

We appreciate valuable comments from the reviewers. Our answers to the comments are provided below. (The reviewers' comments are written in italic. The line numbers in the response are from the revised version of the manuscript.)

## **Response to Anonymous Referee #1**

### *Anonymous Referee #1*

*Received and published: 19 November 2018*

*Overview: Deng et al. present a detailed characterization and analysis of organic aerosol contribution to aerosol particle hygroscopicity through measurements with a Humidity Tandem differential mobility analyzer (HTDMA), Aerosol Mass Spectrometer (AMS) and complementary measurements of black carbon and trace gas species in Wakayama, Japan. The site is one that is very well characterized by previous field campaigns and well described in the literature. This study combines positive matrix factorization (PMF) analysis with aerosol hygroscopicity measurements to understand the time and size – dependent variation of organic hygroscopicity on overall aerosol hygroscopicity. I recommend publication of the study after addressing a few minor issues.*

*General Comments: In general, the discussion of biogenic secondary organic aerosol (aged and fresh BSOA) and the AMS volatility factors (LOOA and MOOA) seem disconnected from each other. As the paper transitions from the PMF analysis to a hygroscopicity based derivation of BSOA (section 4.3 to section 4.4) there doesn't not appear to be a clear transition of tying together of the two concepts or how/why they should or should not be connected. A clearer distinction and transition would be helpful.*

In this study, the fresh BSOA was defined as the enhanced mass of both LOOA and MOOA in the daytime (Sect. 4.2.2). The existence of aged BSOA at the studied site is only briefly explained from the diurnal variation of O:C ratio and MOOA (page 12 lines 16–17), which is, however, not the main point of this study. The discussion on the fractional contribution of aged BSOA to the CCN number concentration is based on a hypothetical condition of BSOA after its transport (the last paragraph in Sect. 4.4), and is not related to the observed relative abundances of LOOA and MOOA. To clarify this

point, the first sentence in the last paragraph of Sect. 4.4 has been modified to: “Furthermore, because fresh BSOA probably become aged after atmospheric transport, the influence of the aging of the estimated fresh BSOA (assuming  $\kappa_{\text{BSOA}}$  was as large as that of  $\kappa_{\text{ROA}}$  (Table S11)) on  $F_{\text{CCN,BSOA}}$  was also evaluated.”

Note that LOOA and MOOA in the manuscript are not volatility factors. They were defined according to the degree of oxygenation (i.e., O:C ratio), as indicated in [page 9 lines 18–20](#): “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 higher O:C ratio (0.95) named more-oxygenated organic aerosol (MOOA).”

*Specific Comments:*

*Page 11 line 4: “observation” conveys a short time period or single time, where the measurements happened over the course of 20 days. A different description (measurement period, campaign, etc.) might be more appropriate.*

The word “observation” has been changed to “measurement period with effective data”. ([page 11 line 4](#))

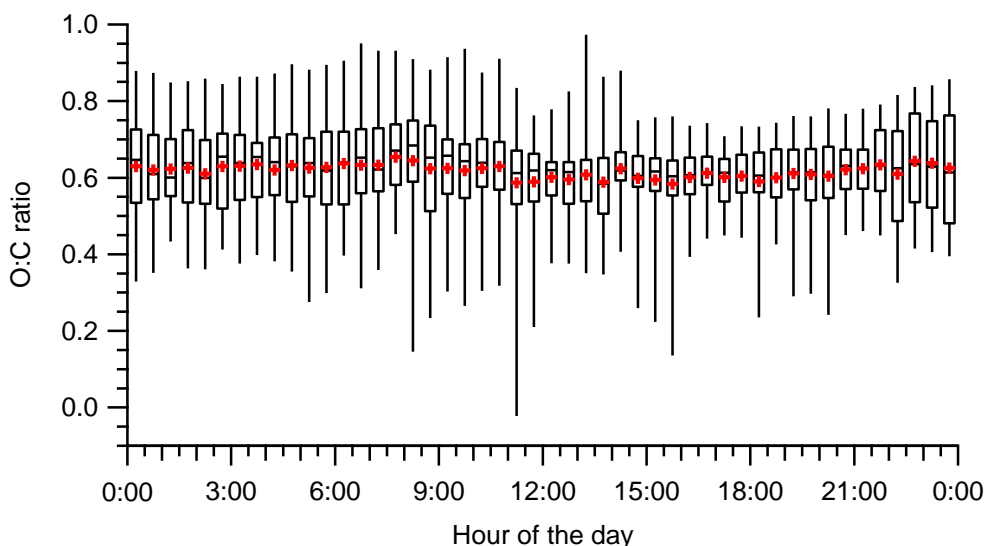
*Page 13 line 8: prior or previous rather than former.*

The “former” has been changed to “prior”. ([page 13 line 10](#))

*Page 13 Figure 2: The O:C ratio seems to vary quite a lot for a value that is an average. What do the percentiles look like (similar to a box and whiskers plot)? This would probably help since the range of change in O:C really isn’t that large (0.58 – 0.64).*

A box and whiskers plot of the diurnal variation of O:C ratio has been added to the supplementary pdf file as Fig. S19, and a relating explanation has been added to the caption of Fig. 2c.

Figure S19 and its caption are as follows:



**Figure S19:** Box and whiskers plot of the diurnal variation of the O:C ratios of bulk OA (only data with  $m_{\text{org}} > 0.3 \mu\text{g m}^{-3}$  are included) for the entire study period. The horizontal lines in the boxes indicate the median values, boundaries of the boxes indicate the 25<sup>th</sup>- and 75<sup>th</sup>-percentiles, and the whiskers indicate the highest and lowest values. The cross symbols in the boxes indicate the mean values.

The caption of Fig. 2c is now as follows: “... (c) LOOA, MOOA, and residual, and the O:C ratio of bulk OA (only data with  $m_{\text{org}} > 0.3 \mu\text{g m}^{-3}$  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.)” (page 13 lines 4–6)

*Page 14 Figure 3: Similar to the issue with figure 2, some of the data is very noisy at the 30 min bins. Specifically, the 30 nm has as much variability point to point as the range of other lines on the graph. Looking at the times series in the Supplementary information (Figure S12), this is because 30 nm also has the lowest data coverage and the 30 min bins do not afford high enough points per average. Either consider longer time bins or remove the 30 nm line from the panel.*

The diurnal variation of  $\kappa_t$  of 30 nm particles in Fig. 3a is now presented in 2-h time resolution. Further, a related explanation has been added to the end of the caption of Fig. 3: “Note that for particles with  $d_{\text{dry}}$  of 30 nm,  $\kappa_t$  is presented in 2-h time resolution because of the low data coverage (Fig. S12).” (page 15 lines 3–4)

*Page 22 Figure 6: It was not initially clear looking at this figure that the aged and*

*fresh lines were different based on different analyses of the data. It wasn't clear why they shouldn't have added up to the OA line. Consider adding to the caption to allow the figure to stand alone better.*

The caption of Fig. 6 has been modified to: “Diurnal variation of the fractional contribution of OA to the total CCN number concentration ( $F_{\text{CCN,OA}}$ ) estimated using time- and size-resolved  $\kappa_{\text{org}}$ , and diurnal variation of the fractional contribution of BSOA to the total CCN number concentration ( $F_{\text{CCN,BSOA}}$ ) estimated assuming fresh BSOA (using size-resolved  $\kappa_{\text{BSOA}}$ ) and aged BSOA (using size-resolved  $\kappa_{\text{ROA}}$ ).” (page 22 lines 2–4)

*Supplement Figure S14: If only the data in the 360 nm panel <0.4 is being used to fit the line, then the other point at 0.9 zooms the graph out and makes the fit look better than it really is (a line fit through a cloud of data points similar to the 300 nm panel). Also, with this graph, the negative  $\kappa_{\text{org}}$  values are non-real and must be the result of issues with the combination of the AMS data and the kappa values. Consider filters for removing these in quality control, or changing the limits on the range of volume fractions of organics required to calculate  $\kappa_{\text{org}}$  (as you mentioned on page 9 line 10).*

We have applied filters to the observed data (Text S4) and to the data used for the derivation of  $\kappa_{\text{org}}$  (page 15 lines 10–11) in the ACPD manuscript. Using stricter filters to rule out the large  $\kappa_{\text{org}}$  in the 360 nm panel in Fig. S14 and/or the negative  $\kappa_{\text{org}}$  values will result in loss of data that are likely real. For example, to omit all negative  $\kappa_{\text{org}}$  values in Fig. S14b, data points with  $\varepsilon_{\text{org}}$  smaller than 0.89 must be excluded. In addition, although the volume additivity assumption used for the derivation of  $\kappa_{\text{org}}$  in general holds well (page 9 lines 11–14), we should not rule out the possibility that the approximation of the additivity assumption of  $\kappa$  results in some negative  $\kappa_{\text{org}}$  as “apparent”  $\kappa$  values. Hence, no modification has been made to this point.

## Response to Anonymous Referee #3

*Anonymous Referee #3*

*Received and published: 6 December 2018*

*The authors presented a comprehensive study of the hygroscopic properties of organic aerosols at a forest site in Wakayama, Japan using a HTDMA and an AMS. The hygroscopicity parameter of fresh biogenic secondary organic aerosols was estimated and its relationship to CCN concentration was also evaluated. The dataset is rich with substantial amount of information, however, the discussion is over spread that the major conclusion becomes blurry. The manuscript is acceptable for publication in ACP after the following concerns are clearly addressed.*

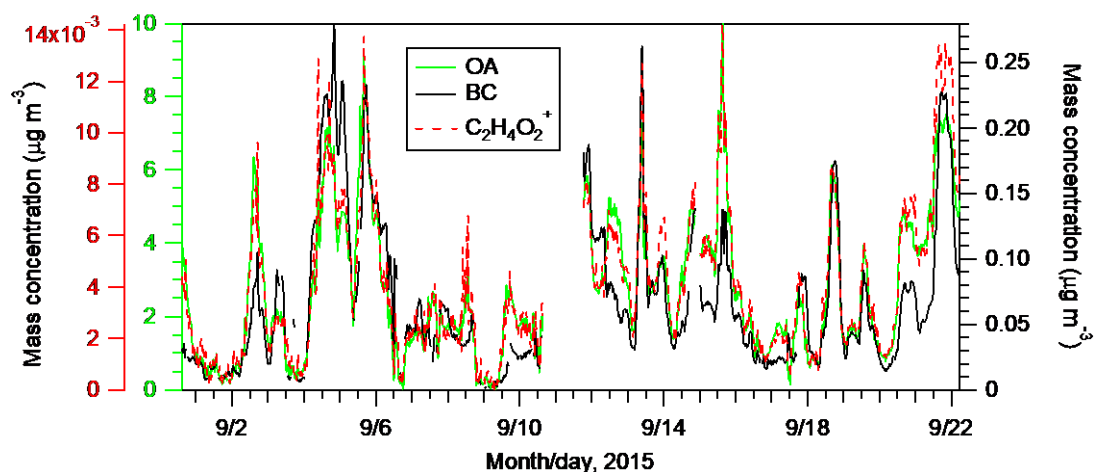
*Major comments: In general, the definition or quantification of BSOA and ROA should be clearly clarified and highlighted with proper references in your manuscript, as most of your discussion is based on this assumption. I suggest to make an individual section introducing it rather a few lines, for instance Page 19, line 9-15.*

BSOA is defined and quantified in Sect. 4.2.2, in association with the derivation of its hygroscopicity. ROA is also defined and quantified in the same section. Although it is also reasonable to make an individual section to define and quantify BSOA and ROA, we have left the original structure to emphasize the characteristics of the hygroscopicity of OA and BSOA and of their contributions to CCN concentrations. Thus, no modification has been made to this point.

*Similarly, in your TextS9, you said ‘The diurnal variation data on the mass concentration of BC was scaled to represent the diurnal variation of non-BSOA-OA’. How did you prove your method is valid, any references? As I see, there is big uncertainty within the estimation of BSOA-OA concentration from this method, which you used further to calculate their CCN contribution. Please carefully clarify. Also, I see you occasionally have BC peaks, correlated with high CO concentration. You might have biomass burning organic aerosols, how did you deal with those or did you filter their contribution or should we neglect their contribution? Please discuss.*

Although we have not found a reference for our method to assess non-BSOA-OA, we regard that the method is appropriate for the purpose of this study. Although a possible contribution of local biomass burning is in contradict to the assumption of the method, it must be small in the studied remote mountain area. The following Fig. R1 supports this idea. The mass fraction of fragment  $C_2H_4O_2^+$ , which is a tracer of biomass burning OA, was low (0.15%), as compared to that in a city site (0.62%) (Xu et al., 2015). Besides,  $C_2H_4O_2^+$  correlated with OA ( $R^2$ : 0.95) more strongly than with BC ( $R^2$ : 0.72). The possible contribution of local anthropogenic pollution to BC was ruled out by using the screening explained in Text S4. No modification has been made concerning this point.

Note that BSOA used for the estimation of the fractional contribution of BSOA to CCN number concentrations was quantified using size-resolved data (Sect. 4.2.2), whereas BSOA-OA in Text S9 was derived from bulk OA mass concentrations.



**Figure R1:** Time series of the mass concentrations of BC, OA, and fragment  $C_2H_4O_2^+$ .

*Your RH values are pretty high, which means supersaturation conditions might be possible reached in the real atmosphere. This indicates that your particles, especially large ones (larger than 300 nm) might already activate under supersaturation and then lose water again due to evaporation after RH decreases. This process will strongly affect your results, did you consider this into your discussion.*

Possible in-cloud processes suggested from high ambient RH conditions could have changed the properties of the observed aerosol, for example by the aging of the freshly formed BSOA (Han et al., 2014). It is now discussed briefly as follows:

“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).” (page 12 lines 15–19)

*The correlation between  $\kappa_{org}$  and  $vLOOA/(vLOOA+vMOOA)$  is not high, and you used this relation to derive  $\kappa_{LOOA}$  and  $\kappa_{MOOA}$ , which may introduce even higher uncertainties. I think your analysis should start from the closure between measured  $\kappa$  and ZSR-derived  $\kappa$ . You can replace  $\kappa_{org}$  with  $\kappa_{LOOA}$  and  $\kappa_{MOOA}$ , and ask your computer to find the best solution for  $\kappa_{LOOA}$  and  $\kappa_{MOOA}$  and to see if these values are different from those of your current analysis. In addition, I don't understand those error bars in your Fig. 5.*

The method recommended by the reviewer (referred to as ALT method) is in essence same as the one we used (referred to as ORIG method). Both of them are based on the volume additivity assumption (page 8 lines 13–15). With the ALT method, the derived  $\kappa_{LOOA}$  and  $\kappa_{MOOA}$  using data same as those in Fig. 5 are 0.090 and 0.23, which are 8.4% higher and 18% lower than the ones derived from the ORIG method. If these two values are applied for the derivation of  $\kappa_{BSOA}$  and  $\kappa_{ROA}$  (Table R1) and  $F_{CCN,BSOA}$  (Table R2), the resulting differences are: the  $\kappa_{BSOA}$  value for 100 nm particles (0.094) is 5.9% higher, whereas the changes for larger particles are negligible;  $\kappa_{ROA}$  are 11–13% lower; using size-averaged  $\kappa_{BSOA}$  overestimated  $F_{CCN,BSOA}$  by 8–13% if compared to those using size-resolved  $\kappa_{BSOA}$  (12–19% using the ORIG method (page 23 line 25));  $F_{CCN,BSOA}$  increased by 35–57% with the assumption of aged BSOA if compared to those under the condition of fresh BSOA (50–84% with ORIG method (page 24 line 4)). Because the main conclusion does not change, the derivation of  $\kappa_{LOOA}$  and  $\kappa_{MOOA}$  in the manuscript is not modified.

