition) in a forest in Wakayama, Japan. Different from the above studies, at a rural site in the southeastern United States, a small diurnal variation of κ_{org} (~0.13 to ~0.17, night to day) under SUPS was observed (Cerully et al., 2015). With respect to the size-dependence of κ_{org}, airborne studies over United States, Canada, Pacific Ocean, and the Gulf of Mexico for a variety of air mass types, presented a decrease of κ_{org} (from 0.13 to 0.06) with increase of the particle modal diameter (from 130 to ~210 nm) under subsaturated water vapor conditions (SUBS) (Shingler et al., 2016). By contrast,

ground-based observations in the City of Nagoya in Japan under SUBS presented relatively low κ_{org} in small particles (0.12–0.15; 60 and 100 nm) and high κ_{org} in large particles (0.17–0.22; 200 and 359 nm) (Kawana et al., 2016). For aerosols in forest areas, whereas Deng et al. (2018) reported a difference of 0.03 in mean κ_{org} between sub-100 nm particles (κ_{org} was 0.19) and ~150 nm particles (κ_{org} was 0.22), Thalman et al. (2017) did not identify any size-dependence of κ_{org} for 94–171 nm particles.

5   The hygroscopicity of laboratory-generated model SOA was also reported to be size-dependent. Frosch et al. (2011) reported that the κ of α–pinene SOA at SUPS at 100 nm (~0.12) was ~0.06 higher than at 200 nm. Zhao et al. (2015) reported that the κ of model SOA at SUPS produced by different precursors at 50, 100, and 200 nm were ~0.17, ~0.11, and ~0.07, respectively. Tritscher et al. (2011) also found that small (50 nm) α-pinene SOA particles had a higher κ than large ones (150 nm) at SUBS, although the difference was small (0.03). Frosch et al. (2013) reported that the κ of β-caryophyllene SOA decreased with

10   increase of SS, which can be interpreted as the increase of κ with the increase of particle diameter, and that the maximum of the difference was about 0.1.

The variations in κ_{org} observed in the aforementioned studies may have great influence on the prediction of CCN. Based on global climate modelling simulations, Liu and Wang (2010) reported that CCN concentration would change within 40 % by changing the κ of SOA by ±50 % (from 0.14 to 0.07 or 0.21). Rastak et al. (2017) reported that the difference of the aerosol

15   radiative effects between κ_{org} of 0.05 and 0.15 was −1.02 W m^{-2}, the order of which is the same as that of the overall climate forcing effect of anthropogenic aerosol during the industrial period. Based on CCN closure studies, Wang et al. (2008) reported that, for above-cloud aerosols with high volume fractions of OA, while the CCN number concentration closure could be achieved using κ_{org} of 0.12, the use of κ_{org} of 0.25 led to overestimation of the CCN number concentration by 50 %. Mei et al. (2013b) reported that the increase of κ_{org} from 0.08 to 0.13 led to 30 % increase of the calculated CCN number concentration

20   and that increase from 0.03 to 0.18 doubled the concentration. It is therefore important to study the temporal variation and size-dependence of κ_{org} in more locations where OA dominates the aerosol chemical composition, to characterize the κ_{org} values and to represent the κ_{org} appropriately in model predictions of CCN number concentrations.

The temporal variation and size-dependence of κ_{org} of ambient aerosol is reported to relate with variations in the chemical composition of OA, which can result from the mixing of aerosols of different origins, formation of SOA, and aging processes (Cerully et al., 2015; Bougiatioti et al., 2016; Shingler et al., 2016; Thalman et al., 2017; Deng et al., 2018). The size-dependent chemical composition of model SOA has been explained by the size-dependent contributions of different organic vapors to particle growth (e.g., Winkler et al., 2012; Ehn et al., 2014; Zhao et al., 2015; Zhao et al., 2016). The size-dependent κ of model SOA has also been explained from the viewpoint of size-dependent chemical composition (Zhao et al., 2015; Frosch et al., 2013) and other factors: the dependence of water activity on particle size, the dependence of the surface tension on the solution concentration, and the evaporation of semi-volatile SOA under high SS conditions (Frosch et al., 2011; Frosch et al., 2013; Zhao et al., 2015). In recent studies, the variation of κ_{org} was explained by the variation of OA subcomponents derived from positive matrix factorization (PMF) analysis of OA mass spectra (Cerully et al., 2015; Bougiatioti et al., 2016). From these studies it is reported that the daily variation of κ_{org} could be well explained by the daily variation in the contributions of the retrieved PMF factors to κ_{org}.

In the forest atmosphere, the oxidation of biogenic volatile organic compounds (BVOC) emitted by vegetation can produce substantial amounts of biogenic secondary organic aerosols (BSOA; Tunved et al., 2006; Pöschl et al., 2010; Han et al., 2014). BSOA is reported to contribute to the growth of newly formed particles in forests (e.g., Han et al., 2013; Yu et al., 2014; Zhou et al., 2015). BSOA may also condense on preexisting background particles or particles transported with inflowing air masses (e.g., Cerully et al., 2015; Thalman et al., 2017). Moreover, BSOA is subject to aging processes that include photochemical oxidation and aqueous phase reactions that must depend on ambient meteorological conditions (e.g., Han et al., 2014; Thalman et al., 2017). Such processes could result in time- and size-dependent variation in the chemical composition of OA and thus time- and size-dependent κ_{org} in the forest atmosphere. However, the characteristics of the temporal variations and size-dependence of κ_{org}, and their relationships to the atmospheric processes of BSOA in forest environments, are not well understood.

We performed field observation at a forest site in Wakayama, Japan in August and September, 2015, and characterized the diurnal variations and size-dependence of κ_{org}. The variations and dependence were interpreted based upon the size-resolved

chemical composition of OA from the viewpoint of BSOA formation. Furthermore, the influence of these variations on the fractional contribution of OA and BSOA to the CCN concentration was assessed. Previous observational studies at the site indicated that BSOA formation was intensive and that aging occurred after formation (Han et al., 2014; Deng et al., 2018). It was also observed that κ_{org} was time and size dependent and that the contribution of OA and BSOA to CCN number

5   concentrations could be substantial (Deng et al., 2018). This work is an extension of previous studies on the hygroscopicity and CCN activity of aerosols, and the contributions of OA and BSOA to the CCN concentration, in the same forest (Kawana et al., 2017; Deng et al., 2018). It is intended to clarify the diurnal variation and size-dependence of the hygroscopicity of OA and their influence on the contributions of OA and BSOA to CCN.

2 Field observation

10   The field observation was performed at Wakayama Forest Research Station, Kyoto University (34.06° N, 135.52° E, about 500 m above sea level), located in the central part of the Kii Peninsula. The observation site is about 70 km south of Osaka (2.7 million inhabitants) and 60 km northwest of the North Pacific. Both coniferous trees (such as *Cryptomeria japonica*, *Chamaecyparis obtuse*, and *Pinus densiflora*) and broad-leaf trees (such as *Quercus serrata* and *Quercus crispula*) are distributed on the Kii Peninsula (Okumura, 2009). The study period was from 1430 Japan Standard Time (JST) on 31 August

15   to 0600 JST on 22 September 2015.

The hygroscopic growth at 85 % relative humidity (RH), number-size distributions, and size-resolved chemical composition of ambient aerosols were measured using a hygroscopicity tandem differential mobility analyzer (HTDMA), a scanning mobility particle sizer (SMPS), and a high-resolution time-of-flight aerosol mass spectrometer (AMS), respectively. Ambient air was aspirated from an inlet about 7.5 m above the ground. The air was transferred through a $PM_{2.5}$ cyclone (URG) installed

20   at the lower end of the 10.4 m stainless-steel inlet tubing (1/2-inch OD) and introduced to the instrument room at a flow rate of 16.7 L min^{-1}. A manifold combined with an assistant pump (ULVAC, DA30S) was used to split the air flow, and the sample flow for the instrument system composed of the HTDMA, SMPS, and AMS was 0.9 L min^{-1}. The sample flow upstream of the AMS was dried with two diffusion driers containing silica gel. The sample flow to the HTDMA and SMPS was dried with three diffusion driers, in series, two with silica gel and one with molecular sieves.