**Table R1: Size-resolved  $\kappa_{\text{BSOA}}$  and  $\kappa_{\text{ROA}}$  calculated from  $\kappa_{\text{LOOA}}$  and  $\kappa_{\text{MOOA}}$  derived using ALT method**

$d_{\text{dry}}$ (nm)	$\kappa_{\text{BSOA}}$	$\kappa_{\text{ROA}}$
100	0.094	0.16
200	0.11	0.16
300	0.12	0.16
360	0.12	0.17

**Table R2: Diurnal variation of the ratios of  $F_{\text{CCN,BSOA}}$  derived using size-resolved  $\kappa_{\text{BSOA}}$ , size-averaged  $\kappa_{\text{BSOA}}$ , and size-resolved aged  $\kappa_{\text{BSOA}}$  to that derived using size-resolved  $\kappa_{\text{BSOA}}$ <sup>1</sup>**

Hour of day	Ratios of $F_{\text{CCN,BSOA}}$ from different assumptions		
	Size-resolved	Size-averaged	Aged, Size-resolved
	$\kappa_{\text{BSOA}}$	$\kappa_{\text{BSOA}}$	$\kappa_{\text{BSOA}}$ <sup>2</sup>
0000–0200 JST	1	1.13	1.56
0200–0400 JST	1	1.12	1.57
0400–0600 JST <sup>3</sup>	1	0.922	1.31
0600–0800 JST <sup>3</sup>	1	1.92	2.76
0800–1000 JST	1	1.13	1.56
1000–1200 JST	1	1.10	1.48
1200–1400 JST	1	1.08	1.36
1400–1600 JST	1	1.08	1.35
1600–1800 JST	1	1.09	1.38
1800–2000 JST	1	1.10	1.43
2000–2200 JST	1	1.11	1.45
2200–0000 JST	1	1.12	1.56

<sup>1</sup>Both  $\kappa_{\text{BSOA}}$  and  $\kappa_{\text{ROA}}$  are from Table R1;

<sup>2</sup>The condition of size-resolved aged  $\kappa_{\text{BSOA}}$  assumes that the value of  $\kappa_{\text{BSOA}}$  equals that of  $\kappa_{\text{ROA}}$ ;

<sup>3</sup>The concentration of BSOA was low (refer to the caption of Fig. 7).

The error bars in Fig. 5 represent the standard deviation of size-resolved  $\kappa_{\text{org}}$  during 1200–2000 JST and 2000–1200 JST. This point was not clearly addressed in the original caption. It has been modified to: “... The size-resolved mean  $\kappa_{\text{org}}$  during 1200–2000 JST and 2000–1200 JST are indicated as filled circles and diamond markers, respectively. The standard deviations of the mean  $\kappa_{\text{org}}$  are indicated by the whiskers. The standard deviations of the mean  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  are presented in Table S6. The size-resolved  $\kappa$  values of BSOA and ROA are indicated by the three-pointed stars and triangles, respectively. The diameters of  $\kappa_{\text{org}}$ ,  $\kappa_{\text{BSOA}}$ , and  $\kappa_{\text{ROA}}$  are differentiated by colors. ...” (page 18 lines 12–15)



*I am not sure about your Section 4.4. You said ‘your particles larger than 70 nm are assumed to be CCN active’, which means you neglected the effect from the chemical composition. Then you started to consider the effect from chemical composition by dividing the spectrum with BSOA-contribution and contributions from other components, see Page 21, line 17-22. To me, this is a little bit in conflict with each other. Secondly, your Fig. S17 are actually based on external mixing state assumption. For your internal mixing aerosol population, particles are having quite similar chemical composition. I don’t see the point that how could BSOA contributes to CCN concentration alone. The logic behind it as I see is the involving of BSOA into organic aerosols will change the hygroscopicity parameter  $\kappa$ , then influence the critical diameter of particles that are able to activate, for instance, not 70 nm anymore, which thus change the potential CCN concentration. If this is true, then your method to derive the contribution of BSOA to CCN concentration is not sound or at least with huge uncertainties. Please carefully clarify. Mei et al., (2013b), who you cited in your introduction, gave a proper way to calculate the CCN concentration due to an elevated korg in their section 5.2.*

The evaluation of the contribution of BSOA to the CCN number concentration was from the viewpoint of its contribution to the aerosol total water uptake (page 21 lines 10–11). For the evaluation, the aerosols were assumed to be internally-mixed in respective diameter ranges (page 14 line 2 and page 21 lines 11–14). Therefore, they have same critical activation diameters under certain water vapor supersaturation condition. Fig. S17 should be understood from the viewpoint of the water uptake fraction. To better address this point, the first sentence in the caption of Fig. S17 has been changed to: “Estimate of the contributions of BSOA to the CCN number concentration from the viewpoint of its size-resolved contribution to the aerosol water uptake.”

The influence of the variation of CCN activation diameter on the prediction of  $F_{\text{CCN,OA}}$  and  $F_{\text{CCN,BSOA}}$  was not assessed in the original manuscript. It was now added as Text S12 (the original Text S12 is now Text S13) as follows:

### **“Text S12. Assessment of the diurnal variation of the CCN activation diameter**

Although the variation of the CCN activation diameter with time influences the prediction of  $F_{CCN,OA}$  and  $F_{CCN,BSOA}$ , the degree was found to be small. In the summertime observation in 2014 (Deng et al., 2018), the range of the diurnal variation of the CCN activation diameter was from 64 to 76 nm, whereas the CCN activation diameter assumed in this study is 70 nm. Applying 64 or 76 nm to an assumed CCN activation diameter results in the deviations of the predicted  $F_{CCN,OA}$  and  $F_{CCN,BSOA}$  only by  $-1.9$ – $2.3$  % and  $-3.1$ – $3.8$  %, respectively.”

A corresponding explanation was also added to the end of the first paragraph of Sect. 4.4: “The diurnal variation of the CCN activation diameter was not considered for the estimate of  $F_{CCN,OA}$  and  $F_{CCN,BSOA}$  (Text S12).”

It is reasonable to use the method in Mei et al. (2013b) to calculate the CCN concentration contributed by BSOA, which was adopted in our previous paper (Deng et al., 2018). However, in this manuscript we instead assessed the fractional contribution of OA and BSOA to the CCN number concentration from the viewpoint of their contributions to the aerosol water uptake over the effective measurement period on a diurnal basis.

#### **Other minor changes:**

- 1) Fig. 6 and the corresponding data in Table S9, and Fig. 7 and the corresponding data in Table S12 have been corrected because the  $\kappa_{ROA}$  at 100 nm was erroneously used as  $\kappa_{BSOA}$  for all the four diameters with the assumption of size-resolved aged BSOA. The size-resolved  $\kappa_{ROA}$  is now used instead.
- 2) The “0.41” in Text S12, which was a typo, has been corrected to “0.15”.
- 3) The reference “Deng et al., 2018” in the reference list has been updated because the status of the paper has been updated.

- 4) JSPS KAKENHI JP18K19852 is now acknowledged.
- 5) Current affiliation of one of the authors has been updated.
- 6) Some minor changes that have no influence on the points of the manuscript are also made.

All changes can be found in the track-change version of the manuscript.

### **References:**

Deng, Y. G., Kagami, S., Ogawa, S., Kawana, K., Nakayama, T., Kubodera, R., Adachi, K., Hussein, T., Miyazaki, Y., and Mochida, M.: Hygroscopicity of Organic Aerosols and Their Contributions to CCN Concentrations Over a Midlatitude Forest in Japan, *Journal of Geophysical Research-Atmospheres*, 123, 9703-9723, 10.1029/2017jd027292, 2018.

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Xu, W. Q., Sun, Y. L., Chen, C., Du, W., Han, T. T., Wang, Q. Q., Fu, P. Q., Wang, Z. F., Zhao, X. J., Zhou, L. B., Ji, D. S., Wang, P. C., and Worsnop, D. R.: Aerosol composition, oxidation properties, and sources in Beijing: results from the 2014 Asia-Pacific Economic Cooperation summit study, *Atmospheric Chemistry and Physics*, 15, 13681-13698, 10.5194/acp-15-13681-2015, 2015.

# 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<sup>1</sup>, Hikari Yai<sup>1</sup>, Hiroaki Fujinari<sup>1</sup>, Kaori Kawana<sup>2,3</sup>, Tomoki Nakayama<sup>4,5</sup>, and Michihiro Mochida<sup>1,4</sup>

<sup>1</sup>Graduate School of Environmental Studies, Nagoya University, Nagoya, Japan

<sup>2</sup>Institute of Low Temperature Science, Hokkaido University, Hokkaido, Japan

<sup>3</sup>Now at [Research and Development Center for Global Change, Japan Agency for Marine-Earth Science and Technology, Yokohama, Japan](#)

<sup>4</sup>Institute for Space-Earth Environmental Research, Nagoya University, Nagoya, Japan

<sup>5</sup>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 ( $\kappa_{\text{org}}$ ) 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  $\kappa_{\text{org}}$  for particles with dry diameters of 100 and 300 nm were on average 0.091 and 0.096, respectively, and the difference of  $\kappa_{\text{org}}$  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  $\kappa_{\text{org}}$ . 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  $\kappa_{\text{org}}$ , the use of time- and size-averaged  $\kappa_{\text{org}}$  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  $\kappa_{\text{org}}$  strongly affect the overall contribution of OA to CCN concentrations. The fractional contribution of fresh BSOA to CCN number

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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  $\kappa$  of OA ( $\kappa_{\text{org}}$ ; 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  $\kappa_{\text{org}}$  presented the lowest value of  $\sim 0.1$  in September and the highest value of  $\sim 0.15$  in December, and that the ranges of the diurnal variations of  $\kappa_{\text{org}}$  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  $\kappa_{\text{org}}$  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  $\kappa_{\text{org}}$  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  $\kappa_{\text{org}}$  ( $\sim 0.13$  to  $\sim 0.17$ , night to day) under SUPS was observed (Cerully et al., 2015). With respect to the size-dependence of  $\kappa_{\text{org}}$ , airborne studies over United States, Canada, Pacific Ocean, and the Gulf of Mexico for a variety of air mass types, presented a decrease of  $\kappa_{\text{org}}$  (from 0.13 to 0.06) with increase of the particle modal diameter (from 130 to  $\sim 210$  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  $\kappa_{\text{org}}$  in small particles (0.12–0.15; 60 and 100 nm) and high  $\kappa_{\text{org}}$  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  $\kappa_{\text{org}}$  between sub-100 nm particles ( $\kappa_{\text{org}}$  was 0.19) and ~150 nm particles ( $\kappa_{\text{org}}$  was 0.22), Thalman et al. (2017) did not identify any size-dependence of  $\kappa_{\text{org}}$  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  $\kappa$  of  $\alpha$ -pinene SOA at SUPS at 100 nm (~0.12) was ~0.06 higher than at 200 nm. Zhao et al. (2015) reported that the  $\kappa$  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)  $\alpha$ -pinene SOA particles had a higher  $\kappa$  than large ones (150 nm) at SUBS, although the difference was small (0.03). Frosch et al. (2013) reported that the  $\kappa$  of  $\beta$ -caryophyllene SOA decreased with  
10 increase of SS, which can be interpreted as the increase of  $\kappa$  with the increase of particle diameter, and that the maximum of the difference was about 0.1.

The variations in  $\kappa_{\text{org}}$  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  $\kappa$  of SOA by  $\pm 50$  % (from 0.14 to 0.07 or 0.21). Rastak et al. (2017) reported that the difference of the aerosol  
15 radiative effects between  $\kappa_{\text{org}}$  of 0.05 and 0.15 was  $-1.02 \text{ W m}^{-2}$ , 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  $\kappa_{\text{org}}$  of 0.12, the use of  $\kappa_{\text{org}}$  of 0.25 led to overestimation of the CCN number concentration by 50 %. Mei et al. (2013b) reported that the increase of  $\kappa_{\text{org}}$  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  $\kappa_{\text{org}}$  in more locations where OA dominates the aerosol chemical composition, to characterize the  $\kappa_{\text{org}}$  values and to represent the  $\kappa_{\text{org}}$  appropriately in model predictions of CCN number concentrations.

The temporal variation and size-dependence of  $\kappa_{\text{org}}$  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  $\kappa$  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  $\kappa_{\text{org}}$  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  $\kappa_{\text{org}}$  could be well explained by the daily variation in the contributions of the retrieved PMF factors to  $\kappa_{\text{org}}$ .

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  $\kappa_{\text{org}}$  in the forest atmosphere. However, the characteristics of the temporal variations and size-dependence of  $\kappa_{\text{org}}$ , 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  $\kappa_{\text{org}}$ . 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  $\kappa_{\text{org}}$  was time and size dependent and that the contribution of OA and BSOA to CCN number 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<sub>2.5</sub> 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<sup>-1</sup>. 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<sup>-1</sup>. 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<sup>-1</sup> 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 °C) and 85.0 ± 0.2 % (20.4 ± 0.5 °C), respectively, and that at the outlet of the sheath flow of DMA2 was 86.0 ± 0.3 % (20.3 ± 0.6 °C). 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<sup>-1</sup> 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<sup>-1</sup> 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<sub>4</sub>), ammonium (NH<sub>4</sub>), nitrate (NO<sub>3</sub>), 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

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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 (1 $\lambda$ -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; Deng et al., 2018). The mixing ratios of target gaseous species, NO-NO<sub>2</sub>-NO<sub>x</sub>, CO, CO<sub>2</sub>, and O<sub>3</sub>, were monitored using commercial instruments (APNA-370, Horiba for NO-NO<sub>2</sub>-NO<sub>x</sub>; model 48ij, Thermo Fisher Scientific for CO; LI-820, LI-COR for CO<sub>2</sub>; model 49ij, Thermo Fisher Scientific for O<sub>3</sub>). 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,  $g_t$ , was defined as the ratio of the particle wet diameter ( $d_{\text{wet}}$ , 85 % RH) to the corresponding dry diameter ( $d_{\text{dry}}$ ). The distributions of  $g_t$  for specific  $d_{\text{dry}}$  ( $n(g_t)$ , i.e., the number distribution of particles as a function of  $g_t$ ) 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  $n(g_t)$  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  $g_t$  probability distribution function,  $g_t$ -PDF, is the normalized  $n(g_t)$ . The  $g_t$ -PDF in this study is presented in linear scale, which was converted from the original logarithmic scale distribution. The time-resolved mean value of  $g_t$  for respective  $d_{\text{dry}}$ ,  $g_{t,m}$ , was calculated as follows.

$$g_{t,m} = \frac{\sum n(g_t)g_t}{\sum n(g_t)} \quad (0.8 \leq g_t \leq 2.2 \text{ for } 30 \leq d_{\text{dry}} \leq 300 \text{ nm, or } 0.8 \leq g_t \leq 2.0 \text{ for } d_{\text{dry}} = 360 \text{ nm}) \quad (1)$$

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 ( $\kappa_i$ ) was calculated following the  $\kappa$ -Köhler theory (Petters and Kreidenweis, 2007).

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

where  $\sigma$  is the surface tension at the solution/air interface,  $M_w$  and  $\rho_w$  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 (Vargafik et al., 1983) was used as  $\sigma$  in Eq. (3). Because  $\kappa_i$  was calculated from  $g_{f,mw}$ , the aerosol mixing state was not considered in the analysis of  $\kappa$  in this study.

### 3.2 Hygroscopicity of OA

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

$$\kappa_t = \varepsilon_{org} \kappa_{org} + \varepsilon_{inorgsalt} \kappa_{inorgsalt} + \varepsilon_{BC} \kappa_{BC} = \varepsilon_{org} \kappa_{org} + \sum_{i=1}^5 \varepsilon_i \kappa_i + \varepsilon_{BC} \kappa_{BC} \quad (4)$$

Here,  $\kappa_i$  is the hygroscopicity parameter of ambient aerosol at 85 % RH calculated using Eq. (3), while  $\kappa_{org}$ ,  $\kappa_{inorgsalt}$ , and  $\kappa_{BC}$  are the hygroscopicity parameters of OA, inorganic salts, and BC, respectively. The volume fractions of OA, inorganic salts, and BC are  $\varepsilon_{org}$ ,  $\varepsilon_{inorgsalt}$ , and  $\varepsilon_{BC}$ , respectively, and  $\varepsilon_i$  and  $\kappa_i$  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  $\varepsilon_{org}$ ,  $\varepsilon_i$ , and  $\varepsilon_{BC}$  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

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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  $\sim 1.0$  (0.98–0.99) to 2.0 times that of  $d_{dry}$ , corresponding to the particle density of  $\sim 1.0$  (0.98–0.99) to  $2.0 \text{ g cm}^{-3}$ , were adopted. More details about the calculations of the size-resolved  $\epsilon_{org}$ ,  $\epsilon_i$ , and  $\epsilon_{BC}$  are presented in Text S5. The derivation of  $\kappa_i$  was based on the online Extended AIM Aerosol Thermodynamics Model II (E-AIM II, [http://www.aim.env.uea.ac.uk/aim/kohler/input\\_kohler.html](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  $\kappa$  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  $\kappa_{org}$  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  $\kappa_{org}$ , the derived  $\kappa_{org}$  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 the chemical composition in the  $d_{va}$  range 69–138 nm (Fig. S4). The result indicates that  $\kappa_{org}$  was not sensitive to change in the selected  $d_{va}$  range when  $\epsilon_{org}$  was greater than 40 %. Note that, although the volume additivity assumption between organics and inorganics may not necessarily hold (Vaishya et al., 2013; the  $\kappa_{org}$  derived in the manner in this study represents the perturbation of  $\kappa_i$  as a result of the presence of organics), the inverse linear correlation between  $\kappa_i$  and  $\epsilon_{org}$  (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  $\kappa_{org}$ , 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 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  $\kappa_{org}$  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  $\kappa_{org}$  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).

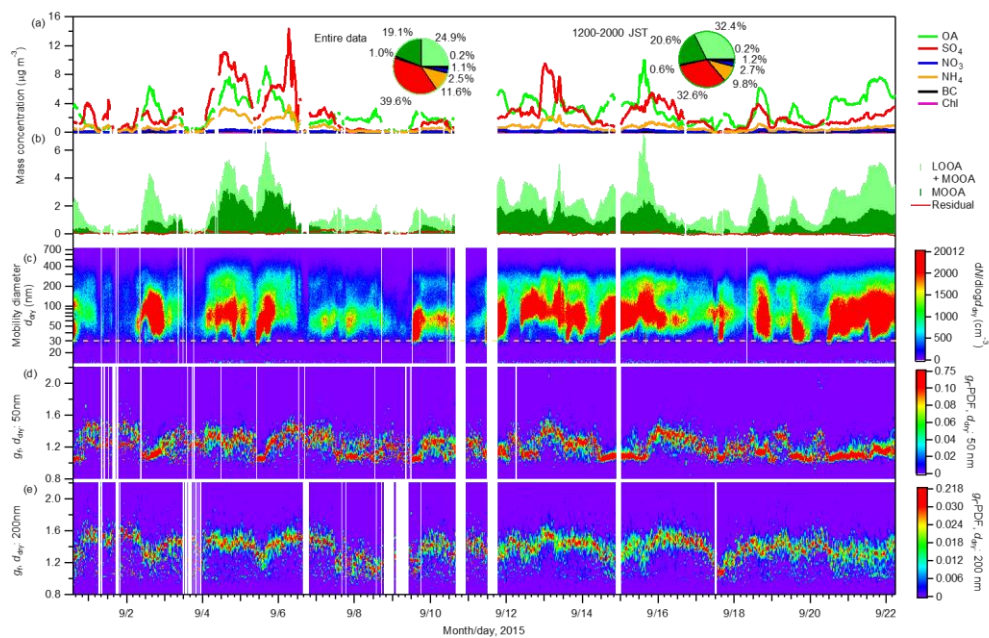


Figure 1: Time series of (a) sub-micrometer mass concentrations of non-refractory aerosol chemical components (OA, SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, and Chl) from the AMS measurement and BC from the PSAP measurement, (b) mass concentrations of LOOA and MOOA, and the residuals from the PMF analysis, (c) aerosol number-size distributions, and  $g_1$ -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  $\pm$  standard deviation (SD) of the temperature and RH of the ambient air were  $18.2 \pm 2.4$  °C and  $94.2 \pm 7.6$  %, 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  $\pm$  SD of the BC concentration during the entire study period was  $0.07 \pm 0.06$   $\mu\text{g m}^{-3}$  (Fig. S7). The mean  $\pm$  SD of the mixing ratios of CO, NO, NO<sub>2</sub>, NO<sub>x</sub>, and O<sub>3</sub> during the entire study period were  $164 \pm 42$ ,  $0.33 \pm 0.12$ ,  $0.56 \pm 0.35$ ,  $0.63 \pm 0.38$ , and  $11.5 \pm 8.4$  ppb, respectively (Fig. S7). The concentration of BC was low, and the mixing ratios of CO and NO<sub>x</sub> 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<sub>x</sub> 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<sub>3</sub> was substantial and presented obvious diurnal variation (Fig. S7). On average, O<sub>3</sub> 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:  $6.2 \pm 4.4$   $\mu\text{g m}^{-3}$ ), 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 ( $N_{\text{CN}}$ ) was  $1241 \pm 1012$   $\text{cm}^{-3}$ . The geometric mean diameter of the aerosols

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ranged from 45 to 154 nm with a mean  $\pm$  SD of  $88 \pm 17$  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 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 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 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 anthropogenic OA to the observed enhancement of OA was small.

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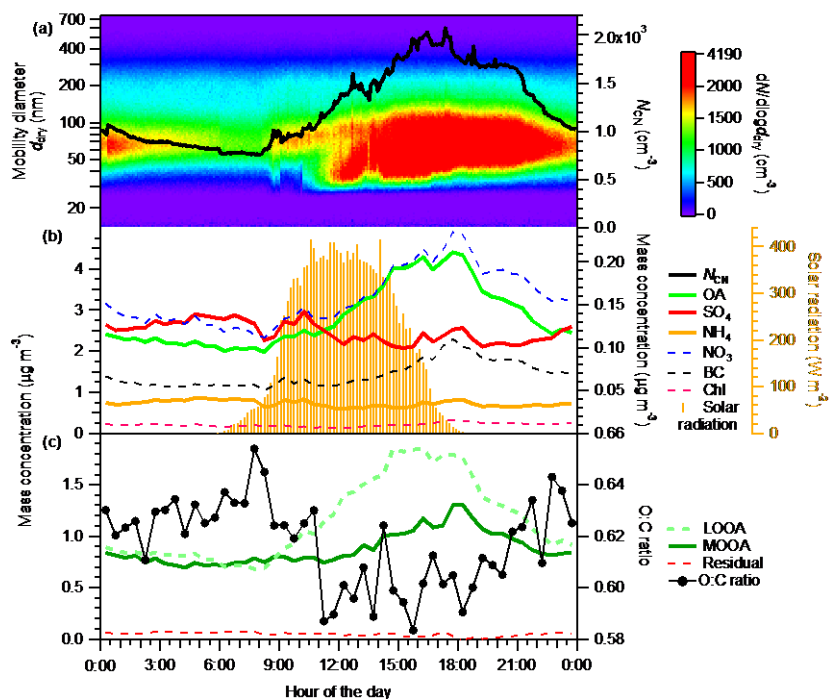


Figure 2: Diurnal variations of (a) number-size distribution (image plot) and number concentration ( $N_{CN}$ , right axis) of ambient aerosols, and the mass concentrations of (b) OA,  $SO_4$ , and  $NH_4$  (left axis), and  $NO_3$ , BC, and Chl (right axis in black), and (c) LOOA, MOOA, and residual, and the O:C ratio of bulk OA (only data with  $m_{org} > 0.3 \mu g m^{-3}$  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).

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#### 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  $\pm$  SD of  $g_{f,m}$  at 30, 50, 70, 100, 200, 300,

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and 360 nm were  $1.13 \pm 0.08$ ,  $1.21 \pm 0.09$ ,  $1.22 \pm 0.09$ ,  $1.26 \pm 0.10$ ,  $1.36 \pm 0.10$ ,  $1.40 \pm 0.08$ , and  $1.42 \pm 0.08$ , respectively.

The unimodal pattern of the  $g_r$ -PDF indicated the internal mixing state of the observed aerosol at the respective particle diameters. Decreases of  $g_{r,m}$  (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, 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  $g_{r,mw}$  ( $\kappa_i$ ) also increased with the increase of aerosol particle diameters (Fig. 3a). Similar diurnal variation patterns were observed for all the diameters studied. The  $\kappa_i$  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 diurnal variation pattern and size-dependence of  $\kappa_i$  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  $\kappa_i$ . Although  $\kappa_{inorgsalt}$  is much greater than  $\kappa_{org}$  (Petters and Kreidenweis, 2007), the high  $\varepsilon_{org}$  makes the influence of OA on  $\kappa_i$  significant. Thus, the variation of  $\kappa_{org}$  (Sect. 4.2) may also contribute to the variation of  $\kappa_i$ . For particles with  $d_{dry} \leq 70$  nm, decrease of the particle hygroscopicity with decrease of the particle diameter is also explained by the accompanying increase of  $\varepsilon_{org}$  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,  $\kappa_i$  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).

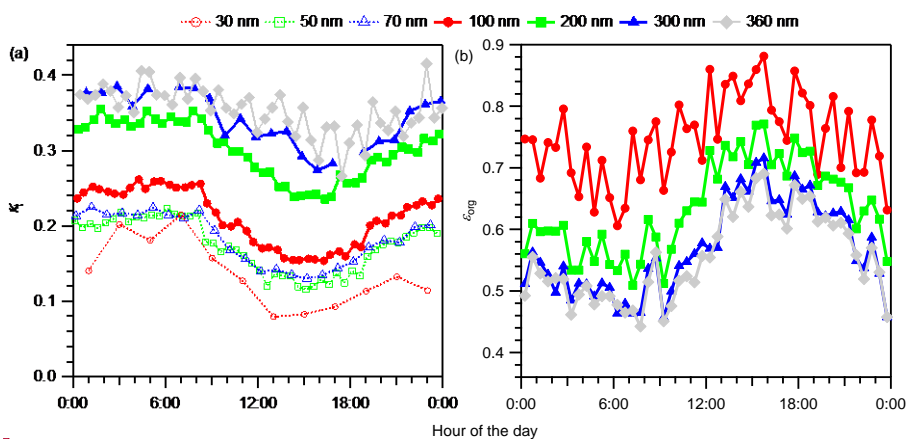


Figure 3: Diurnal variations of (a) size-resolved hygroscopicity of aerosols ( $\kappa$ ) and (b) size-resolved volume fractions of OA ( $\epsilon_{\text{org}}$ ) for the entire study period. Note that for particles with  $d_{\text{aer}}$  of 30 nm,  $\kappa$  is presented in 2-h time resolution because of the low data coverage (Fig. S12).

5

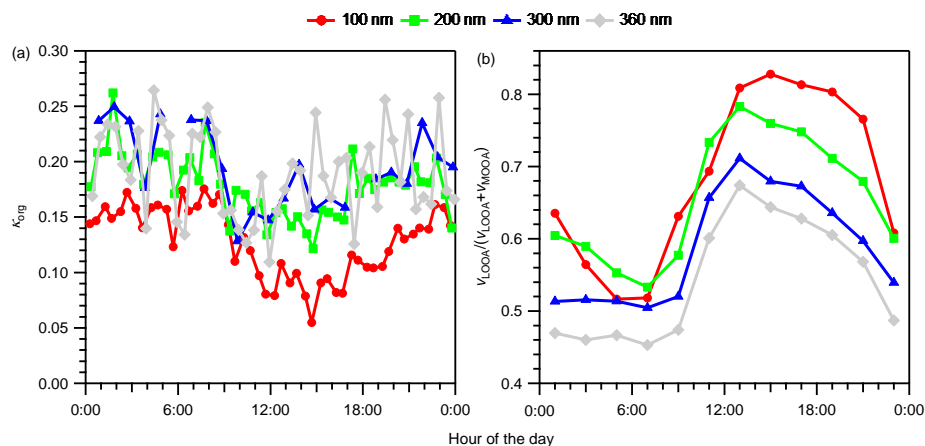
## 4.2 Hygroscopicity of organic aerosol components

### 4.2.1 Variation of $\kappa_{\text{org}}$ and its relation to the chemical structure of OA

The diurnal variation of  $\kappa_{\text{org}}$  and the volume fraction of LOOA in OA,  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$ , where  $v_{\text{LOOA}}$  and  $v_{\text{MOOA}}$  refer to the volume concentrations of LOOA and MOOA, respectively, for the entire study period are presented in Fig. 4. Data with  $\epsilon_{\text{org}} < 0.40$  were excluded from the  $\kappa_{\text{org}}$  values presented because the uncertainty that originated from subtraction of the contribution of inorganic components was considered large in the low  $\epsilon_{\text{org}}$  range (Mei et al., 2013a). The  $\kappa_{\text{org}}$  decreased rapidly from approximately 0800 JST in the morning when the mass concentrations of OA and LOOA started to increase (Fig. 2). The  $\kappa_{\text{org}}$  reached daily minima during 1000–1800 JST, and increased after the minima (Fig. 4a). The  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  in Fig. 4b presents the opposite diurnal variation pattern. The characteristics of the size-dependence of  $\kappa_{\text{org}}$  and  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  were dependent on time periods. To characterize the size-dependence of  $\kappa_{\text{org}}$  and  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$ , the mean values of  $\kappa_{\text{org}}$  and  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  during 1200–2000 JST and 2000–1200 JST were plotted separately in the  $\kappa_{\text{org}} - v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$

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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  $\kappa_{org}$  and  $v_{LOOA}/(v_{LOOA}+v_{MOOA})$ . Although the differences of  $\kappa_{org}$  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  $\kappa_{org}$  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  $\kappa_{org}$  and  $v_{LOOA}/(v_{LOOA}+v_{MOOA})$  were not clear. The clearer size-dependence of both  $\kappa_{org}$  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  $\kappa_{org}$  and  $v_{LOOA}/(v_{LOOA}+v_{MOOA})$  during 1200–2000 JST indicate that the variation of  $\kappa_{org}$  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  $\kappa_{org}$ , while the presence of MOOA with high oxygenation state (O:C ratio of 0.95) increased the observed  $\kappa_{org}$ . A similar relationship was observed in a former study at the observation site:  $\kappa_{org}$  was positively correlated with the O:C ratio of the organics (Deng et al., 2018).