In the HTDMA, the dried aerosol (RH < 1.8 %) was passed through the first differential mobility analyzer (DMA1; 3081, TSI), where the aerosol was classified, and quasi-monodisperse particles of 30, 50, 70, 100, 200, 300, and 360 nm in diameter (d_{dry}) were obtained. The setting for the classification was fixed for 5 min at each diameter. In each hour, the sequential diameter setting of DMA1 was 30, 50, 70, 100, 200, 360, 30, 50, 100, 200, 300, and 360 nm. During 0550–0554 JST and 1750–1754 JST, the setting of DMA1 was for system performance check. The classified aerosol was passed through a Nafion humidifier (MD-110-24S-4, Perma Pure) where it was humidified to ~85% RH. The aerosol was then introduced to a second DMA (DMA2; 3081, TSI) coupled to a condensation particle counter (CPC, 3775, TSI), which was operated by scanning the voltage of DMA2. For both DMA1 and DMA2, the aerosol flow rate was 0.3 L min^{-1} and the sheath-to-sample flow ratio was 10:1. The residence time of the monodisperse particles from the outlet of the humidifier to the inlet of DMA2, where the RH was considered to be ~85 %, was approximately 11 s. The sheath air flow of DMA2 was also humidified using another Nafion humidifier (PD-100T-12MSS, Perma Pure). The RH (temperature) measured (HMP237, Vaisala) at the inlets of aerosol flow and sheath flow to DMA2 were 85.0 ± 0.2 % (20.3 ± 0.5 ℃) and 85.0 ± 0.2 % (20.4 ± 0.5 ℃), respectively, and that at the outlet of the sheath flow of DMA2 was 86.0 ± 0.3 % (20.3 ± 0.6 ℃). For analysis of the particle hygroscopic growth, RH of 85 % was applied. The SMPS for the measurement of aerosol number-size distributions was composed of a third DMA (DMA3; 3080, 3081, TSI) and a CPC 3772 (TSI). The aerosol flow (RH < 1.6 %) was 0.3 L min^{-1} and the sheath to aerosol flow ratio was 10:1. At the inlet of CPC 3772, the sample flow was diluted to 1 L min^{-1} with purified dry air, which was generated using a compressor (RD-45-N, IAC) and an air dryer (QD 30-50, IAC). The aerosol number-size distributions were measured for a dry diameter range of 13.8–749.9 nm every 5 min. The performances of the three DMAs were assessed using standard size PSL particles before and after the observation (Text S1). Furthermore, an aqueous solution of ammonium sulfate (AS) (99.999 % purity, Sigma-Aldrich) was nebulized and the generated aerosols were dried and introduced to the HTDMA, to assess the consistency of the sizing of the two DMAs under dry condition, and to validate the RH setting before the observation (Text S2). The setup and calibration procedures of the AMS were the same as those for the observations in 2014 (Deng et al., 2018). The V-mode (MS and PToF modes) data was analyzed using the Igor high resolution data analysis package (PIKA1.20Q, Igor 6.37) to obtain the bulk and size-resolved mass concentrations of the chemical components (sulfate (SO$_4$), ammonium (NH$_4$), nitrate (NO$_3$), chloride (Chl), and OA), and the atomic ratios of O to C (O:C ratio) and H to C (H:C ratio) for organics. In

addition, high-resolution bulk OA mass spectra observed in V-mode were subjected to PMF analysis (Paatero and Tapper, 1994; Ulbrich et al., 2009) (Sect. 3.3, Text S3). The RH of the sample flow was lower than 0.5 %.

A single wavelength particle soot absorption photometer (1λ-PSAP, 567 nm, Radiance Research Inc.) with a thermodenuder maintained at 300 °C, was deployed to obtain the mass concentration of sub-micrometer black carbon (BC; Kondo et al. 2009;

5 Deng et al., 2018). The mixing ratios of target gaseous species, $NO-NO_2-NO_x$, CO, CO_2, and O_3, were monitored using commercial instruments (APNA-370, Horiba for $NO-NO_2-NO_x$; model 48ij, Thermo Fisher Scientific for CO; LI-820, LI-COR for CO_2; model 49ij, Thermo Fisher Scientific for O_3). Meteorological data were collected (Kyoto University, 2017). Air temperature, RH (HMP-155, Vaisala), precipitation (RH-5E, IKEDA-KEIKI), and solar radiation (CMP3-L, Campbell) were used in this study.

10 All the observation data except meteorological data were screened to eliminate data that might have been under the strong influence of local anthropogenic emissions, for example, from vehicles. This was performed by omitting data with spikes in the number concentrations of aerosols from their size distribution data, and in the mass concentration of BC (Text S4).

3 Data analysis

3.1 Hygroscopicity of ambient aerosols

15 The hygroscopic growth factor of aerosol particles, g_f, was defined as the ratio of the particle wet diameter (d_{wet}, 85 % RH) to the corresponding dry diameter (d_{dry}). The distributions of g_f for specific d_{dry} ($n(g_f)$, i.e., the number distribution of particles as a function of g_f) were retrieved using the Twomey algorithm as presented by Mochida et al. (2010) with consideration of the shape of the transfer functions of the two DMAs. The difference in the processing is that the transfer function and the $n(g_f)$ in this study were analyzed and presented in the fine mode of 1024 diameter bins per decade while 64 bins per decade were used

20 in Mochida et al. (2010). The g_f probability distribution function, g_f-PDF, is the normalized $n(g_f)$. The g_f-PDF in this study is presented in linear scale, which was converted from the original logarithmic scale distribution. The time-resolved mean value of g_f for respective d_{dry}, $g_{f,m}$, was calculated as follows.

$$g_{f,m} = \frac{\sum n(g_f)g_f}{\sum n(g_f)} \quad (0.8 \le g_f \le 2.2 \text{ for } 30 \le d_{dry} \le 300 \text{ nm, or } 0.8 \le g_f \le 2.0 \text{ for } d_{dry} = 360 \text{ nm}) \tag{1}$$

For ambient particles, time-resolved mean-water-volume equivalent g_f ($g_{f,mw}$, i.e., the average of g_f that corresponds to the mean water volume retained by particles of certain d_{dry}) was also calculated using Eq. (2) (Kawana et al., 2016).

$$g_{f,mw} = \left[\frac{\sum n(g_f)(g_f^3 - 1)}{\sum n(g_f)} + 1 \right]^{\frac{1}{3}} \quad (0.8 \leq g_f \leq 2.2 \text{ for } 30 \leq d_{dry} \leq 300 \text{ nm, or } 0.8 \leq g_f \leq 2.0 \text{ for } d_{dry} = 360 \text{ nm}) \quad (2)$$

The hygroscopicity parameter of ambient particles at 85 % RH (κ_t) was calculated following the κ-Köhler theory (Petters and Kreidenweis, 2007).

$$\kappa_t = \left(g_{f,mw}^3 - 1 \right) \left[\frac{\exp\left(\frac{4\sigma M_w}{RT\rho_w d_{wet}} \right)}{0.85} - 1 \right] \quad (3)$$

where σ is the surface tension at the solution/air interface, M_w and ρ_w are the molecular mass and density of pure water, respectively, d_{wet} is the product of $g_{f,mw}$ and d_{dry}, R is the universal gas constant, and T is the temperature in kelvin. In this study, the mean temperature at the inlets of aerosol flow and sheath flow of DMA2, weighted by their flowrates, was applied as T (294 K) and the surface tension of pure water at this temperature (Vargaftik et al., 1983) was used as σ in Eq. (3). Because κ_t was calculated from $g_{f,mw}$, the aerosol mixing state was not considered in the analysis of κ in this study.

3.2 Hygroscopicity of OA

The hygroscopicity parameter of organics, κ_{org}, was calculated using Eq. (4) assuming the volume additivity of water retained by different aerosol components (Petters and Kreidenweis, 2007).

$$\kappa_t = \varepsilon_{org}\kappa_{org} + \varepsilon_{inorgsalt}\kappa_{inorgsalt} + \varepsilon_{BC}\kappa_{BC} = \varepsilon_{org}\kappa_{org} + \sum_{i=1}^{5} \varepsilon_i \kappa_i + \varepsilon_{BC}\kappa_{BC}$$

$$(4)$$

Here, κ_t is the hygroscopicity parameter of ambient aerosol at 85 % RH calculated using Eq. (3), while κ_{org}, $\kappa_{inorgsalt}$, and κ_{BC} are the hygroscopicity parameters of OA, inorganic salts, and BC, respectively. The volume fractions of OA, inorganic salts, and BC are ε_{org}, $\varepsilon_{inorgsalt}$, and ε_{BC}, respectively, and ε_i and κ_i are the volume fraction and hygroscopicity parameter of the inorganic salts: ammonium nitrate (AN), sulfuric acid (SA), ammonium hydrogen sulfate (AHS), letovicite (LET), and ammonium sulfate (AS). The ε_{org}, ε_i, and ε_{BC} were calculated based on the size-resolved mass concentrations of organics, sulfate, nitrate, and ammonium from the AMS, and the sub-micrometer BC mass concentrations from the PSAP. BC was

assumed to have the same mass-size distribution as OA. The aerosol particles were assumed to be spherical and without voids. PToF mode data in vacuum aerodynamic diameter (d_{va}) ranges that were ~1.0 (0.98–0.99) to 2.0 times that of d_{dry}, corresponding to the particle density of ~1.0 (0.98–0.99) to 2.0 g cm^{-3}, were adopted. More details about the calculations of the size-resolved ε_{org}, ε_i, and ε_{BC} are presented in Text S5. The derivation of κ_i was based on the online Extended AIM Aerosol

5   Thermodynamics Model II (E-AIM II, http://www.aim.env.uea.ac.uk/aim/kohler/input_kohler.html; Clegg et al., 1998; Wexler and Clegg, 2002) as presented in Text S6 and Table S3. The κ of BC was assumed to be zero. Because of the low signal intensity of the PToF data in the sub-100-nm d_{va} range (Text S7), the κ_{org} was only derived for particles with d_{dry} of 100, 200, 300, and 360 nm. Furthermore, to assess the influence of the choice of the d_{va} range on the derivation of κ_{org}, the derived κ_{org} for particles with d_{dry} of 100 nm using the chemical composition in the d_{va} range 98–197 nm, was compared with that using

10   the chemical composition in the d_{va} range 69–138 nm (Fig. S4). The result indicates that κ_{org} was not sensitive to change in the selected d_{va} range when ε_{org} was greater than 40 %. Note that, although the volume additivity assumption between organics and inorganics may not necessarily hold (Vaishya et al., 2013; the κ_{org} derived in the manner in this study represents the perturbation of κ_t as a result of the presence of organics), the inverse linear correlation between κ_t and ε_{org} (correlation coefficients: −0.45 to −0.83; Fig. S5) suggests that the additivity holds well for the aerosols studied.

15 **3.3 PMF analysis of OA mass spectra**

To characterize the diurnal variations and size-dependence of κ_{org}, the high-resolution OA bulk mass spectra derived from the V-mode AMS data were subjected to PMF analysis (Text S3), followed by derivation of the size-resolved contributions of the PMF factors to the OA mass concentration (Text S8). A two-factor PMF solution was adopted, which resolved two oxygenated OA factors: one with a lower atomic O:C ratio (0.47) named less-oxygenated organic aerosol (LOOA), and the other with a

20 higher O:C ratio (0.95) named more-oxygenated organic aerosol (MOOA). The low relative residual (2.6 %) for the bulk mass spectra supports the use of the two PMF factors to illustrate the observed OA. Note that the two OA factors resolved here represent two different groups of OA chemical structures, not necessarily two different OA sources (Zhang et al., 2011). The use of a PMF result with more factors could make illustration of the variation of κ_{org} complex and was not adopted. The PToF mode OA mass spectra in 2 h time resolution were attributed to the two PMF factors through multivariable linear regression

(Text S8). For particles with d_{dry} equals to or larger than 100 nm, the variation of κ_{org} was discussed with regard to the variations of the two PMF factors. Furthermore, the hygroscopicity parameters for the two OA fractions were derived, and then used to estimate the hygroscopicity of freshly formed BSOA (Sect. 4.2).
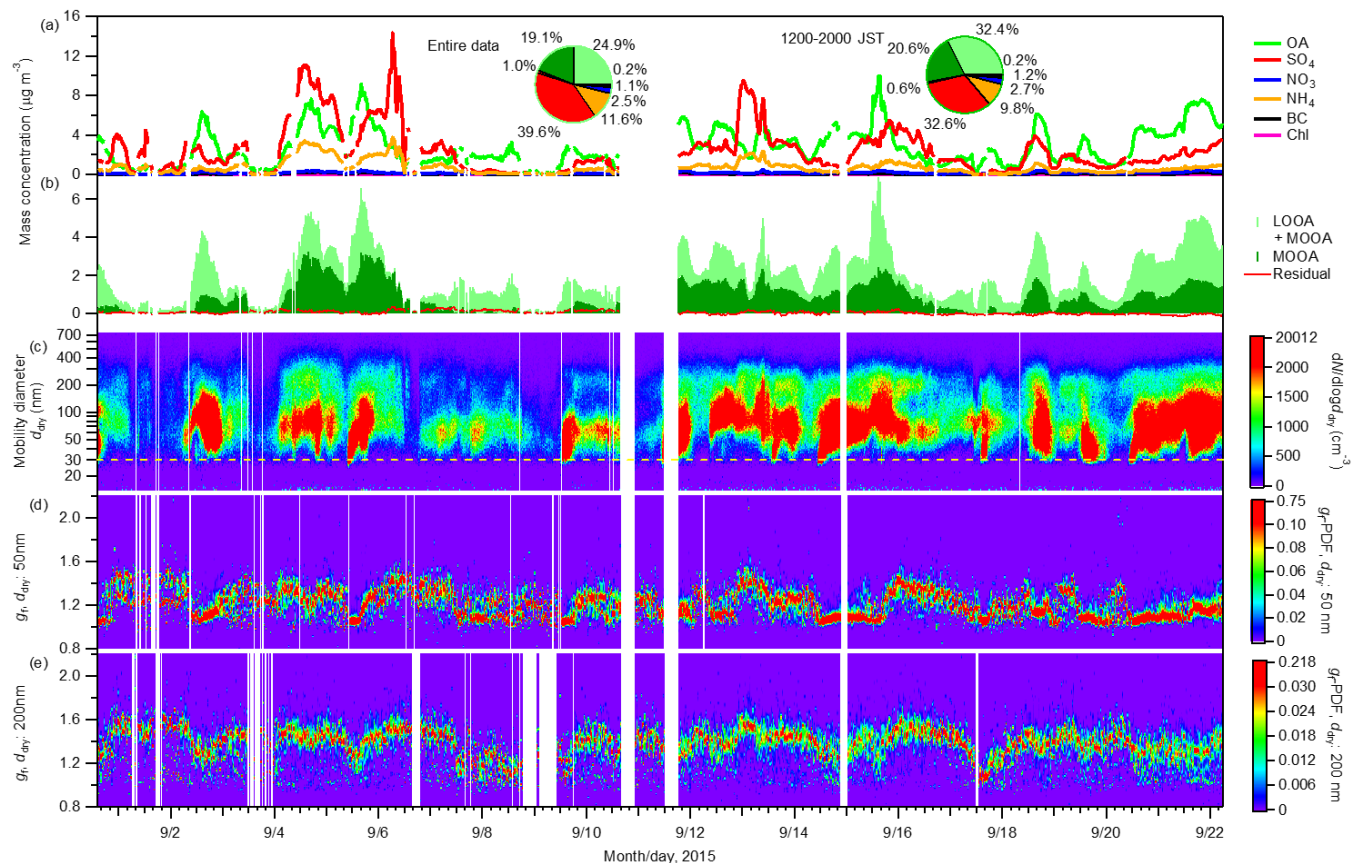
Figure 1: Time series of (a) sub-micrometer mass concentrations of non-refractory aerosol chemical components (OA, SO₄, NO₃, NH₄, and Chl) from the AMS measurement and BC from the PSAP measurement, (b) mass concentrations of LOOA and MOOA, and the residuals from the PMF analysis, (c) aerosol number-size distributions, and g_f-PDF of aerosol particles with d_{dry} of (d) 50 nm and (e) 200 nm. The two pie charts in panel (a) present the mass fractions of chemical components for the entire study period and for the afternoon hours (1200–2000 JST) during the study period. The dashed line in panel (c) represents a diameter of 30 nm.

4 Results and discussions

4.1 Overview of the observations

4.1.1 Meteorological conditions, gaseous species, and aerosol chemical composition

During the measurement period with effective data, the mean ± standard deviation (SD) of the temperature and RH of the
ambient air were 18.2 ± 2.4 °C and 94.2 ± 7.6 %, respectively. Precipitation events occurred intermittently during 1–3, 6–10,
and 16–17 September (Fig. S7). Backward air mass trajectories (Fig. S9) generated using NOAA's HYSPLIT atmospheric
transport and dispersion modeling system (Draxler and Hess, 1998) indicate that, except on 1 and 17 September, most of the
air masses that arrived at the observation site had traveled from the Japan archipelago (and even from the Asian continent)
within five days, and may have transported aged anthropogenic pollutants to the observation site. The mean ± SD of the BC
concentration during the entire study period was 0.07 ± 0.06 µg m^{-3} (Fig. S7). The mean ± SD of the mixing ratios of CO, NO,
NO_2, NO_x, and O_3 during the entire study period were 164 ± 42, 0.33 ± 0.12, 0.56 ± 0.35, 0.63 ± 0.38, and 11.5 ± 8.4 ppb,
respectively (Fig. S7). The concentration of BC was low, and the mixing ratios of CO and NO_x were modest. A daily maximum
of BC appeared in the afternoon hours (Fig. 2), which however might have been caused by the charring of OA at the heating
temperature of 300 °C. The mixing ratios of CO and NO_x tended to be relatively high during 1000–2200 JST (Fig. S8), which
might have been caused by the transport of anthropogenic pollution to the surface site by enhanced vertical convection in the
daytime. The concentration of O_3 was substantial and presented obvious diurnal variation (Fig. S7). On average, O_3 peaked
during noon with the solar radiation (Fig. S8), indicating the occurrence of photochemical reactions during the daytime.

The time series of the mass concentrations of aerosol chemical components and aerosol number-size distributions are presented
in Fig. 1. Among non-refractory aerosol chemical components derived from the AMS and BC derived from the PSAP (total
concentration: 6.2 ± 4.4 µg m^{-3}), organics on average accounted for the largest fraction (45.0 %; of which LOOA and MOOA
accounted for 24.9 % and 19.1 %, respectively), followed by sulfate (39.6 %) and ammonium (11.6 %). The contribution of
nitrate, BC, and chloride were minor: their mass fractions were on average 2.5 %, 1.1 %, and 0.2 %, respectively. The
contribution of OA to the sub-micrometer aerosol mass increased and that of sulfate decreased in the afternoon hours (1200–
2000 JST). The mean aerosol number concentration (N_{CN}) was 1241 ± 1012 cm^{-3}. The geometric mean diameter of the aerosols

ranged from 45 to 154 nm with a mean $\pm$ SD of 88 ± 17 nm. No strong burst of small particles (i.e., $d_{dry} < 30$ nm) was identified during the observation, which is different from the two former observations in 2010 and 2014 (Han et al., 2013; Deng et al., 2018).