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**Figure 4: Diurnal variations of (a) size-resolved hygroscopicity of OA ( $\kappa_{\text{org}}$ ) and (b) size-resolved volume fractions of LOOA in OA ( $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$ ) for the entire study period. For  $\kappa_{\text{org}}$  in panel (a), only data with  $\kappa_{\text{org}} > 0.40$  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  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$ .**

5 The hygroscopicity parameters of LOOA ( $\kappa_{\text{LOOA}}$ ) and MOOA ( $\kappa_{\text{MOOA}}$ ) were determined to evaluate the variations of  $\kappa_{\text{org}}$  that can be explained by the relative contributions of LOOA and MOOA to OA. For the determination of  $\kappa_{\text{LOOA}}$  and  $\kappa_{\text{MOOA}}$ ,  $\kappa_{\text{org}}$  was plotted against  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  and their correlation was analyzed based on linear regression analysis (Figs. 5 and S14). For particles with  $d_{\text{dry}}$  of 100, 200, 300, and 360 nm, the correlation coefficients between  $\kappa_{\text{org}}$  and  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  were  $-0.50$ ,  $-0.58$ ,  $-0.27$ , and  $-0.099$ , respectively. Relatively high correlations were observed for particles with  $d_{\text{dry}}$  of 100 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  $\kappa_{\text{org}}$  in those diameter ranges, than in those of 300 and 360 nm. The regression line for particles with  $d_{\text{dry}}$  of both 100 and 200 nm (Fig. 5) were used to derive  $\kappa_{\text{LOOA}}$  and  $\kappa_{\text{MOOA}}$  by applying  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  of zero and unity to the obtained regression equation, respectively. The derived  $\kappa_{\text{LOOA}}$  and  $\kappa_{\text{MOOA}}$  were 0.083 and 0.28, respectively. This result is in between the results if particles with  $d_{\text{dry}}$  of only 100 nm (derived  $\kappa_{\text{LOOA}}$  and  $\kappa_{\text{MOOA}}$  were 0.060 and 0.25, respectively) and only 200 nm (derived  $\kappa_{\text{LOOA}}$  and  $\kappa_{\text{MOOA}}$  were 0.095 and 0.34, respectively) were used. Compared with the  $\kappa$  of PMF factors reported by Jimenez et al. (2009), the derived  $\kappa_{\text{LOOA}}$  and  $\kappa_{\text{MOOA}}$  are within the ranges of  $\kappa$  for semi-volatile oxygenated OA (0.04–0.18) and low-volatility oxygenated OA (0.18–0.35), respectively (Fig. 5). The size-resolved  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  and the above derived  $\kappa_{\text{LOOA}}$  and  $\kappa_{\text{MOOA}}$  were used to reconstruct the diurnal variation data and mean values of size-resolved  $\kappa_{\text{org}}$  during 1200–2000 JST based on the volume additivity assumption. The reconstructed  $\kappa_{\text{org}}$  and the  $\kappa_{\text{org}}$  described above (measured  $\kappa_{\text{org}}$ ) 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  $\kappa_{\text{org}}$ . For 100 and 200 nm particles, the relative contribution of LOOA and MOOA to OA can explain the majority of the variations of  $\kappa_{\text{org}}$  (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  $\kappa_{\text{org}}$  of 300 and 360 nm particles are explained less by the relative contributions 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  $\kappa_{\text{org}}$  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  $\kappa_{org}$ . The slope and  $r^2$  of the regression line over the mean reconstructed and observed  $\kappa_{org}$  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  $\kappa_{org}$  is explained by the relative contribution of LOOA and MOOA

5 to OA by at least ~ 40 % during the time period.

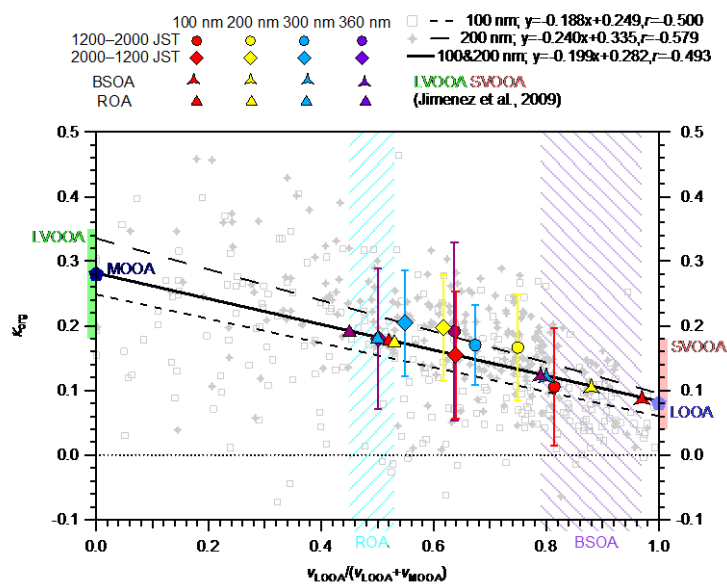


Figure 5:  $\kappa_{org}$  versus  $V_{LOOA}/(V_{LOOA}+V_{MOOA})$  for particles with  $d_{dry}$  of 100 nm (gray open squares) and 200 nm (gray cross markers) over the entire study period. The time resolution of individual data is 2 h. Only data with  $\kappa_{org} > 0.40$  are considered. The short-dashed, 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  $\kappa$  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  $\kappa_{org}$  during 1200–2000 JST and 2000–1200 JST are indicated as filled circles and diamond markers, respectively. The standard deviations of the mean  $\kappa_{org}$  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  $\kappa$  values of BSOA and ROA are indicated by the three-pointed stars and triangles, respectively. The diameters of  $\kappa_{org}$ ,  $\kappa_{BSOA}$ , and  $\kappa_{ROA}$  are differentiated by colors. The ranges of  $\kappa$  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.

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#### 4.2.2 Hygroscopicity of biogenic secondary organic aerosols

The hygroscopicity parameter of freshly formed BSOA ( $\kappa_{\text{BSOA}}$ ) was calculated as the volume weighted mean of  $\kappa_{\text{LOOA}}$  and  $\kappa_{\text{MOOA}}$ . 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  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  of ROA was estimated to be 0.52, 0.53, 0.50, and 0.45 for particles with  $d_{\text{dry}}$  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  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  of BSOA. The estimated  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  of the BSOA were 0.97, 0.88, 0.80, and 0.79 for particles with  $d_{\text{dry}}$  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  $\kappa_{\text{BSOA}}$  (and  $\kappa_{\text{ROA}}$ ) were calculated using the derived  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  of BSOA (ROA) for particles with different  $d_{\text{dry}}$  and  $\kappa_{\text{LOOA}}$  and  $\kappa_{\text{MOOA}}$ , and found to be 0.089 (0.18), 0.11 (0.18), 0.12 (0.18), and 0.12 (0.19) for particles with  $d_{\text{dry}}$  of 100, 200, 300, and 360 nm, respectively. The result indicates that  $\kappa_{\text{BSOA}}$  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  $\kappa_{\text{ROA}}$  (Fig. 5; colored triangles) was less obvious than that of  $\kappa_{\text{BSOA}}$ . The  $\kappa_{\text{BSOA}}$  derived at 85 % RH for particles with  $d_{\text{dry}}$  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  $94\pm 11$  nm) at the same site (Deng

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

#### 4.3 Ranges of the variations of $\kappa_i$ , $\kappa_{\text{org}}$ , and $\kappa_{\text{BSOA}}$

10 The ranges of the diurnal variations of  $\kappa_i$  and  $\kappa_{\text{org}}$ , the difference between their maxima and minima, were obtained from their diurnal variation data with 2 h resolution (Table S8). The variation ranges of  $\kappa_i$  were 0.14, 0.091, 0.084, 0.10, 0.11, 0.11, and 0.070 for particles with  $d_{\text{dry}}$  of 30, 50, 70, 100, 200, 300, and 360 nm, respectively. The variation ranges of  $\kappa_{\text{org}}$  for particles with  $d_{\text{dry}}$  of 100, 200, 300, and 360 nm were 0.091, 0.079, 0.096, and 0.11, respectively. The size-dependence of  $\kappa_i$  and  $\kappa_{\text{org}}$  were quantified by the mean  $\kappa_i$  and  $\kappa_{\text{org}}$  values for the entire study period (Table S8). The difference of  $\kappa_i$  between particles  
15 with  $d_{\text{dry}}$  of 100 and 300 nm was 0.13, and that of  $\kappa_{\text{org}}$  was 0.056.

The ranges of both the diurnal variations and the size-dependence of  $\kappa_i$  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  $d_{\text{dry}}$  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  $\kappa_{\text{org}}$  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  $\kappa_i$  and  $\kappa_{\text{org}}$  are discussed; other factors such as the absolute values of  $\kappa_i$  or  $\kappa_{\text{org}}$  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  $d_{\text{dry}}$  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  $\kappa_{BSOA}$  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  $\kappa_{BSOA}$  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  $g_t$  distributions and time- and size-resolved  $g_{t,m}$  (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  $\kappa_{org}$  ( $\kappa_{BSOA}$ ) divided by  $\kappa_t$  [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  $dN_{CN}/d\log d_{dry}$  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  $dN_{CN}/d\log d_{dry}$  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).



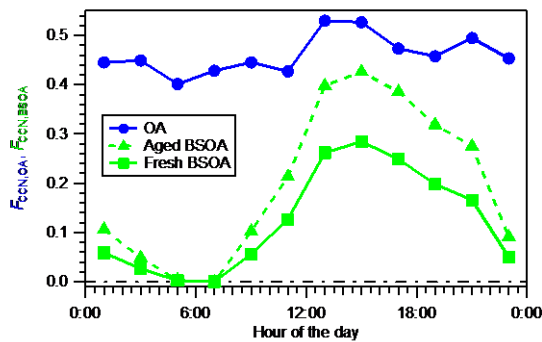
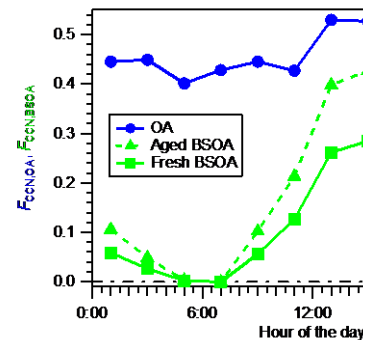
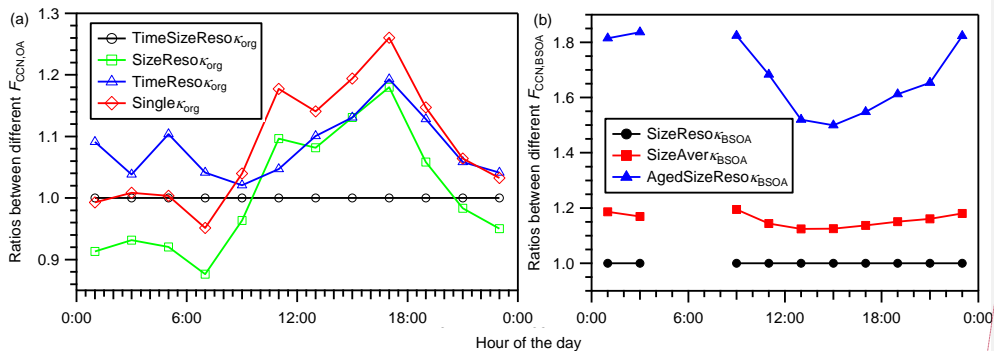


Figure 6: Diurnal variation of the fractional contribution of OA to the total CCN number concentration ( $F_{CCN,OA}$ ) estimated using time- and size-resolved  $\kappa_{org}$ , and diurnal variation of the fractional contribution of BSOA to the total CCN number concentration ( $F_{CCN,BSOA}$ ) estimated assuming fresh BSOA (using size-resolved  $\kappa_{BSOA}$ ) and aged BSOA (using size-resolved  $\kappa_{ROA}$ ).

The diurnal variation of  $F_{CCN,OA}$  estimated using time- and size-resolved  $\kappa_{org}$  and that of  $F_{CCN,BSOA}$  using size-resolved  $\kappa_{BSOA}$  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  $\epsilon_{BSOA}$  (Fig. S18), compared to that of  $\epsilon_{org}$  (Fig. 3). The  $F_{CCN,BSOA}$  of 0.28 during 1200–1600 JST indicates a significant contribution of BSOA to the CCN number concentration.



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Figure 7: (a) Diurnal variation of the ratios of the  $F_{CCN,OA}$  derived using time- and size-resolved  $\kappa_{org}$  (TimeSizeReso $\kappa_{org}$ ), time-averaged and size-resolved  $\kappa_{org}$  (SizeReso $\kappa_{org}$ ), size-averaged and time-resolved  $\kappa_{org}$  (TimeReso $\kappa_{org}$ ), and time- and size-averaged  $\kappa_{org}$  (Single $\kappa_{org}$ ) to that derived using the time- and size- resolved  $\kappa_{org}$  (TimeSizeReso $\kappa_{org}$ ). (b) Diurnal variation of the ratios of the  $F_{CCN,BSOA}$  derived using size-resolved  $\kappa_{BSOA}$  (SizeReso $\kappa_{BSOA}$ ), size-averaged  $\kappa_{BSOA}$  (SizeAver $\kappa_{BSOA}$ ), and aged size-resolved  $\kappa_{BSOA}$  (AgedSizeReso $\kappa_{BSOA}$ ) to that derived using the size-resolved  $\kappa_{BSOA}$  (SizeReso $\kappa_{BSOA}$ ). In panel (b), the condition of aged size-resolved  $\kappa_{BSOA}$  assumes that the value of  $\kappa_{BSOA}$  equals that of  $\kappa_{ROA}$ , and the data during 0400–0800 JST, when the concentration of BSOA was low (volume concentration less than  $0.01 \times 10^{-6} \text{ cm}^3 \text{ m}^{-3}$ ; Fig. S18), are not presented (data are presented in Table S12).

Because obvious diurnal variations and size-dependence of  $\kappa_{org}$  were found and because  $\kappa_{BSOA}$  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  $\kappa_{org}$  and  $\kappa_{BSOA}$  were assessed. To assess the influence of the variation of  $\kappa_{org}$  on  $F_{CCN,OA}$ , the diurnal variations of  $F_{CCN,OA}$  was estimated using (0a, base case) time- and size-resolved  $\kappa_{org}$ , (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)  $\kappa_{org}$ , (2a) time-resolved, size-averaged  $\kappa_{org}$ , and (3a) time- and size-averaged  $\kappa_{org}$  (Table S10). Cases (1a)–(3a) were compared with the base case (0a), as presented in Fig. 7a. Using time-averaged  $\kappa_{org}$  (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  $\kappa_{org}$  (case 2a), the  $F_{CCN,OA}$  was overestimated by 2–19% on a diurnal basis. Using time- and size-averaged  $\kappa_{org}$  (i.e., a single mean  $\kappa_{org}$ , 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  $\kappa_{org}$  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  $\kappa_{BSOA}$  on  $F_{CCN,BSOA}$ , the diurnal variations of  $F_{CCN,BSOA}$  was estimated using (0b, base case) size-resolved  $\kappa_{BSOA}$  and (1b) size-averaged  $\kappa_{BSOA}$  (Table S11). Case (1b) was compared with case (0b), as presented in Fig. 7b. Using size-averaged  $\kappa_{BSOA}$  caused overestimation of  $F_{CCN,BSOA}$  by 12–19%, which relates to the decrease of the estimated  $\kappa_{BSOA}$  and the increase of  $dN_{CN}/d\log d_{dry}$  (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  $\kappa_{BSOA}$  was as large as that of  $\kappa_{ROA}$  (Table S11)) on  $F_{CCN,BSOA}$  was also evaluated. Here, the

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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.

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## 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 ( $\kappa$ ) and of OA ( $\kappa_{org}$ ) 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  $\kappa_{org}$  of 100–360 nm particles were 0.079–0.11 and the  $\kappa_{org}$  of 300 nm particles was 0.056 larger than that of the 100 nm particles. The diurnal variations and size-dependence of  $\kappa$  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  $\kappa_{org}$ . The hygroscopicity of fresh BSOA ( $\kappa_{BSOA}$ ) 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  $\kappa_{\text{org}}$ , the use of time- and size-averaged  $\kappa_{\text{org}}$  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  $\kappa_{\text{org}}$  in the prediction of the contribution of OA to the CCN number concentration. The use of size-averaged  $\kappa_{\text{BSOA}}$  overestimated the contribution of fresh BSOA to the CCN number concentration by 12–19 % compared with the use of size-resolved  $\kappa_{\text{BSOA}}$ . 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  $\kappa_{\text{org}}$  at the observation site under the influence of the formation of BSOA. Also revealed was the importance of the variation of  $\kappa_{\text{org}}$  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  $\kappa_{\text{org}}$  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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**Text S1. Performance check of the DMAs**

Before and after the atmospheric observation, the accuracy of the sizing by three DMAs was assessed using standard size PSL particles (JSR SIZE STANDARD PARTICLES: SC-0055-D, SC-0100-D, and SC-032-S; Thermo Scientific™: 3500A). The mode diameters from fittings for the measurement data (Kawana et al., 2014) were compared with the manufacturer warranty (Table S1), which is interpreted as prescribed ranges of mean diameter  $\pm$  the expanded uncertainty ( $k = 2$ ). The mode diameters after the atmospheric observation agreed with those before the observation within 0.84 %. The results obtained before the atmospheric observation are as follows. For DMA1, whereas the measured mode diameter of SC-0100-D was within the prescribed range, the measured mode diameters of SC-0055-D and SC-032-S were 1.0 % larger than the upper end of the prescribed range and 0.76 % lower than the lower end of the prescribed range, respectively. For DMA2, the measured mode diameter of SC-0055-D was 1.5 % larger than the upper end of the prescribed range, and the measured mode diameters of SC-0100-D, SC-032-S, and 3500A were 0.85, 3.2, and 2.2 % lower than the lower end of the prescribed ranges, respectively. For DMA3, the measured mode diameter of SC-0055-D was 6.9 % larger than the upper end of the prescribed diameter range, and the measured mode diameters for all three of the other PSL standards were within the prescribed ranges.