5   The diurnal variation of the number-size distributions and the mass concentrations of the chemical components of aerosols are presented in Fig. 2. The N_{CN}, OA, and LOOA presented similar diurnal variation patterns. Their daily minima were observed between 0600 and 0830 JST. After 0830 JST, they increased monotonically and reached their maxima during 1500–1800 JST. Then they gradually decreased until approximately 0600 JST of the next day. MOOA also increased slowly (following the trend of LOOA) in the daytime and reached its maximum around 1800 JST. The pattern of the enhancement of OA in the
10   daytime followed that of the solar radiation (Fig. 2b), indicating that the enhancement of OA was caused by the formation of BSOA through photochemical reactions of BVOC (Han et al., 2014; Deng et al., 2018). This is supported by an analysis indicating that anthropogenic pollution was not the main contributor to the enhancement of OA, at least during the period 1200–1600 JST (Text S9), and by the report that primary biogenic OA is mainly in the supermicrometer aerosol diameter range in a forest environment, for the Amazon at least (Pöschl et al., 2010). Furthermore, the stronger enhancement of LOOA
15   than of MOOA indicates that the freshly formed BSOA was mainly composed of LOOA and had a low oxygenation state. The O:C ratio of OA increased slowly from around noon to midnight (Fig. 2c), together with the appearance of MOOA, indicating the aging of freshly formed BSOA (Han et al., 2014). Because of high RH conditions (Fig. S7), aqueous phase reactions including in-cloud processes could have played an important role in the aging of fresh BSOA (Han et al., 2014), which could have modified the hygroscopicity of ambient aerosols (Jimenez et al., 2009; Farmer et al., 2015). Although no abrupt increase
20   of sub-30 nm particles was observed, the increase in the number concentration of 30–50 nm particles around noon indicates the formation of new particles near the observation site. These particles probably had grown by the condensation of BSOA formed from BVOC at the time they were transported to the observation site. The concentrations of nitrate and chloride stayed low, although they also presented maxima in the afternoon. Sulfate, which may have been strongly influenced by transported anthropogenic aerosol, did not present an obvious diurnal variation. This result supports the view that the contribution of
25   anthropogenic OA to the observed enhancement of OA was small.
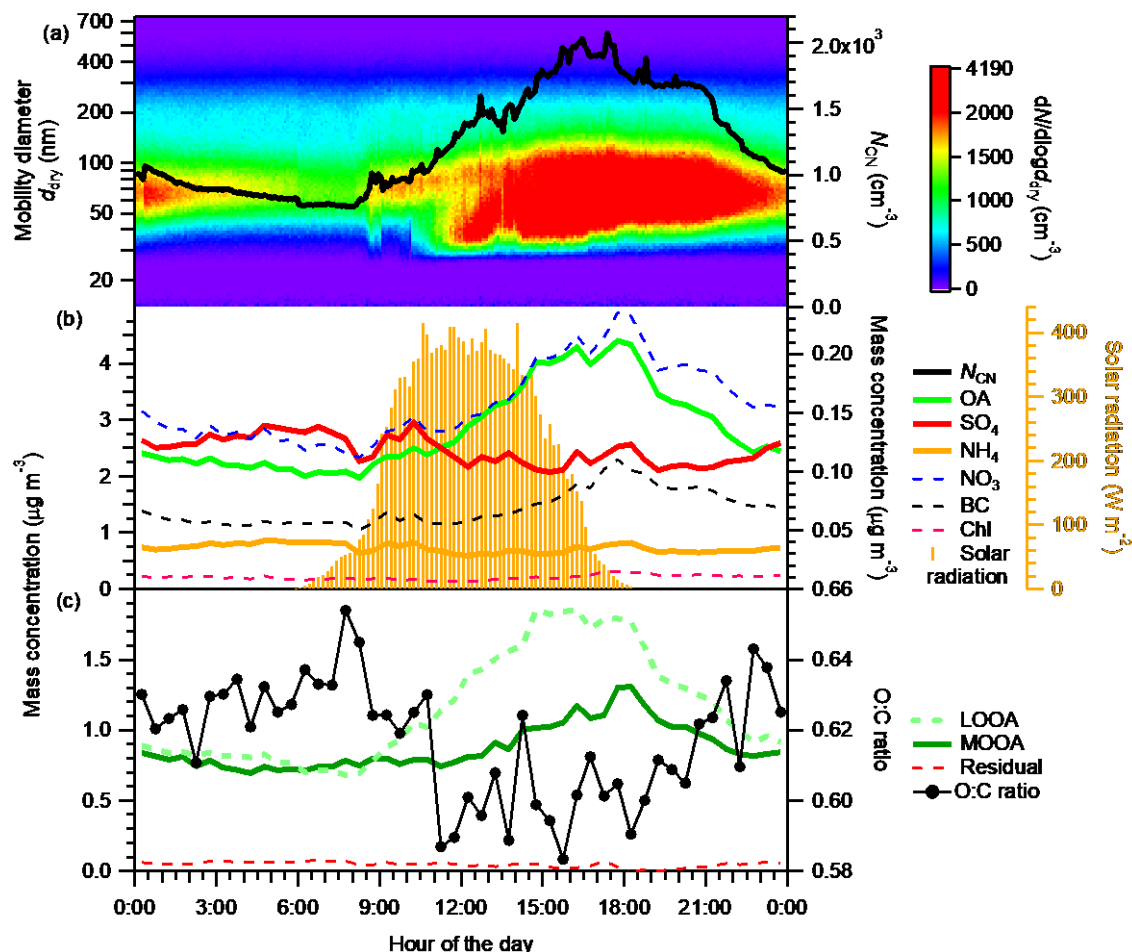
Figure 2: Diurnal variations of (a) number-size distribution (image plot) and number concentration (N_{CN}, right axis) of ambient aerosols, and the mass concentrations of (b) OA, SO₄, and NH₄ (left axis), and NO₃, BC, and Chl (right axis in black), and (c) LOOA, MOOA, and residual, and the O:C ratio of bulk OA (only data with $m_{org} > 0.3$ µg m⁻³ are included) averaged for the entire study period. (A box and whiskers plot of the diurnal variation of O:C ratio is presented in Fig. S19.) The diurnal variation of solar radiation averaged for the entire period is superimposed in panel (b).

4.1.2 Hygroscopicity of atmospheric aerosols

Similar to a prior observation at the same site in 2010 (Kawana et al., 2017), the hygroscopic growth factor g_f presented unimodal distributions at respective particle diameters (Figs. 1d, 1e, and S11), and the mean hygroscopic growth factor $g_{f,m}$ of the aerosols increased with increase of the particle diameters (Fig. S12). The mean ± SD of $g_{f,m}$ at 30, 50, 70, 100, 200, 300,

and 360 nm were 1.13 ± 0.08, 1.21 ± 0.09, 1.22 ± 0.09, 1.26 ± 0.10, 1.36 ± 0.10, 1.40 ± 0.08, and 1.42 ± 0.08, respectively. The unimodal pattern of the g_f-PDF indicated the internal mixing state of the observed aerosol at the respective particle diameters. Decreases of $g_{f,m}$ (Fig. S12) were observed for all particles during periods of intensive BSOA formation (i.e., episodes when the mass concentration of OA especially LOOA greatly increased; such episodes were observed on 31 August,

5 and on 2, 5, 7, 9, 14, 15, 17, 18, 19, 20, and 21 September; Fig. 1b).

The hygroscopicity parameter of ambient aerosol particles that corresponds to $g_{f,mw}$ (κ_t) also increased with the increase of aerosol particle diameters (Fig. 3a). Similar diurnal variation patterns were observed for all the diameters studied. The κ_t started to decrease around 0800 JST, then reached daily minima between 1300 and 1900 JST. Then it increased continually until around 0200 JST of the next day, and remained high until 0800 JST the next morning. For particles with $d_{dry} \geq 100$ nm, the

10 diurnal variation pattern and size-dependence of κ_t were opposite to those of the volume fraction of OA (Fig. 3b) and were similar to those of the volume fraction of total inorganic salts (Fig. S13). The results suggest that, at least for ambient aerosol particles with $d_{dry} \geq 100$ nm, OA and inorganic salts had low and high hygroscopicity, respectively, resulted in the variations of κ_t. Although $\kappa_{inorgsalt}$ is much greater than κ_{org} (Petters and Kreidenweis, 2007), the high ε_{org} makes the influence of OA on κ_t significant. Thus, the variation of κ_{org} (Sect. 4.2) may also contribute to the variation of κ_t. For particles with $d_{dry} \leq 70$ nm,

15 decrease of the particle hygroscopicity with decrease of the particle diameter is also explained by the accompanying increase of ε_{org} and the decrease of $\varepsilon_{inorgsalt}$ (Levin et al., 2014). This is indicated by the substantially lower mean mass fraction of inorganic salts than of organics in the corresponding d_{va} range of less than 150 nm (Fig. S2). In particular, for particles with d_{dry} of 30 nm, κ_t remained constant in a low range (0.079–0.089) from 1300 JST to 1700 JST with a mean value of 0.082. BSOA formed during this period probably dominated the particle mass (Kawana et al., 2017; Han et al., 2014).
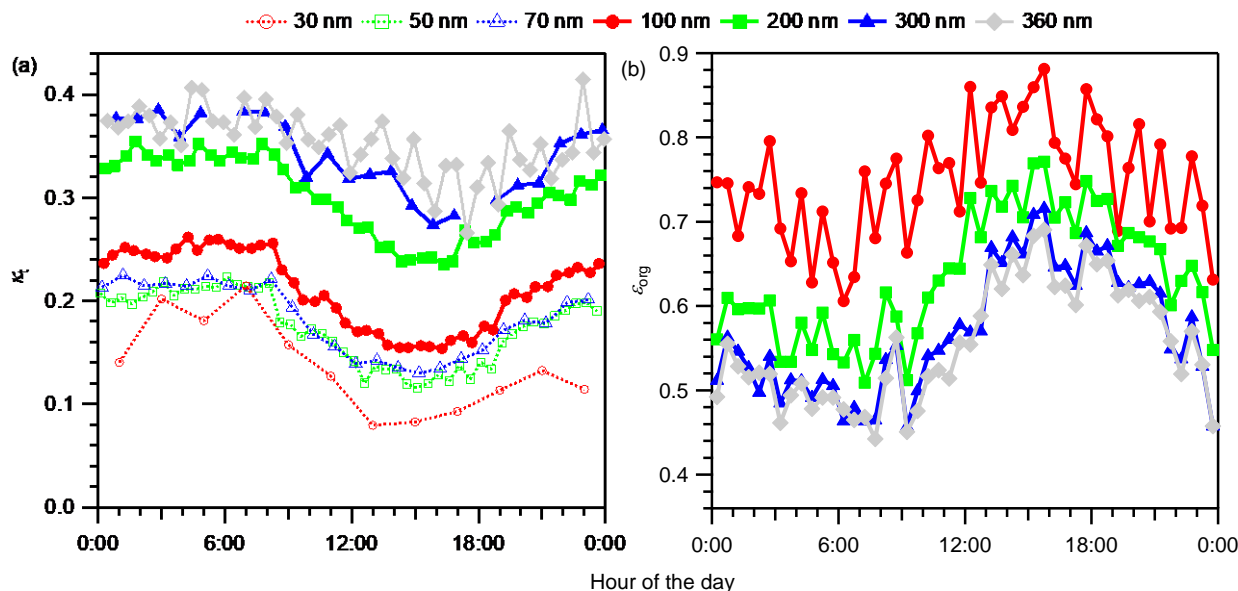
Figure 3: Diurnal variations of (a) size-resolved hygroscopicity of aerosols (κ_t) and (b) size-resolved volume fractions of OA (ε_{org}) for the entire study period. Note that for particles with d_{dry} of 30 nm, κ_t is presented in 2-h time resolution because of the low data coverage (Fig. S12).

4.2 Hygroscopicity of organic aerosol components

4.2.1 Variation of κ_{org} and its relation to the chemical structure of OA

The diurnal variation of κ_{org} and the volume fraction of LOOA in OA, $v_{LOOA}/(v_{LOOA}+v_{MOOA})$, where v_{LOOA} and v_{MOOA} refer to the volume concentrations of LOOA and MOOA, respectively, for the entire study period are presented in Fig. 4. Data with

10    $\varepsilon_{org} < 0.40$ were excluded from the κ_{org} values presented because the uncertainty that originated from subtraction of the contribution of inorganic components was considered large in the low ε_{org} range (Mei et al., 2013a). The κ_{org} decreased rapidly from approximately 0800 JST in the morning when the mass concentrations of OA and LOOA started to increase (Fig. 2). The κ_{org} reached daily minima during 1000–1800 JST, and increased after the minima (Fig. 4a). The $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ in Fig. 4b presents the opposite diurnal variation pattern. The characteristics of the size-dependence of κ_{org} and $v_{LOOA}/(v_{LOOA}+v_{MOOA})$

15   were dependent on time periods. To characterize the size-dependence of κ_{org} and $v_{LOOA}/(v_{LOOA}+v_{MOOA})$, the mean values of κ_{org} and $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ during 1200–2000 JST and 2000–1200 JST were plotted separately in the κ_{org} - $v_{LOOA}/(v_{LOOA}+v_{MOOA})$

space for different d_{dry} (Fig. 5), and the difference in the diurnal variation data between particles with different diameters were evaluated using a 10 % two-sided t-test (Table S7). During 1200–2000 JST, opposite size-dependences were observed between the mean κ_{org} and $v_{LOOA}/(v_{LOOA}+v_{MOOA})$. Although the differences of κ_{org} between 200 and 300 nm particles (p-value: 0.71) and 300 and 360 nm particles (p-value: 0.15) were not significant, the differences of κ_{org} between 100 and 200 nm particles (p-value: 0.01) and 200 and 360 nm particles (p-value: 0.07), and the differences of $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ between particles with all different diameters (p-value: <0.02), were significant during that period. During 2000–1200 JST, the size-dependences of κ_{org} and $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ were not clear. The clearer size-dependence of both κ_{org} and $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ during 1200–2000 JST than during 2000–1200 JST, was explained by the formation of BSOA during the afternoon hours. The patterns of diurnal variation and of size-dependence between κ_{org} and $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ during 1200–2000 JST indicate that the variation of κ_{org} could be explained at least in part by the relative contributions of LOOA and MOOA to OA. That is, the presence of LOOA with low oxygenation state (O:C ratio of 0.47) lowered the observed κ_{org}, while the presence of MOOA with high oxygenation state (O:C ratio of 0.95) increased the observed κ_{org}. A similar relationship was observed in a former study at the observation site: κ_{org} was positively correlated with the O:C ratio of the organics (Deng et al., 2018).
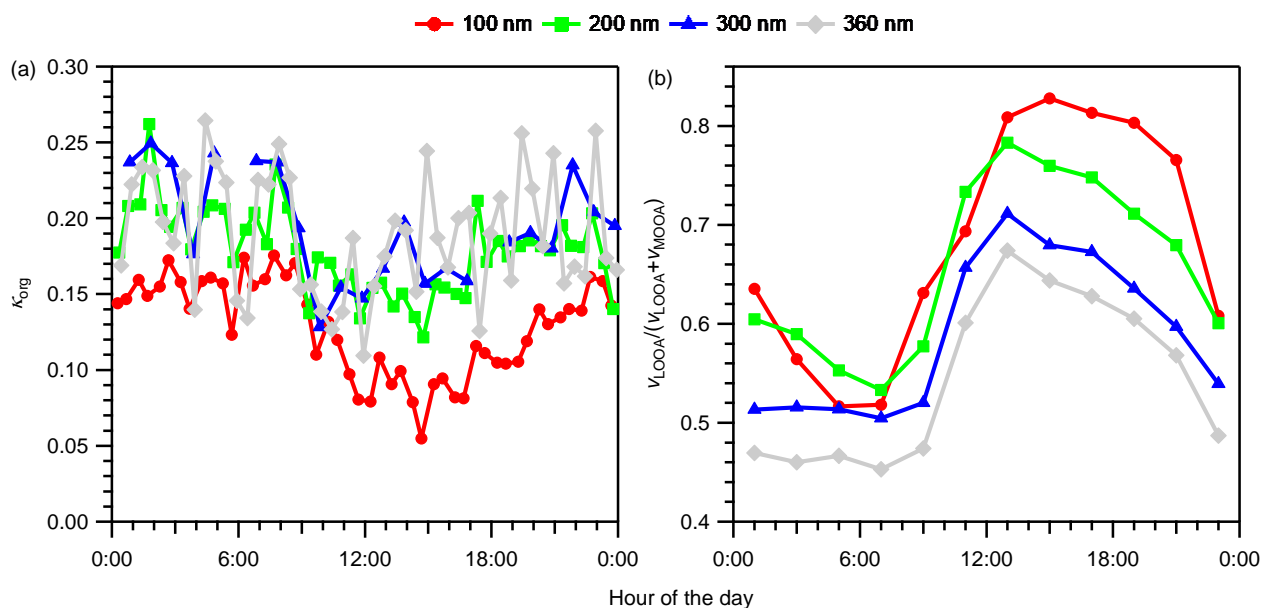
Figure 4: Diurnal variations of (a) size-resolved hygroscopicity of OA (κ_{org}) and (b) size-resolved volume fractions of LOOA in OA ($v_{LOOA}/(v_{LOOA}+v_{MOOA})$) for the entire study period. For κ_{org} in panel (a), only data with $\varepsilon_{org} > 0.40$ were considered. The values in panel (b) were calculated from the diurnal variations of the average volume concentrations of LOOA and MOOA (Fig. S16), not from the averages of $v_{LOOA}/(v_{LOOA}+v_{MOOA})$.