**Text S2. Performance check of HTDMA using ammonium sulfate particles**

Before the atmospheric observation, 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 difference in the sizing between the two DMAs under dry condition and to validate the control of RH in the HTDMA. The diameter setting for the measurements was the same as that of ambient particles (Sect. 2). The mean growth factors ( $g_{f,m}$ ) of the AS particles under both dry and wet conditions were

retrieved using the same method as that for ambient particles (Sect. 3.1). The  $g_{f,m}$  of the dry AS aerosol particles with diameters of 30–360 nm were 1.2–4.1 % deviated from unity (Table S2). The deviations were used to correct the difference of sizing between DMA1 and DMA2 for the  $g_f$  of AS and ambient aerosol particles measured at 85 % RH. The respective  $g_{f,m}$  of AS particles at 85 % RH with  $d_{dry}$  of 30, 50, 70, 100, 200, 300, and 360 nm were 1.52, 1.54, 1.54, 1.54, 1.55, 1.57, and 1.59, which agree within 2.0 % with the calculated values ( $g_{f,AS}$ ; Table S2) based on the Extended AIM Aerosol Thermodynamics Model II (E-AIM II, <http://www.aim.env.uea.ac.uk/aim/model2/model2a.php>; Clegg et al., 1998; Wexler and Clegg, 2002). The derivation of the hygroscopic growth factor of AS particles using the E-AIM II model is presented in Text S6.

### **Text S3. PMF analysis of organic mass spectra**

The bulk mass spectra of organics observed in V-mode were subjected to PMF analysis (PMF Evaluation Tool v3.04A). For the analysis, high resolution fragment ions with signal to noise ratio (SNR) smaller than 0.2 were omitted, fragments with SNR in the range of 0.2–2 were down-weighted by a factor of three, and fragments related to CO<sub>2</sub> (i.e., CO<sub>2</sub>, CO, H<sub>2</sub>O, HO, and O) were down-weighted so that fragment CO<sub>2</sub> only contributed once. The obtained two-factor solution, with a more-oxygenated OA component (MOOA) and a less-oxygenated OA component (LOOA), with seed = 1 and fpeak = 0, was adopted for the explanation of OA composition. The two-factor PMF results are summarized in Fig. S1.

### **Text S4. Data screening methods**

All the data except for the meteorological data obtained during the atmospheric observation were subjected to the screening to exclude data under possible influence from intermittent local anthropogenic emissions. For the SMPS data with 5 min resolution, and the BC and gaseous species data with 30 min resolution, if

the data value at one point was more than 30 % deviated from both the former data point and the next data point in the time series, the data at that time point was deleted. The chemical composition data derived from AMS measurements with 30 min resolution were deleted whenever the BC data were deleted. The hygroscopic growth data derived from the HTDMA measurements were deleted whenever the SMPS data were deleted. Furthermore, if the total count of particles measured using the CPC in the HTDMA in the diameter range of 0.80–2.2 times of  $d_{dry}$  (or 0.80–2.0 times of  $d_{dry}$  for particles with  $d_{dry}$  of 360 nm) during a single scan was less than eight, the HTDMA data was not used, either. Here, the  $d_{dry}$  were corrected for the difference of sizing between DMA1 and DMA2.

#### **Text S5. Derivation of size-resolved volume fractions of the chemical components**

The size-resolved volume fractions of inorganic salts ( $\epsilon_i$ ), organics ( $\epsilon_{org}$ ), and BC ( $\epsilon_{BC}$ ) were calculated as follows. First, BC was assumed to be internally mixed with non-refractory aerosol components and to have the same mass-size distribution as OA. The aerosol particles were assumed to be spherical and without voids. Using the PToF mode data from the AMS, the mass concentrations of aerosol components in the vacuum aerodynamic diameter ( $d_{va}$ ) ranges that are ~1.0 (0.98–0.99) to 2.0 times of  $d_{dry}$  were obtained: the ranges of  $d_{va}$  for particles with  $d_{dry}$  of 100, 200, 300, and 360 nm were 98–197, 197–395, 295–589, and 353–707 nm, respectively. Second, the mole amounts of sulfate, nitrate, and ammonium in 1 m<sup>3</sup> of air were derived. Third, the amount of ammonium nitrate (AN), ammonium sulfate (AS), letovicite (LET), ammonium hydrogen sulfate (AHS), and sulfuric acid (SA) per mole in 1 m<sup>3</sup> of air was determined, assuming that nitrate was fully neutralized with ammonium, and that sulfate could present in the form of AS, LET, AHS, and/or SA according to the amount of remaining ammonium. The detected non-refractory chloride was not considered because of its low concentration compared with the concentrations of the other non-refractory components. The contribution of sea salt and minerals to the sub-micrometer aerosol

particles was likely small (Han et al., 2014; Deng et al., 2018) and was also not considered. Fourth, the volumes of BC, OA, and LET were derived using their respective densities and the volumes of AN, AS, AHS, and SA were derived using their respective molar volumes. The density of BC was assumed to be  $1.77 \text{ g cm}^{-3}$  (Park et al., 2004). The density of organics ( $\rho_{\text{org}}$ ) was estimated to be  $1.32 \pm 0.09 \text{ g cm}^{-3}$  using the O:C and H:C ratios of organics derived from AMS measurements (Kuwata et al., 2012), and the mean value of  $1.32 \text{ g cm}^{-3}$  was adopted for this study. The density of LET was assumed to be  $1.83 \text{ g cm}^{-3}$  (Padró et al., 2010). The molar volumes of AN, AS, AHS, and pure liquid SA, which are the same as the ones used in the E-AIM II model, were adopted in this study. Finally, the volume fractions of each species were obtained.

#### **Text S6. Derivation of $g_{\text{t,AS}}$ and $\kappa$ using the E-AIM II model**

The hygroscopic growth factor of pure ammonium sulfate particles ( $g_{\text{t,AS}}$ ) and the hygroscopicity parameter of each inorganic salt ( $\kappa$ ) at 85 % RH were derived based on the output of the E-AIM II model and the  $\kappa$ -Köhler equation (Petters and Kreidenweis, 2007) as follows.

The water activity ( $a_w$ ) range from 0.8000 to 0.8499 at a resolution of 0.0001 was applied to the E-AIM II model for unit mole of each inorganic salt at the temperature of 294 K. For the calculation, the partition of  $\text{HNO}_3$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{SO}_4$  into the vapor phase was prevented and the formation of solid AS was also prevented. The hygroscopic growth factor ( $g_t$ ) corresponding to each  $a_w$  was derived from the ratio of total wet volume ( $V_{\text{wet}}$ ) to the dry molar volume of the pure salt. The  $\kappa_1$  corresponding to each  $a_w$  was derived from Equation 2 of Petters and Kreidenweis (2007). The exponential part of the  $\kappa$ -Köhler equation was derived on the assumption that the partial molar volume of water equals the molar volume of pure water. Here,  $a_w$  was calculated based on the relationship that the RH above the particle surface equals the product of the  $a_w$  and the exponential part of the  $\kappa$ -Köhler equation representing the Kelvin effect. For particles

with respective  $d_{\text{dry}}$ , an  $a_w$  value at which the RH above the particle surface was nearest to 85 % ( $a_{w,85}$ ) was obtained by applying a wet diameter represented by the product of  $d_{\text{dry}}$  and  $g_f$ . The hygroscopicity parameter value at  $a_{w,85}$  was defined as  $\kappa_1$  (Table S3). For AS, the  $g_f$  at  $a_{w,85}$  was defined as  $g_{f,AS}$  (Table S2). For the derivation of  $\kappa_1$ , the surface tension of the solution was applied, whereas for the derivation of  $\kappa_f$  (Sect. 3.1) the surface tension of pure water was applied. The uncertainty of the surface tension should not introduce large uncertainty in the derived  $\kappa_{\text{org}}$  because the difference of  $\kappa_1$  obtained using the surface tension of pure water and that obtained using the surface tension of the solution was small (within 0.38 %, Table S3).

#### **Text S7. Determination of the range of $d_{va}$ for the calculation of $\kappa_{\text{org}}$**

The PToF mode AMS data over a lower  $d_{va}$  range was subjected to low signal intensity (Fig. S2) when it was adopted for the derivation of size-resolved  $\kappa_{\text{org}}$ . To determine the applicable range of  $d_{va}$  for this study, the mean mass-size distribution data of OA during the entire study period was compared to that of a baseline region (Fig. S3). The baseline region here is the transition region between the regions dominated by gaseous species and particle signals of OA, and corresponds to the PToF time region of 0.00135458–0.00150458 s. To eliminate data under the strong influence of the signals from gaseous species, the  $d_{va}$  of 98 nm (where the mass ratio of the mean observed OA to mean baseline OA became greater than three) was adopted as the lower limit of the  $d_{va}$  range for the derivation of  $\kappa_{\text{org}}$ . In Fig. S3, the mean mass-size distribution of OA for filtered air (collected by connecting a HEPA filter (TSI) to the inlet tubing outside the instrument room) is also presented for comparison. Only in the  $d_{va}$  range of 90–716 nm, the mean values of the observed OA mass in each  $d_{va}$  bin were greater than that of OA for the filtered air. This also indicates the strong influence of the signals from gaseous species at  $d_{va}$  smaller than ~90 nm. Because the OA data of filtered air was noisy, it was not used for the determination of the applicable  $d_{va}$  range.

### **Text S8. Derivation of size-resolved PMF factors**

To explain the diurnal variation and size-dependence of  $\kappa_{\text{org}}$  from the compositional characteristics of OA, size-resolved PMF factors (LOOA and MOOA) were derived through multivariable linear regression analysis as follows.

First, the fragment profiles of LOOA and MOOA from bulk OA mass spectra were converted to the profiles in unit  $m/z$  resolution by summing up the intensity of the fragment ion signals at the same unit  $m/z$ . Then, for each time period in 2 h time resolution and for each PToF size bin  $i$ , the contributions from LOOA ( $a_i$ ) and MOOA ( $b_i$ ) were derived using the Solver function in Microsoft Excel by minimizing the value of the following formula:

$$\sum_{j=12}^{115} [x_{ij} - (a_i f_{1j} + b_i f_{2j})]^2$$

Where  $x_{ij}$  is the measured signal intensity in size bin  $i$  at  $m/z = j$ , and  $f_{1j}$  and  $f_{2j}$  are the respective normalized signal intensity of LOOA and MOOA at  $m/z = j$ . The unit of  $x_{ij}$ ,  $a_i$ , and  $b_i$  was  $\mu\text{g m}^{-3}$ , whereas  $f_{1j}$  and  $f_{2j}$  were dimensionless.

The size-resolved LOOA and MOOA were derived for the  $d_{\text{va}}$  range from  $\leq 10$  nm to around 900 nm (Fig. S6). However, only the  $d_{\text{va}}$  range above 98 nm was adopted for the analysis. This is because the uncertainty of the contributions from LOOA and MOOA in the lower  $d_{\text{va}}$  range was presumably relatively large, given the low organic signal intensity (Fig. S3) and high residual to measured OA mass ratio (Fig. S6).

### **Text S9. Assessment of the contributions of BSOA and anthropogenic OA to the enhancement of OA in the daytime**

The contributions of BSOA and anthropogenic OA to the enhancement of OA in the daytime (in relation to the background period) were assessed using BC as a tracer of OA that did not come from BSOA

formation (non-BSOA-OA). Here, the non-BSOA-OA was considered the sum of regional OA and other anthropogenic OA. The diurnal variation data on the mass concentration of BC was scaled to represent the diurnal variation of non-BSOA-OA. For the scaling, the observed OA during the background period (i.e., 0600–0800 JST, when the daily minima of  $m_{\text{org}}$  appeared) was assumed to be composed only of non-BSOA-OA. The scaling factor was calculated to be 36.5. The mass concentrations of non-BSOA-OA ( $m_{\text{non-BSOA,bulk}}$ ) and BSOA ( $m_{\text{BSOA,bulk}}$ ) were then estimated using the following equations.

$$m_{\text{non-BSOA,bulk}} = m_{\text{BC}} \times 36.5 \quad (\text{S1})$$

$$m_{\text{BSOA,bulk}} = m_{\text{org}} - m_{\text{non-BSOA,bulk}} \quad (\text{S2})$$

Note that  $m_{\text{BSOA,bulk}}$  and  $m_{\text{non-BSOA,bulk}}$  are different from the mass concentrations of the BSOA and ROA defined from the size-resolved LOOA/MOOA data (Sect. 4.2.2 and Text S10). The  $m_{\text{BSOA,bulk}}$  may be negatively biased because the charring of OA during the PSAP measurement may have resulted in a positive bias of  $m_{\text{BC}}$ . The increase of the OA mass concentration in the daytime ( $m_{\text{org,ENH}}$ ) was estimated by subtracting the  $m_{\text{org}}$  during the background period from that during the period of interest. The ratio of  $m_{\text{BSOA,bulk}}$  to  $m_{\text{org,ENH}}$  was in the range 0.6–0.9 during 1200–1600 JST, and it was in the range 0.1–0.5 during 1600–2030 JST (Fig. S10). The result indicates that BSOA was the main contributor to the enhancement of OA at least during 1200–1600 JST. In a later period, a larger contribution from anthropogenic OA is not ruled out.

#### **Text S10. Derivation of $v_{\text{BSOA}}$ and $v_{\text{ROA}}$ from $v_{\text{LOOA}}$ and $v_{\text{MOOA}}$**

Because the observed OA can be assumed to be contributed either by LOOA and MOOA, or by BSOA and ROA, the sum of LOOA and MOOA should equal the sum of BSOA and ROA. The size-resolved  $v_{\text{BSOA}}$  and  $v_{\text{ROA}}$  can be derived from the size-resolved  $v_{\text{LOOA}}$  and  $v_{\text{MOOA}}$ . From the analysis in Sect. 4.2.2, 0.97 (0.52), 0.88 (0.53), 0.80 (0.50), and 0.79 (0.45) of the volume of BSOA (ROA) for particles with  $d_{\text{dry}}$

of 100, 200, 300, and 360 nm were assigned to LOOA, and the balances were assigned to MOOA. The relations are expressed by the equations:

$$v_{\text{BSOA}} + v_{\text{ROA}} = v_{\text{LOOA}} + v_{\text{MOOA}} \quad (\text{S3})$$

$$a \times v_{\text{BSOA}} + b \times v_{\text{ROA}} = v_{\text{LOOA}} \quad (\text{S4})$$

Where  $v_{\text{BSOA}}$ ,  $v_{\text{ROA}}$ ,  $v_{\text{LOOA}}$ , and  $v_{\text{MOOA}}$  are the size-resolved volume concentrations of BSOA, ROA, LOOA, and MOOA, respectively, and  $a$  and  $b$  represent the size-resolved volume fractions of BSOA and ROA, respectively, that were assigned to LOOA. The volume concentrations of BSOA and ROA were estimated using the equations:

$$v_{\text{BSOA}} = [(1 - b) / (a - b)] \times v_{\text{LOOA}} - [b / (a - b)] \times v_{\text{MOOA}} \quad (\text{S5})$$

$$v_{\text{ROA}} = [(a - 1) / (a - b)] \times v_{\text{MOOA}} + [a / (a - b)] \times v_{\text{LOOA}} \quad (\text{S6})$$

Equations (S5) and (S6) were used to estimate the contributions of BSOA to aerosol water uptake and to the CCN number concentration (Sect. 4.4 and Text S11).