5   The hygroscopicity parameters of LOOA (κ_{LOOA}) and MOOA (κ_{MOOA}) were determined to evaluate the variations of κ_{org} that can be explained by the relative contributions of LOOA and MOOA to OA. For the determination of κ_{LOOA} and κ_{MOOA}, κ_{org} was plotted against $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ and their correlation was analyzed based on linear regression analysis (Figs. 5 and S14). For particles with d_{dry} of 100, 200, 300, and 360 nm, the correlation coefficients between κ_{org} and $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ were −0.50, −0.58, −0.27, and −0.099, respectively. Relatively high correlations were observed for particles with d_{dry} of 100

10   and 200 nm, probably because higher particle number concentrations (Fig. 1c) and higher OA volume fractions (Fig. 3) led to smaller uncertainties in the derived κ_{org} in those diameter ranges, than in those of 300 and 360 nm. The regression line for particles with d_{dry} of both 100 and 200 nm (Fig. 5) were used to derive κ_{LOOA} and κ_{MOOA} by applying $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ of zero and unity to the obtained regression equation, respectively. The derived κ_{LOOA} and κ_{MOOA} were 0.083 and 0.28, respectively. This result is in between the results if particles with d_{dry} of only 100 nm (derived κ_{LOOA} and κ_{MOOA} were 0.060

15   and 0.25, respectively) and only 200 nm (derived κ_{LOOA} and κ_{MOOA} were 0.095 and 0.34, respectively) were used. Compared with the κ of PMF factors reported by Jimenez et al. (2009), the derived κ_{LOOA} and κ_{MOOA} are within the ranges of κ for semi-volatile oxygenated OA (0.04–0.18) and low-volatility oxygenated OA (0.18–0.35), respectively (Fig. 5). The size-resolved $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ and the above derived κ_{LOOA} and κ_{MOOA} were used to reconstruct the diurnal variation data and mean values of size-resolved κ_{org} during 1200–2000 JST based on the volume additivity assumption. The reconstructed κ_{org} and the

20   κ_{org} described above (measured κ_{org}) were compared and their correlations were evaluated through linear regression analysis (Fig. S15). The slope and r^2 of the regression line are used to assess the ability of LOOA and MOOA to explain the variations of κ_{org}. For 100 and 200 nm particles, the relative contribution of LOOA and MOOA to OA can explain the majority of the variations of κ_{org} (the slope and r^2 for 100 nm particles were 0.72 and 0.79, respectively and those for 200 nm particles were 0.63 and 0.68, respectively). The variations of κ_{org} of 300 and 360 nm particles are explained less by the relative contributions

25   of LOOA and MOOA to OA (the slope and r^2 for 300 nm particles were 0.31 and 0.48, respectively; for 360 nm particles were 0.16 and 0.07, respectively). The slope and r^2 of the regression line between reconstructed and measured κ_{org} for particles with

all four d_{dry} were 0.39 and 0.44, respectively. This result indicates that the relative contribution of LOOA and MOOA can explain around 40 % of the observed diurnal variations of κ_{org}. The slope and r^2 of the regression line over the mean reconstructed and observed κ_{org} of the four different sizes during afternoon hours (1200–2000 JST) were 0.39 and 0.84, respectively, which indicates that the size-dependence of κ_{org} is explained by the relative contribution of LOOA and MOOA to OA by at least ~ 40 % during the time period.
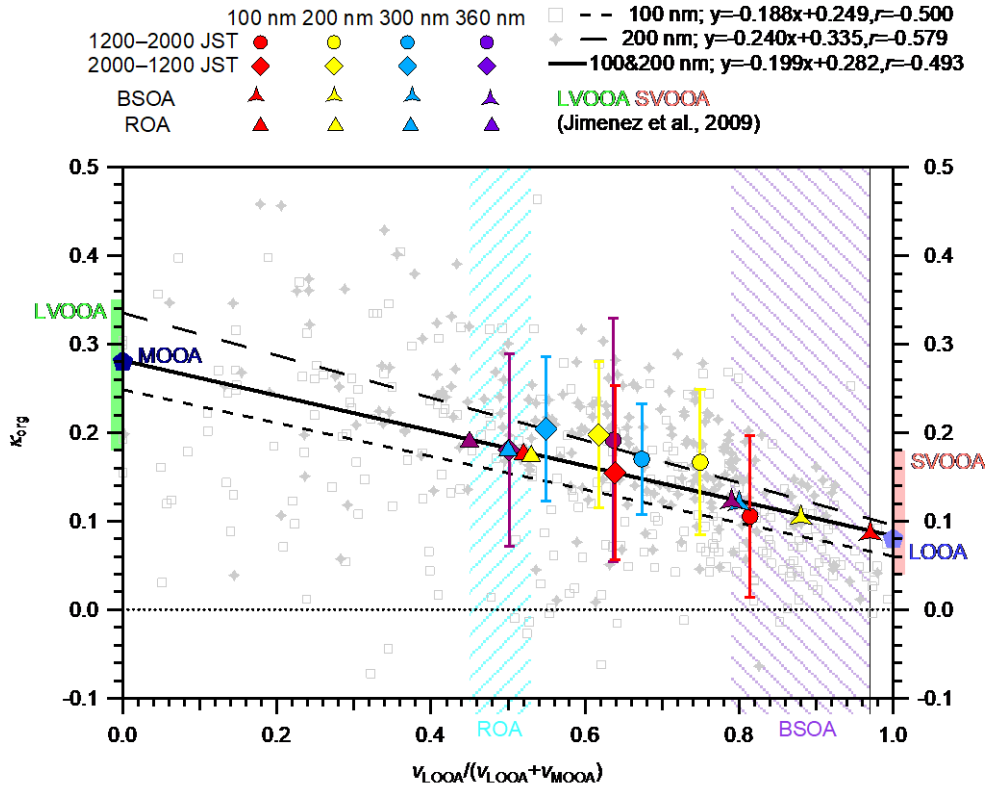
Figure 5: κ_{org} versus $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ for particles with d_{dry} of 100 nm (gray open squares) and 200 nm (gray cross markers) over the entire study period. The time resolution of individual data is 2 h. Only data with $\varepsilon_{org} > 0.40$ are considered. The short-dashed, long-dashed, and solid lines are the regression lines for particles with d_{dry} of 100 nm, 200 nm, and the sum of the particles with the two sizes, respectively. The κ values of LOOA and MOOA derived from the regression lines (Sect. 4.2.1) are indicated by the light and dark blue pentagons, respectively. The size-resolved mean κ_{org} during 1200–2000 JST and 2000–1200 JST are indicated as filled circles and diamond markers, respectively. The standard deviations of the mean κ_{org} are indicated by the whiskers. The standard deviations of the mean $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ are presented in Table S6. The size-resolved κ values of BSOA and ROA are indicated by the three-pointed stars and triangles, respectively. The diameters of κ_{org}, κ_{BSOA}, and κ_{ROA} are differentiated by colors. The ranges of κ for low-volatility oxygenated OA (LVOOA) and semi-volatile oxygenated OA (SVOOA) from Jimenez et al. (2009) are superimposed on the left and right axes, respectively. The shaded areas represent the estimated ranges of $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ for ROA (left slash pattern) and BSOA (right slash pattern) of 100–360 nm particles.

4.2.2 Hygroscopicity of biogenic secondary organic aerosols

The hygroscopicity parameter of freshly formed BSOA (κ_{BSOA}) was calculated as the volume weighted mean of κ_{LOOA} and κ_{MOOA}. As discussed in Sect. 4.1.1, the enhanced OA mass in the daytime can be regarded as fresh BSOA. To simplify the analysis, the remaining part of the observed OA can be regarded as regionally transported OA (ROA), which may contain some aged, locally formed BSOA (Deng et al., 2018). To estimate the size-resolved contributions of LOOA and MOOA to BSOA and ROA, the size-resolved diurnal variations of sulfate was assumed as a tracer of regionally transported aerosol, and was scaled to represent the diurnal variations of LOOA and MOOA that constitute ROA (LOOA-ROA and MOOA-ROA; Fig. S16). For the scaling, the period of 0600–0800 JST, when OA and its subcomponents reached their daily minima (Figs. 2 and S16), was regarded as the background period, and all the LOOA and MOOA during the period were considered constituents of ROA. The remaining fractions of LOOA and MOOA were regarded as constituents of BSOA, referred to as LOOA-BSOA and MOOA-BSOA, respectively. The $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ of ROA was estimated to be 0.52, 0.53, 0.50, and 0.45 for particles with d_{dry} of 100, 200, 300, and 360 nm, respectively (the range is presented by a left-slash pattern in Fig. 5). The period when the diurnal variations of the size-resolved concentration of LOOA reached their maxima (i.e., 1400–1600 JST; Fig. S16) was chosen to estimate the size-resolved $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ of BSOA. The estimated $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ of the BSOA were 0.97, 0.88, 0.80, and 0.79 for particles with d_{dry} of 100, 200, 300, and 360 nm, respectively (the range is presented by a right-slash pattern in Fig. 5). Although the estimated BSOA could have aged to some extent, it was defined as fresh BSOA. The κ_{BSOA} (and κ_{ROA}) were calculated using the derived $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ of BSOA (ROA) for particles with different d_{dry} and κ_{LOOA} and κ_{MOOA}, and found to be 0.089 (0.18), 0.11 (0.18), 0.12 (0.18), and 0.12 (0.19) for particles with d_{dry} of 100, 200, 300, and 360 nm, respectively. The result indicates that κ_{BSOA} may increase with increase of the particle diameter as a result of the size-dependent contribution of LOOA and MOOA to BSOA (Fig. 5; colored three-pointed stars), which however needs to be confirmed by further studies. The size-dependence of the estimated κ_{ROA} (Fig. 5; colored triangles) was less obvious than that of κ_{BSOA}. The κ_{BSOA} derived at 85 % RH for particles with d_{dry} of 100 nm in this study (0.089) was slightly smaller than that in a previous study for particles with similar diameters under SUPS condition (0.10 at 94±11 nm) at the same site (Deng

et al., 2018). The derived κ_{ROA} is similar to the average κ_{org} during the nighttime (Fig. 4). The size-resolved volume concentrations of BSOA (v_{BSOA}) and ROA (v_{ROA}) were also estimated using those size-resolved $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ values of BSOA and ROA (Text S10). The obtained volume fraction of BSOA in aerosol particles (ε_{BSOA}; Fig. S18) presented diurnal variation patterns that were similar to those of $v_{LOOA}/(v_{LOOA}+v_{MOOA})$. Furthermore, the size dependence of ε_{BSOA} during

5 afternoon hours was also similar to that of $v_{LOOA}/(v_{LOOA}+v_{MOOA})$. Because both the volume concentrations and hygroscopicity of BSOA and ROA were derived from that of LOOA and MOOA, the variation of the relative contributions of the estimated BSOA and ROA to OA can explain 40 % of the diurnal variation and size-dependence of the measured κ_{org}.