#### **Text S11. Estimation of the contributions of OA and BSOA to CCN concentrations**

The contributions of OA and BSOA to the CCN number concentration were estimated from their size-resolved fractional contributions to aerosol water uptake and from the measured aerosol number-size distributions. The analysis was performed for diurnal variation data with 2 h resolution. A schematic of the estimate is presented in Fig. S17. For the estimate, the observed aerosol particles were assumed to be internally mixed, and all the particles with  $d_{\text{dry}}$  larger than 70 nm were assumed to be CCN active. The contributions of OA (BSOA) to the water uptake of particles with  $d_{\text{dry}}$  of 100, 200, 300, and 360 nm were applied for the diameter ranges of 70–150, 150–250, 250–330, 330–430 nm, respectively. For the diameter ranges larger than 430 nm, the CCN number concentration contributed by OA (BSOA) was not considered because of the low aerosol number concentrations. In each diameter range, the fractional contribution of



OA (BSOA) to  $dN_{CN}/d\log d_{dry}$  equals the fractional contribution of OA (BSOA) to the total aerosol water uptake, which was represented as the product of the volume fraction of OA (BSOA) and  $\kappa_{org}$  ( $\kappa_{BSOA}$ ) divided by  $\kappa_i$  [i.e.,  $\varepsilon_{org}\kappa_{org}/\kappa_i$  ( $\varepsilon_{BSOA}\kappa_{BSOA}/\kappa_i$ )]. The total fractional contribution of OA (BSOA) to the total CCN number concentration,  $F_{CCN,OA}$  ( $F_{CCN,BSOA}$ ), equals the integration of the product of the water uptake fraction and  $dN_{CN}/d\log d_{dry}$  above the assumed CCN activation diameter (70 nm), divided by the total CCN number concentration.

For the above analysis, the water uptake of each aerosol component was represented by the product of the volume fraction of the aerosol component ( $\varepsilon_i$ ) and its hygroscopicity ( $\kappa_i$ ), that is,  $\varepsilon_i\kappa_i$ . The mean  $\varepsilon_i$  in each 2 h time section of the day was derived as follows. First, the mean values of the volume concentrations of each inorganic species, organics, and organic fractions (AN, AS, LET, AHS, SA, BC, OA, LOOA, and MOOA;  $\bar{v}_i$ ) were calculated from the 2 h resolution data. Second, the mean volume concentrations of LOOA ( $\bar{v}_{LOOA}$ ) and MOOA ( $\bar{v}_{MOOA}$ ) were scaled so that their sum equals the mean volume concentration of OA ( $\bar{v}_{OA}$ ). Third, the mean volume concentrations of BSOA ( $\bar{v}_{BSOA}$ ) and ROA ( $\bar{v}_{ROA}$ ) were estimated using Eqs. (S5) and (S6). Then,  $\varepsilon_i$  was calculated directly from those  $\bar{v}_i$ . The  $\kappa$  of the inorganic salts under the condition of 0.42 % SS, and at the temperature of the HTDMA measurement in this study, were used to consider the difference of  $\kappa$  between sub- and super-saturated water vapor conditions. Here, the  $\kappa$  for AN, AS, LET, AHS, and SA were calculated to be 0.73, 0.60, 0.63, 0.62, and 0.65, respectively, following the method in Deng et al. (2018). The difference of the  $\kappa$  of organics under sub- and super-saturated conditions was not considered. The  $\kappa$  values of OA and BSOA used for the calculation are presented in Tables S10 and S11, respectively. The contributions of OA and BSOA to the water uptake were calculated as  $\varepsilon_{org}\kappa_{org}/\kappa_{i, \text{reconst,org}}$  and  $\varepsilon_{BSOA}\kappa_{BSOA}/\kappa_{i, \text{reconst,BSOA}}$ , respectively, where,

$$\kappa_{i, \text{reconst,org}} = \varepsilon_{AN}\kappa_{AN} + \varepsilon_{AS}\kappa_{AS} + \varepsilon_{LET}\kappa_{LET} + \varepsilon_{AHS}\kappa_{AHS} + \varepsilon_{SA}\kappa_{SA} + \varepsilon_{org}\kappa_{org} \quad (S7)$$

$$\kappa_{i, \text{reconst,BSOA}} = \varepsilon_{AN}\kappa_{AN} + \varepsilon_{AS}\kappa_{AS} + \varepsilon_{LET}\kappa_{LET} + \varepsilon_{AHS}\kappa_{AHS} + \varepsilon_{SA}\kappa_{SA} + \varepsilon_{BSOA}\kappa_{BSOA} + \varepsilon_{ROA}\kappa_{ROA}$$

(S8)

**Text S12. Assessment of the diurnal variation of the CCN activation diameter,**

Although the variation of the CCN activation diameter with time influences the prediction of  $F_{CCN,OA}$  and  $F_{CCN,BSOA}$ , the degree was found to be small. In the summertime observation in 2014 (Deng et al., 2018), the range of the diurnal variation of the CCN activation diameter was from 64 to 76 nm, whereas the CCN activation diameter assumed in this study is 70 nm. Applying 64 or 76 nm to an assumed CCN activation diameter results in the deviations of the predicted  $F_{CCN,OA}$  and  $F_{CCN,BSOA}$  only by -1.9-2.3 % and -3.1-3.8 %, respectively.

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**Text S13. Assessment of the change of CCN activation diameter accompanying the aging of BSOA**

The aging of BSOA may change the CCN activation diameter and influence the prediction of  $F_{CCN,BSOA}$ . However, the change and the influence are considered to be small as explained below. If the range of  $\kappa$  of 0.17 to 0.35 (i.e., the  $\kappa$  range of (mean - SD) to (mean + SD) under 0.42 % SS condition in Deng et al. (2018)), and the approximate maximum  $\kappa_{BSOA}$  of 0.6 (Fig. S18) are applied, the increase of  $\kappa_{BSOA}$  by 0.09 (i.e., the difference between  $\kappa_{BSOA}$  and  $\kappa_{ROA}$  for particles with  $d_{dry}$  of 100 nm) leads to a decrease in the CCN activation diameter by 3-7 nm. The resulting decrease leads to increase of the predicted  $F_{CCN,BSOA}$  by 0.15-3.8 %, which is regarded as small.

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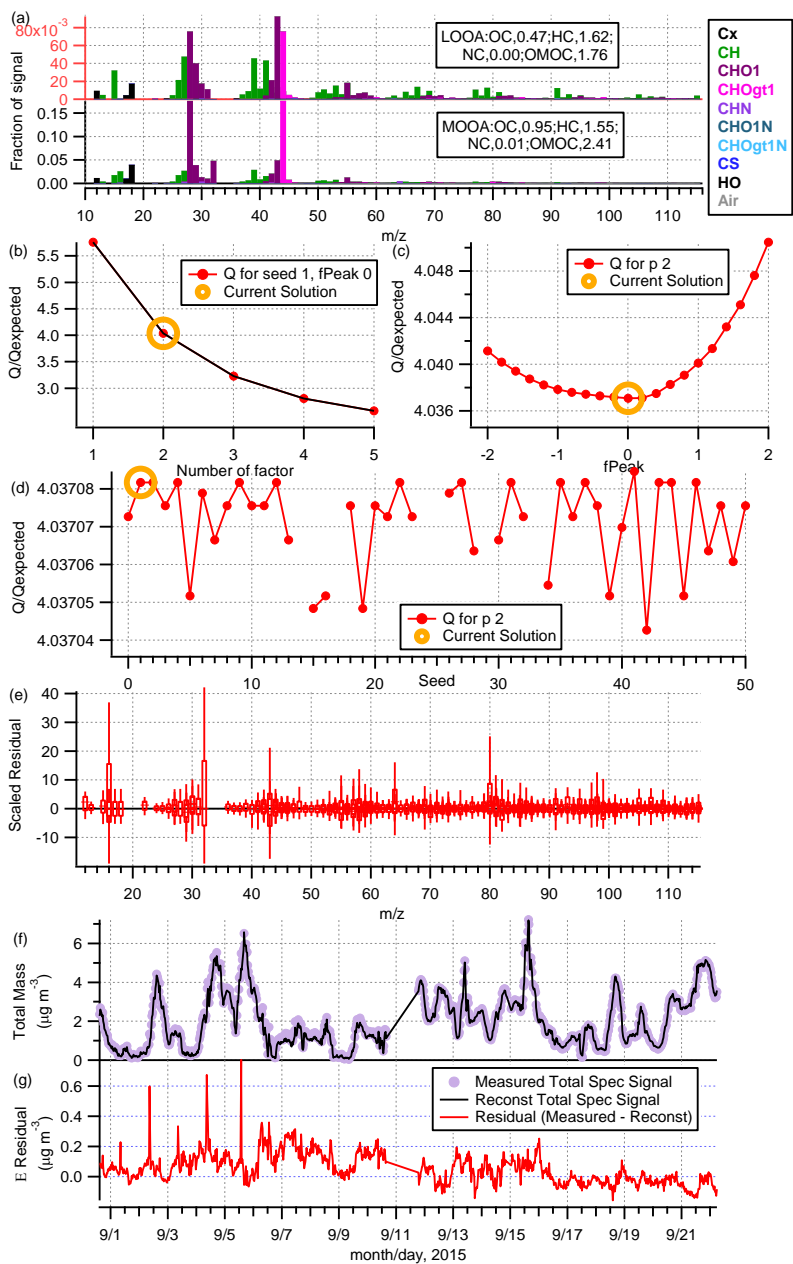
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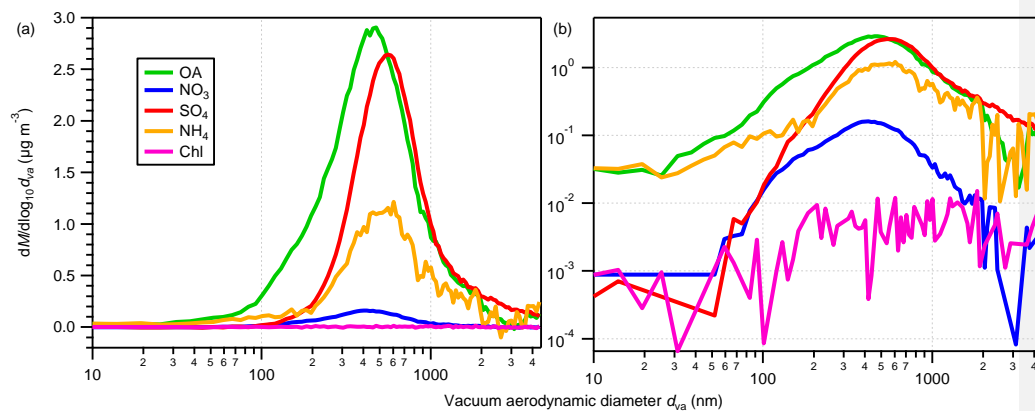
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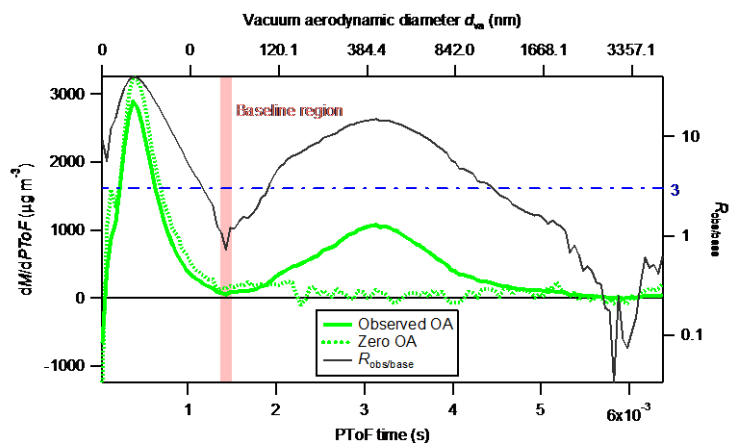
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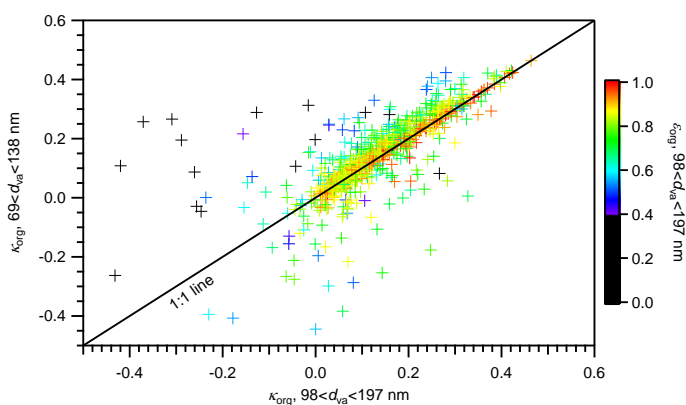
**Figure S1:** Summary of the two-factor result from the PMF analysis: (a) organic mass spectra of LOOA and MOOA colored according to ion groups (fpeak = 0 and SEED = 1), and the atomic ratios of O to C, H to C, and N to C, as well as OM to OC ratio for each factor; (b) Q/Qexpected as a function of the number of factors, where Q is the sum of the weighted squared residuals and Qexpected is the expected Q value; (c) Q/Qexpected as a function of the fpeak values with SEED = 1 and the number of factor = 2; (d) Q/Qexpected as a function of the SEED values with fpeak = 0 and the number of factor = 2; (e) distributions of the scaled residual for each m/z (fpeak = 0 and SEED = 1); time series of (f) the measured organic mass concentrations and those reconstructed (= LOOA + MOOA) (fpeak = 0 and SEED = 1), and (g) residual OA (= measured - reconstructed) (fpeak = 0 and SEED = 1).



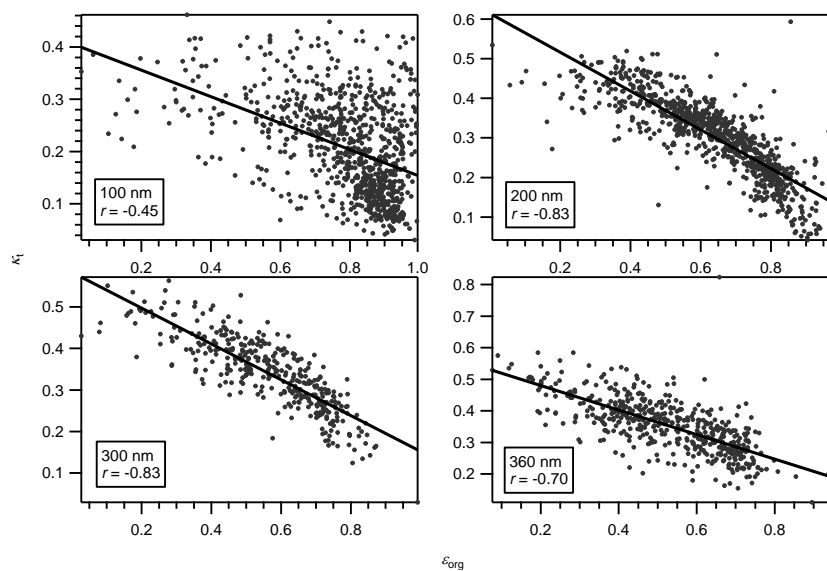
**Figure S2:** Mean mass-size distributions of organics (OA), sulfate ( $\text{SO}_4$ ), ammonium ( $\text{NH}_4$ ), nitrate ( $\text{NO}_3$ ), and chloride (Chl) in (a) linear and (b) logarithmic scales over the entire study period.



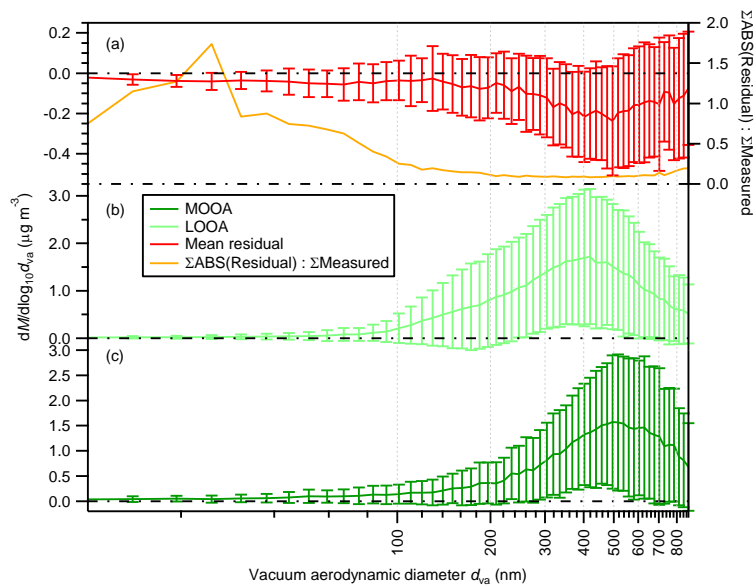
**Figure S3:**  $dM/dPToF$  ( $M$  and  $PToF$  here refer to mass concentration and PToF time, respectively) versus PToF time for the observed OA and OA measured by placing a HEPA filter in the inlet tubing outside the instrument room (zero OA), averaged for the entire study period. The region shaded in pink indicates the PToF time region chosen as a baseline for evaluation of the effective PToF diameter range. (Note that this is not the DC marker region.) The dark solid curve is the absolute value of the ratio of the observed OA at respective PToF time to the mean of the observed OA in the baseline region ( $R_{obs/base}$ ). The blue dash-dotted line indicates the  $R_{obs/base}$  value of three. The vacuum aerodynamic diameter that corresponds to the PToF time is presented on the top axis.



**Figure S4:**  $\kappa_{org}$  of 100 nm particles derived based on the chemical composition in the vacuum aerodynamic diameter ( $d_{va}$ ) range of 69–138 nm versus that of 98–197 nm. Data points with  $\kappa_{org}$  smaller than  $-0.50$  or  $\kappa_{org}$  higher than  $0.60$  are not presented.

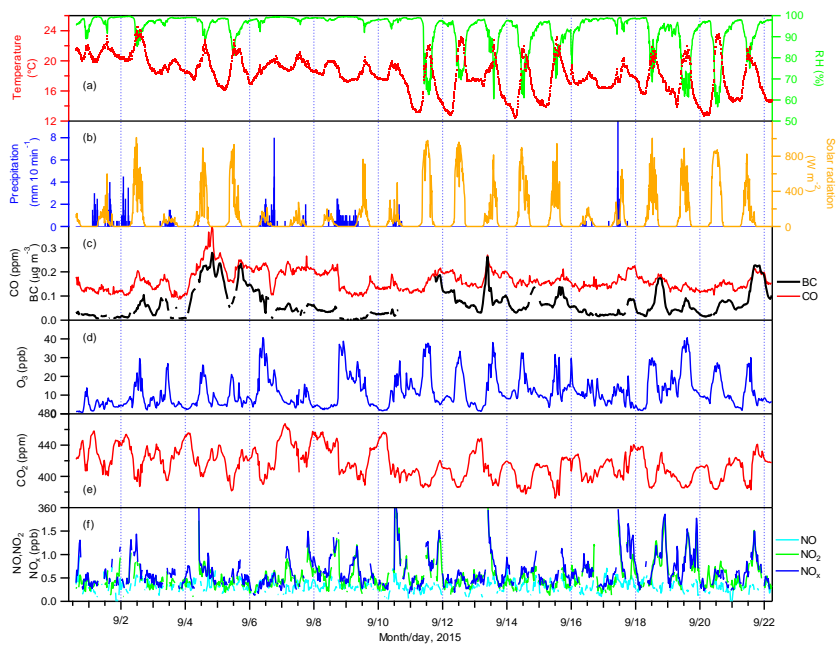


**Figure S5:**  $\kappa_1$  versus  $\epsilon_{org}$  for particles with  $d_{dry}$  of 100, 200, 300, and 360 nm for the entire study period. In each panel, marks and a solid line represent individual data and the corresponding linear regression line, respectively. The correlation coefficient ( $r$ ) of each is also presented.

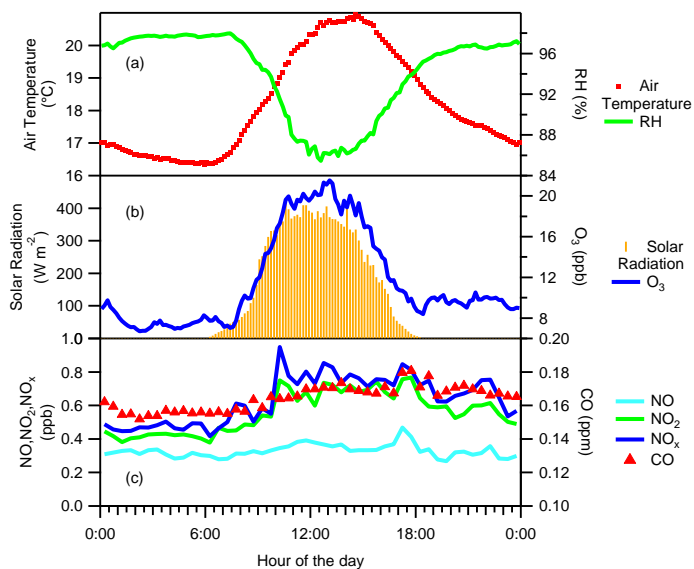


**Figure S6:** Mean mass-size distributions of (a) residual, (b) LOOA, and (c) MOOA over the entire study period. The residual is the difference between the measured and reconstructed (i.e., LOOA + MOOA) mass concentrations of OA in each size bin. The error bars indicate the standard deviation. The ratios of the sum of the absolute value of the residual to the measured mass concentration of OA are superimposed in panel (a) (right axis).

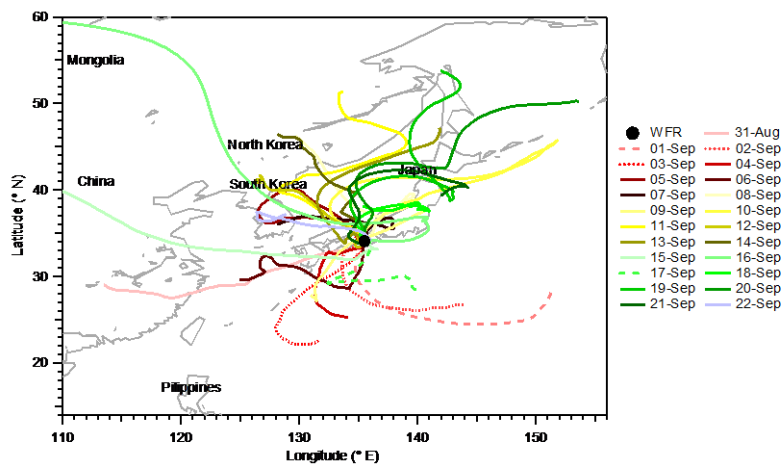




**Figure S7:** Time series of (a) air temperature and relative humidity (RH), (b) precipitation and solar radiation, (c) mass concentration of BC, and mixing ratios of (c) CO, (d) O<sub>3</sub>, (e) CO<sub>2</sub>, and (f) NO, NO<sub>2</sub>, and NO<sub>x</sub>.

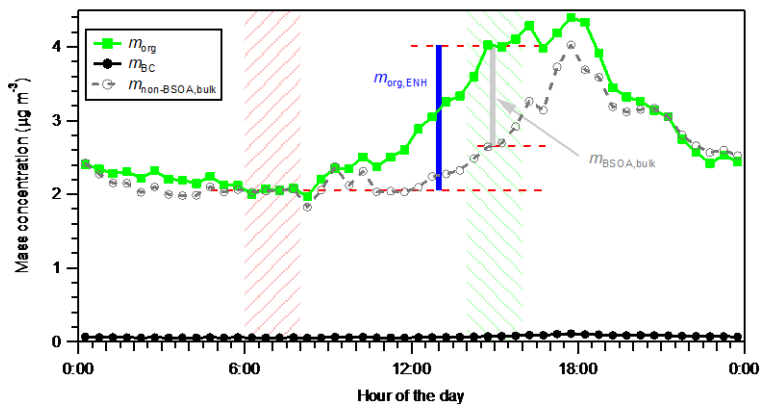


**Figure S8:** Diurnal variations of (a) air temperature and relative humidity (RH), (b) solar radiation and the mixing ratios of O<sub>3</sub>, and (c) mixing ratios of NO, NO<sub>2</sub>, NO<sub>x</sub>, and CO over the entire study period.

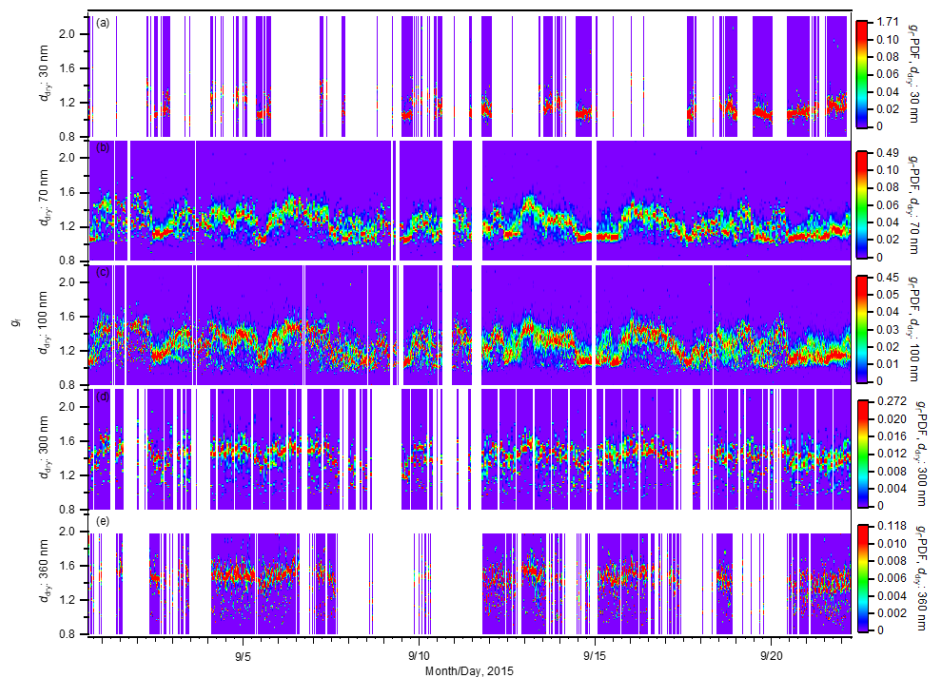


**Figure S9:** Five-day backward air mass trajectories from 500 m agl (above ground level) over Wakayama Forest Research Station at one-day intervals. The arrival time of the air masses at the study site was 1500 JST. The solid circle denotes the location of the study site. Solid trajectories are for days when more than 22 of the 24 hourly trajectories are from terrestrial regions. Dashed trajectories are for days when more

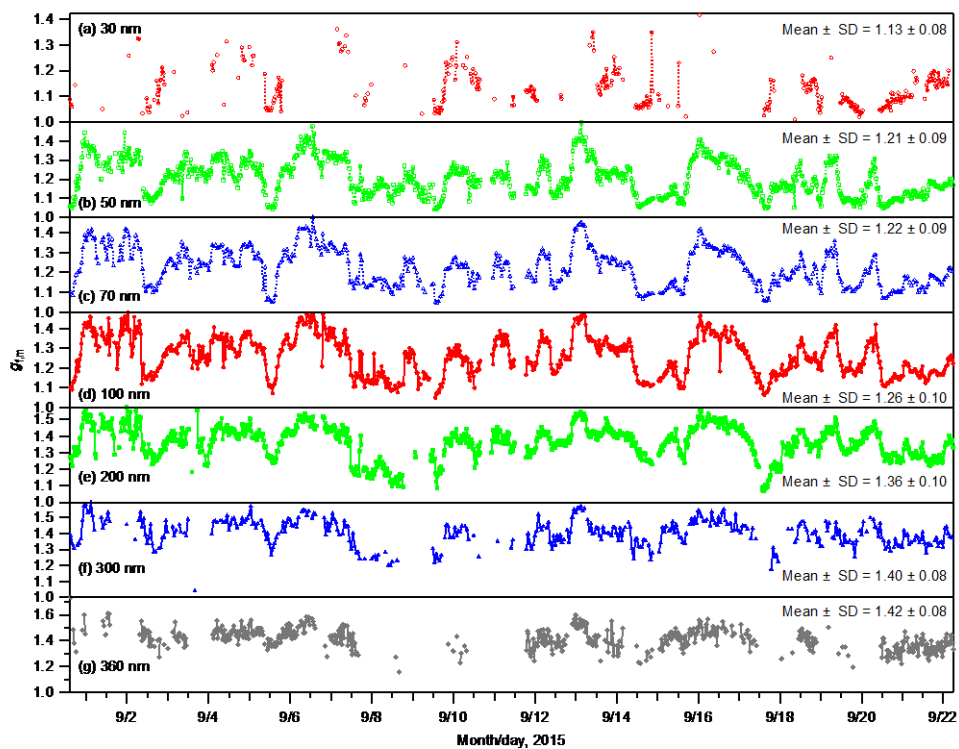
than 21 of the 24 hourly trajectories are from the North Pacific. Dotted trajectories are for days when 10 of the 24 hourly trajectories are from the North Pacific. The map is based on GSHHG 2.3.4; the shoreline polygon data at crude resolution is used. We consider an air mass is from the North Pacific if the trajectory never passes over terrestrial area that appears on the map before it reaches the Kii Peninsula. The trajectories were produced using NOAA's HYSPLIT atmospheric transport and dispersion modeling system (Draxler and Hess, 1998).



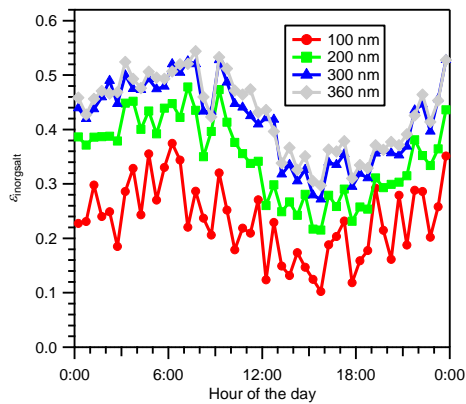
**Figure S10.** Diurnal variation of the mass concentrations of OA ( $m_{org}$ ), BC ( $m_{BC}$ ), and non-BSOA-OA ( $m_{non-BSOA,bulk}$ ; Text S9) during the entire study period. The left-slash pattern represents the background period. As an example, the vertical bars represent the estimates of the total enhancement of OA ( $m_{org,ENH}$ ; blue) and the enhancement contributed by BSOA ( $m_{BSOA,bulk}$ ; gray) for the period 1400–1600 JST (right slash pattern).