4.3 Ranges of the variations of κ_t, κ_{org}, and κ_{BSOA}

10 The ranges of the diurnal variations of κ_t and κ_{org}, the difference between their maxima and minima, were obtained from their diurnal variation data with 2 h resolution (Table S8). The variation ranges of κ_t were 0.14, 0.091, 0.084, 0.10, 0.11, 0.11, and 0.070 for particles with d_{dry} of 30, 50, 70, 100, 200, 300, and 360 nm, respectively. The variation ranges of κ_{org} for particles with d_{dry} of 100, 200, 300, and 360 nm were 0.091, 0.079, 0.096, and 0.11, respectively. The size-dependence of κ_t and κ_{org} were quantified by the mean κ_t and κ_{org} values for the entire study period (Table S8). The difference of κ_t between particles

15 with d_{dry} of 100 and 300 nm was 0.13, and that of κ_{org} was 0.056.

The ranges of both the diurnal variations and the size-dependence of κ_t are similar to those reported from a previous study at the same site in 2010 (the mean of the differences between 0900–2100 JST and 2100–0900 JST on NPF event days and on nonevent days for the d_{dry} range of 28.9–359 nm was in the range of 0.09–0.13, and the difference between Aitken mode and accumulation mode particles was 0.12) (Kawana et al., 2017), which pointed out the importance of the variation of particle

20 hygroscopicity with time and size to the CCN number concentration. The ranges of both the diurnal variations and the size-dependence of κ_{org} are comparable to the range of 0.05 (from 0.08 to 0.13) that could lead to 30 % or more bias in the predicted CCN number concentration if not considered (Mei et al., 2013b). Here, only the ranges of the variation of κ_t and κ_{org} are discussed; other factors such as the absolute values of κ_t or κ_{org} should also be important to the prediction of CCN number concentrations. If SS is 0.1–1 %, typical maximum values in cloud systems (Farmer et al., 2015), the d_{dry} of 100 nm is close

to the mode diameters of the CCN number-size distributions in previous studies at the same site (Kawana et al., 2017; Deng et al., 2018). Whereas the d_{dry} of 300 nm is close to the mode mobility diameters of the mass-size distributions of OA and other aerosol components in this study (Fig. S2). The difference in the two types of mode diameters indicates that significant bias could be introduced if the bulk aerosol composition and/or OA composition is used for the prediction of CCN number concentrations.

The difference of the estimated κ_{BSOA} between particles with d_{dry} of 100 nm and 300 nm was estimated to be 0.031. The difference implies the importance of the size-dependence of κ_{BSOA} in the prediction of the contribution of BSOA to the CCN number concentration.

4.4 Contributions of OA and BSOA to CCN concentrations

The contributions of OA and BSOA to CCN number concentrations were assessed from the viewpoint of their contributions to the aerosol water uptake, which are size-dependent. For the estimate, the observed aerosols were assumed to be internally mixed. This is supported by a result from a previous study at the observation site: there was almost no difference in the prediction of the number fractions of CCN between the use of time- and size-resolved g_f distributions and time- and size-resolved $g_{f,m}$ (Kawana et al., 2017). In two previous observations at the same site, the average CCN activation diameters of aerosols under 0.41 and 0.42 % SS were 71 and 68 nm, respectively (Kawana et al., 2017; Deng et al., 2018). Based on these facts, all the particles with d_{dry} greater than 70 nm were assumed to be CCN active. The estimated total CCN number concentration is referred to as $N_{CCN,t}$. For each size range (Text S11), the contribution of OA (BSOA) to the aerosol water uptake was represented as the product of the volume fraction of OA (BSOA) and κ_{org} (κ_{BSOA}) divided by κ_t [i.e., $\varepsilon_{org}\kappa_{org}/\kappa_t$ ($\varepsilon_{BSOA}\kappa_{BSOA}/\kappa_t$)], and was used to represent the fractional contribution of OA (and BSOA) to $dN_{CN}/dlogd_{dry}$ in the size range.

The fractional contribution of OA (and BSOA) to $N_{CCN,t}$, hereafter referred to as $F_{CCN,OA}$ ($F_{CCN,BSOA}$), was derived by integrating the product of $dN_{CN}/dlogd_{dry}$ and $\varepsilon_{org}\kappa_{org}/\kappa_t$ ($\varepsilon_{BSOA}\kappa_{BSOA}/\kappa_t$) above the CCN activation diameter (70 nm) and by dividing the obtained value by $N_{CCN,t}$. Details for the estimation of $F_{CCN,OA}$ and $F_{CCN,BSOA}$ are presented in Text S11. The diurnal variation of the CCN activation diameter was not considered for the estimate of $F_{CCN,OA}$ and $F_{CCN,BSOA}$ (Text S12).
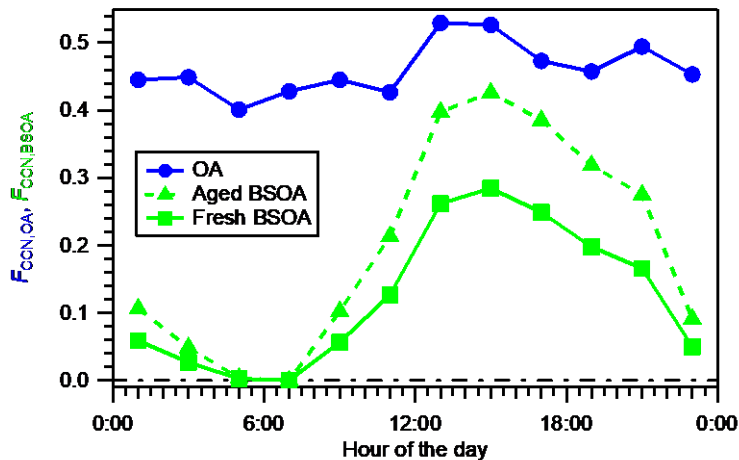
Figure 6: Diurnal variation of the fractional contribution of OA to the total CCN number concentration ($F_{CCN,OA}$) estimated using time- and size-resolved κ_{org}, and diurnal variation of the fractional contribution of BSOA to the total CCN number concentration ($F_{CCN,BSOA}$) estimated assuming fresh BSOA (using size-resolved κ_{BSOA}) and aged BSOA (using size-resolved κ_{ROA}).

The diurnal variation of $F_{CCN,OA}$ estimated using time- and size-resolved κ_{org} and that of $F_{CCN,BSOA}$ using size-resolved k_{BSOA} are presented in Fig. 6. Both $F_{CCN,OA}$ and $F_{CCN,BSOA}$ reached their maxima during 1200–1600 JST, when intensive BSOA formation was observed. The magnitude of the variation of $F_{CCN,BSOA}$ (from 0.00 to 0.28) was larger than that of $F_{CCN,OA}$ (from 0.40 to 0.53). This is explained by the larger magnitude of the diurnal variation range of ε_{BSOA} (Fig. S18), compared to that of

10 ε_{org} (Fig. 3). The $F_{CCN,BSOA}$ of 0.28 during 1200–1600 JST indicates a significant contribution of BSOA to the CCN number concentration.
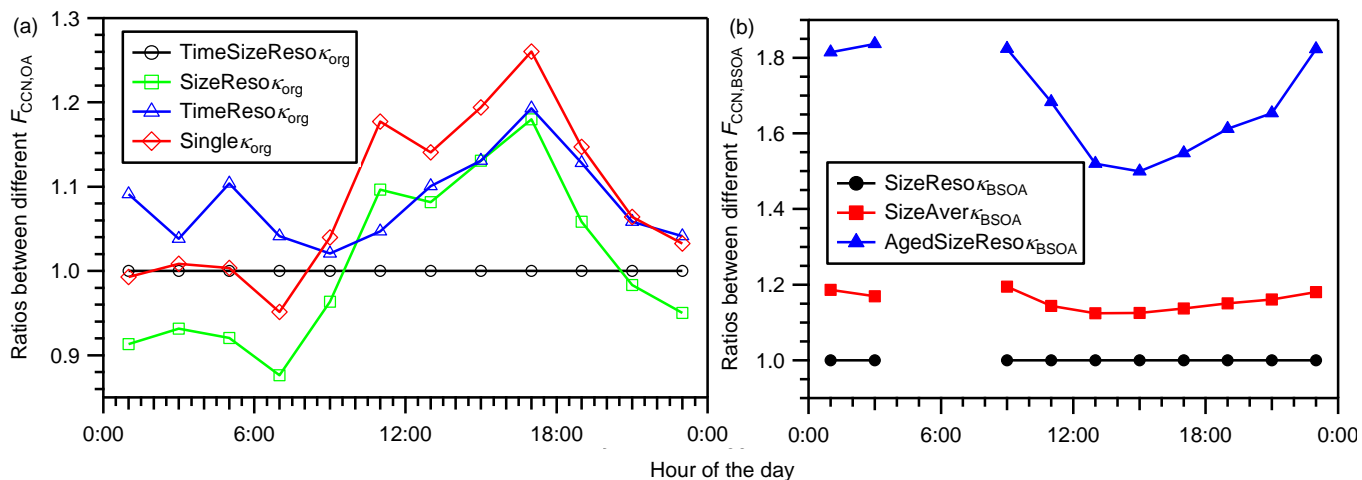
Figure 7: (a) Diurnal variation of the ratios of the $F_{CCN,OA}$ derived using time- and size-resolved κ_{org} (TimeSizeResoκ_{org}), time-averaged and size-resolved κ_{org} (SizeResoκ_{org}), size-averaged and time-resolved κ_{org} (TimeResoκ_{org}), and time- and size-averaged κ_{org} (Singleκ_{org}) to that derived using the time- and size- resolved κ_{org} (TimeSizeResoκ_{org}). **(b)** Diurnal variation of the ratios of the $F_{CCN,BSOA}$ derived using size-resolved κ_{BSOA} (SizeResoκ_{BSOA}), size-averaged κ_{BSOA} (SizeAverκ_{BSOA}), and aged size-resolved κ_{BSOA} (AgedSizeResoκ_{BSOA}) to that derived using the size-resolved κ_{BSOA} (SizeResoκ_{BSOA}). In panel (b), the condition of aged size-resolved κ_{BSOA} assumes that the value of κ_{BSOA} equals that of κ_{ROA}, and the data during 0400–0800 JST, when the concentration of BSOA was low (volume concentration less than 0.01×10^{-6} cm^3 m^{-3}; Fig. S18), are not presented (data are presented in Table S12).

Because obvious diurnal variations and size-dependence of κ_{org} were found and because κ_{BSOA} was also estimated to be size-dependent (Sect. 4.2), the sensitivities of the estimated $F_{CCN,OA}$ and $F_{CCN,BSOA}$ on the variations of κ_{org} and κ_{BSOA} were assessed. To assess the influence of the variation of κ_{org} on $F_{CCN,OA}$, the diurnal variations of $F_{CCN,OA}$ was estimated using (0a, base case) time- and size-resolved κ_{org}, (1a) size-resolved, time-averaged (note that the average here refers to the arithmetic mean, it is the same in other places of this paragraph) κ_{org}, (2a) time-resolved, size-averaged κ_{org}, and (3a) time- and size-averaged κ_{org} (Table S10). Cases (1a)–(3a) were compared with the base case (0a), as presented in Fig. 7a. Using time-averaged κ_{org} (case 1a), the $F_{CCN,OA}$ was overestimated by 18% during 1600–1800 JST and underestimated by 12 % during 0600–0800 JST. Using size-averaged κ_{org} (case 2a), the $F_{CCN,OA}$ was overestimated by 2–19 % on a diurnal basis. Using time- and size-averaged κ_{org} (i.e., a single mean κ_{org}, case 3a), $F_{CCN,OA}$ was overestimated by 26 % during 1600–1800 JST and underestimated by 4.9 % during 0600–0800 JST. The deviation of case (3a) from the base case (0a) resulted from the factors leading to the deviations of cases (1a) and (2a). The magnitudes of the deviations, defined here as the difference between the lowest and highest values of the ratios in Fig. 7a, for (1a), (2a), and (3a) are 30, 17, and 31 %, respectively. The substantial differences suggest that the diurnal variations and size-dependence of κ_{org} are important for accurate prediction of the contribution of OA to the CCN number concentration in modelling studies. To assess the influence of the size-dependence of κ_{BSOA} on $F_{CCN,BSOA}$, the diurnal variations of $F_{CCN,BSOA}$ was estimated using (0b, base case) size-resolved κ_{BSOA} and (1b) size-averaged κ_{BSOA} (Table S11). Case (1b) was compared with case (0b), as presented in Fig. 7b. Using size-averaged κ_{BSOA} caused overestimation of $F_{CCN,BSOA}$ by 12–19 %, which relates to the decrease of the estimated κ_{BSOA} and the increase of dN_{CN}/dlogd_{dry} (Fig. S17) with decrease in the dry particle diameter.

Furthermore, because fresh BSOA probably become aged after atmospheric transport, the influence of the aging of the estimated fresh BSOA (assuming κ_{BSOA} was as large as that of κ_{ROA} (Table S11)) on $F_{CCN,BSOA}$ was also evaluated. Here, the

estimation of $F_{CCN,BSOA}$ in the aged condition ignored the possible change in the CCN activation diameter accompanying the aging processes (Text S13). The possible change in the aerosol size distribution accompanying the aging process was also not considered here. Aged BSOA can contribute more to the aerosol water uptake and thus to the CCN number concentration. Assuming that the BSOA was as aged as ROA, the estimated $F_{CCN,BSOA}$ was 50–84% larger than that estimated assuming fresh BSOA (Fig. 7b), and it could have been 0.43 if the aerosol observed during 1400–1600 JST aged (Fig. 6). The result suggests that, whereas the contribution of BSOA to CCN was substantial at the study site, the magnitude of the contribution might be increased substantially by aging of the BSOA during transport after its formation in the forest.

5 Summary and conclusions

The size-resolved hygroscopicity at 85 % RH, chemical composition, and number-size distributions of atmospheric aerosols were observed at a forest site in Wakayama, Japan in August and September, 2015. The diurnal variation and size-dependence in the hygroscopicity of the observed aerosol and organic aerosol components (OA) were discussed in view of the formation of BSOA. The fractional contributions of OA and BSOA to the total CCN number concentration were discussed in view of the variations of the hygroscopicity parameter of OA and BSOA.

Similar to two previous observations at the same site (Han et al., 2013, 2014; Kawana et al., 2017; Deng et al., 2018), OA was the dominant sub-micrometer aerosol component, followed by sulfate. While the mass concentration of sulfate, on average, did not vary much in a day, the mass concentration of OA increased substantially in the afternoon hours, which was presumably explained by the condensation of BSOA. The hygroscopicity of ambient aerosol (κ_t) and of OA (κ_{org}) increased with increase of the dry particle diameter and presented daily minima in the afternoon hours. In this study, the ranges of the diurnal variations of κ_{org} of 100–360 nm particles were 0.079–0.11 and the κ_{org} of 300 nm particles was 0.056 larger than that of the 100 nm particles. The diurnal variations and size-dependence of κ_t can be explained by the relative contributions of OA and inorganic salts in the observed aerosol. The relative contributions of the estimated fresh BSOA and regional OA can explain 40 % of the diurnal variation and size-dependence of κ_{org}. The hygroscopicity of fresh BSOA (κ_{BSOA}) was estimated to increase (0.089–0.12) with increase of the dry particle diameter (100–300 nm).

The fractional contributions of OA and fresh BSOA to CCN number concentrations estimated from the viewpoint of their contributions to the water uptake by the aerosol were in the ranges 0.40–0.53 and 0.00–0.28, respectively. Compared with the use of time- and size-resolved κ_{org}, the use of time- and size-averaged κ_{org} overestimated the contribution of OA to the CCN number concentration by up to 26 % (1600–1800 JST) and underestimated the contribution by up to 4.9 % (0600–0800 JST).

5   These results indicate the importance of the diurnal variations and size-dependence of κ_{org} in the prediction of the contribution of OA to the CCN number concentration. The use of size-averaged κ_{BSOA} overestimated the contribution of fresh BSOA to the CCN number concentration by 12–19 % compared with the use of size-resolved κ_{BSOA}. If aging of BSOA after atmospheric transport occurs, the contribution of fresh BSOA to the CCN number concentration could be increased by 50–84 %, and could have reached a high value of 0.43 if the aerosol observed during 1400–1600 JST aged.

10   This study revealed the large magnitude of the diurnal variation and size-dependence of κ_{org} at the observation site under the influence of the formation of BSOA. Also revealed was the importance of the variation of κ_{org} to the estimation of the contribution of OA to the CCN number concentration from the viewpoint of the size-resolved contribution of OA to the water uptake of aerosols. Because both the diurnal variation and size-dependence of κ_{org} in the studied forest are different from those in some other forest environments (Cerully et al., 2015; Thalman et al., 2017), further studies on the variation of the

15   hygroscopicity of organics and on the contributions of OA and BSOA to the CCN concentrations should be performed in other forest environments. Furthermore, the size-dependence of the hygroscopicity of fresh BSOA estimated here should be confirmed by additional studies.

Data availability. All of the final derived data supporting the findings of this study are available in the article or in its supporting

20   information file.

Author contributions. MM and YD designed the experiments, and YD, HY, MM, HF, and TN performed them. YD analyzed the data with contributions from MM, TN, and KK. YD prepared the manuscript with contributions from MM, KK, and TN.

Competing interests. The authors declare that they have no conflict of interest.

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