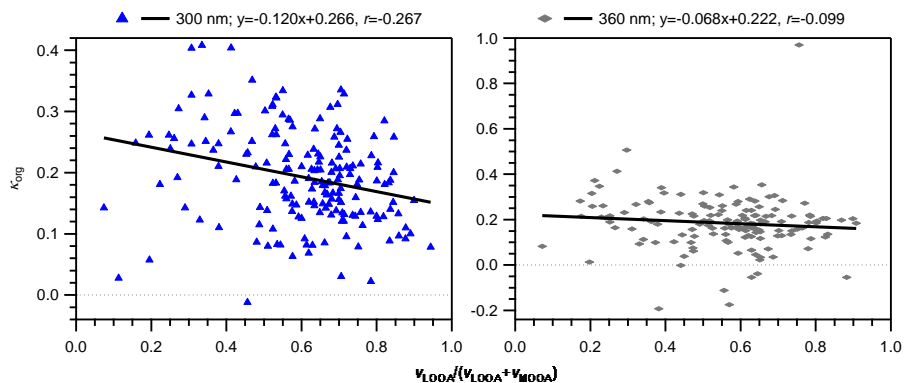
**Figure S11:** Time series of the probability distribution functions of the hygroscopic growth factors ( $g$ -PDF) of aerosol particles with  $d_{dry}$  of (a) 30, (b) 70, (c) 100, (d) 300, and (e) 360 nm.



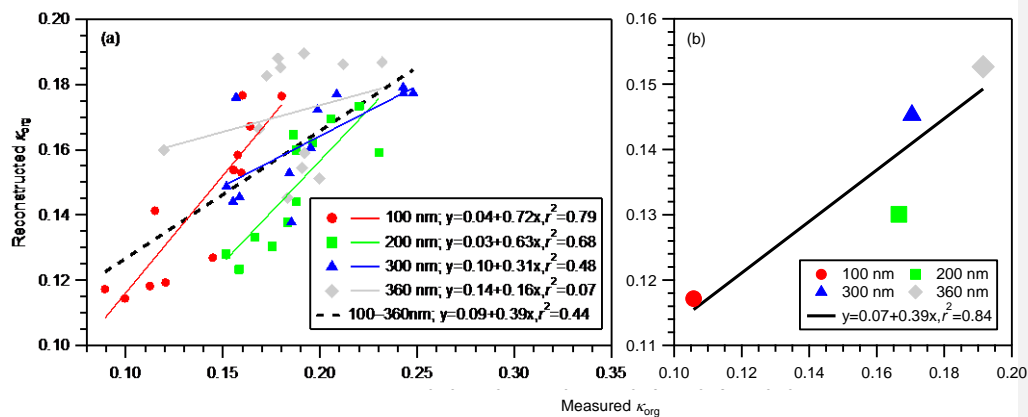
**Figure S12:** Time series of the mean growth factors ( $g_{f,m}$ ) of aerosol particles with different dry diameters. The mean  $\pm$  SD values over the entire study period for each diameter are also presented.



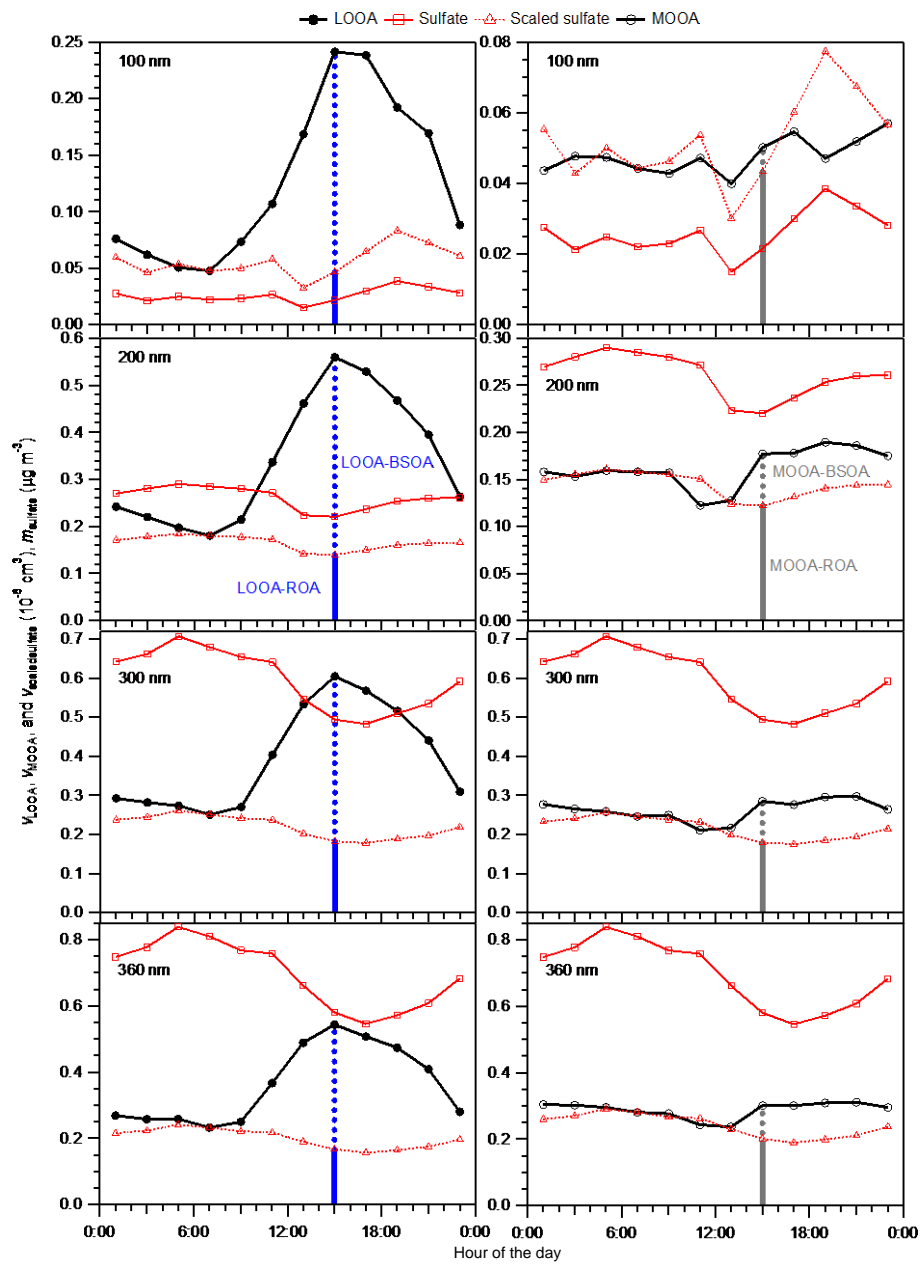
**Figure S13:** Diurnal variation of the size-resolved volume fractions of total inorganic salts ( $\epsilon_{\text{inorgsalt}}$ ) during the entire study period.



**Figure S14:** The  $\kappa_{\text{org}}$  versus  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  for particles with  $d_{\text{dry}}$  of 300 and 360 nm. The time resolution of the data is 2 h. In each panel, marks and a solid line represent individual data and the corresponding linear regression line, respectively. The regression equation and correlation coefficient of each are also presented. Only data with  $\epsilon_{\text{org}}$  greater than 0.40 are used.

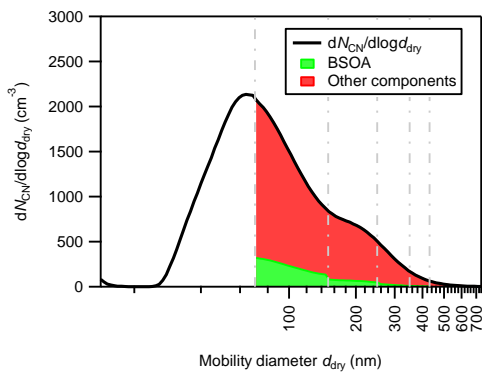


**Figure S15:** The  $\kappa_{\text{org}}$  reconstructed using  $\kappa_{\text{LOOA}}$ ,  $\kappa_{\text{MOOA}}$ , and size-resolved  $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$  (reconstructed  $\kappa_{\text{org}}$ ) versus the  $\kappa_{\text{org}}$  derived from measured  $\kappa_i$  and aerosol chemical composition (measured  $\kappa_{\text{org}}$ ; Sect. 3.2). In panel (a), markers represent size-resolved diurnal variation data at 2 h resolution, solid lines are linear regression lines for particles with respective diameters, and the dashed line is the linear regression line for all 100–360 nm particles. In panel (b), markers represent the size-resolved mean  $\kappa_{\text{org}}$  during 1200–2000 JST, and the solid line is the linear regression line for the size-resolved mean  $\kappa_{\text{org}}$ . Respective regression equations and coefficients of determination ( $r^2$ ) are also presented. Only  $\kappa_{\text{org}}$  data with  $\varepsilon_{\text{org}}$  greater than 0.40 are used for the comparison.



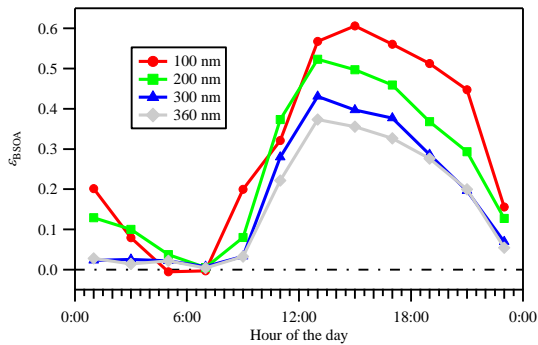


**Figure S16:** Diurnal variation of the volume concentrations of LOOA and MOOA and the mass concentration of sulfate for particles with  $d_{dry}$  of 100, 200, 300, and 360 nm over the entire study period. The scaled sulfate represents the diurnal variation of ROA that was contributed by LOOA (left panels) or MOOA (right panels). The scaling factor for the scaled sulfate in each panel is the mean volume concentration of OA during 0600–0800 JST, divided by the mean mass concentration of sulfate in the same period. The volume concentrations of LOOA and MOOA were derived from the respective mass concentrations (Text S8). The densities of LOOA and MOOA were calculated using their O:C and H:C ratios following Kuwata et al. (2012) and were 1.24 and 1.54 g cm<sup>-3</sup>, respectively.

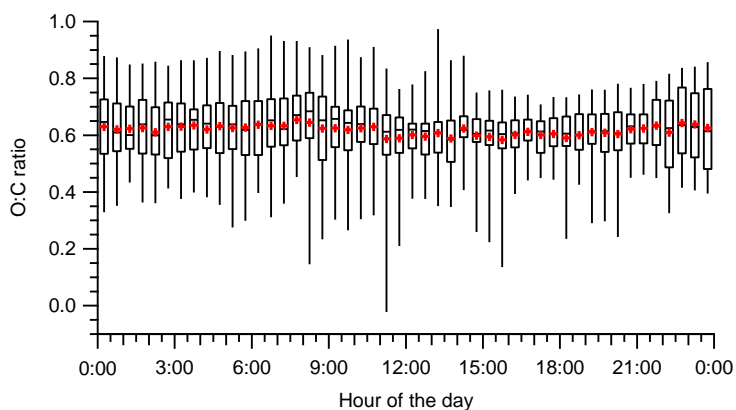


**Figure S17:** Estimate of the contributions of BSOA to the CCN number concentration, from the viewpoint of its size-resolved contribution to the aerosol water uptake. The solid line indicates the mean aerosol number-size distribution during the entire study period. Shaded areas in green represent the fraction of CCN contributed by BSOA and in red, that contributed by other components assuming a CCN activation diameter of 70 nm (Text S11).

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**Figure S18:** The diurnal variation of the volume fractions of BSOA ( $\phi_{\text{BSOA}}$ ) for particles with  $d_{\text{dry}}$  of 100, 200, 300, and 360 nm over the entire study period (Text S11).



**Figure S19:** Box and whiskers plot of the diurnal variation of the O:C ratios of bulk OA (only data with  $m_{\text{org}} > 0.3 \mu\text{g m}^{-3}$  are included) for the entire study period. The horizontal lines in the boxes indicate the median values, boundaries of the boxes indicate the 25<sup>th</sup>- and 75<sup>th</sup>-percentiles, and the whiskers indicate the highest and lowest values. The cross symbols in the boxes indicate the mean values.

**Table S1:** Mode diameters<sup>a</sup> of PSL size standards measured by DMAs in the HTDMA (DMA1 and DMA2) and the SMPS (DMA3) (mean  $\pm$  SD, nm)

Manufacturer warranty	DMA1		DMA2		DMA3	
	Before <sup>c</sup>	After <sup>d</sup>	Before <sup>c</sup>	After <sup>d</sup>	Before <sup>c</sup>	After <sup>d</sup>
55 ( $\pm 1$ ) <sup>b</sup>	56.6 $\pm$ 0.4	56.2 $\pm$ 0.4	56.8 $\pm$ 0.4	-	59.9 $\pm$ 0.2	-
100 ( $\pm 3$ ) <sup>b</sup>	98.0 $\pm$ 0.2	98.4 $\pm$ 0.1	97.0 $\pm$ 0.1	96.2 $\pm$ 0.2	101.2 $\pm$ 0.3	101.1 $\pm$ 0.1
309 ( $\pm 9$ ) <sup>b</sup>	297.7 $\pm$ 0.8	298.0 $\pm$ 0.4	290.4 $\pm$ 1.2	-	303.6 $\pm$ 0.3	-
498 ( $\pm 9$ ) <sup>b</sup>	-	-	478.4 $\pm$ 5.8	-	499.6 $\pm$ 4.4	-

<sup>a</sup> The mean  $\pm$  SD of the mode diameters from fittings are presented (unit: nm).

<sup>b</sup> Mean diameter ( $\pm$  the expanded uncertainty;  $k = 2$ ).

<sup>c</sup> Before the atmospheric observations.

<sup>d</sup> After the atmospheric observations.

**Table S2:** The  $g_{\text{t,m}}$  of ammonium sulfate (AS) particles measured under dry condition ( $g_{\text{t,m,dryAS}}$ ) and at 85 % RH ( $g_{\text{t,m,wetAS}}$ ), and calculated  $g_{\text{t}}$  of AS particles at 85 % RH ( $g_{\text{t,AS}}$ )

$d_{\text{dry}}$ (nm)	30	50	70	100	200	300	360
$g_{\text{t,m,dryAS}}$	0.959	0.976	0.984	0.985	0.988	0.982	0.981
$g_{\text{t,m,wetAS}}^{\text{a}}$	1.52	1.54	1.54	1.54	1.55	1.57	1.59

$g_{t,AS}^a$	1.49	1.52	1.54	1.55	1.57	1.57	1.57
<b>Difference (%)<sup>b</sup></b>	2.0	1.3	0	-0.65	-1.3	0	1.3

<sup>a</sup> Corrected for the difference of sizing between DMA1 and DMA2.

<sup>b</sup>  $((g_{t,m,wetAS} - g_{t,AS}) / g_{t,AS}) \times 100$ .

**Table S3: The  $\kappa$  values of inorganic salts ( $\kappa$ ) at 85 % RH derived using the surface tension of the solution and of pure water**

$d_{dry}$ (nm)	$\kappa$ , with surface tension of solution				$\kappa$ , with surface tension of pure water			
	100	200	300	360	100	200	300	360
AN	0.553	0.555	0.555	0.556	0.553	0.555	0.556	0.556
AS	0.533	0.527	0.525	0.524	0.531	0.526	0.524	0.524
LET	0.550	0.545	0.543	0.543	0.549	0.544	0.543	0.543
AHS	0.612	0.607	0.605	0.605	0.612	0.607	0.605	0.605
SA	0.972	0.959	0.955	0.953	0.971	0.959	0.955	0.953

**Table S4: Data in Fig. 3 of the main manuscript** ("DataInFigure3ofTheManuscript.xlsx").

**Table S5: Data in Fig. 4 of the main manuscript** ("DataInFigure4ofTheManuscript.xlsx").

**Table S6: Data in Fig. 5 of the main manuscript** ("DataInFigure5ofTheManuscript.xlsx").

**Table S7: Comparisons of  $\kappa_{org}$  and  $v_{LOOA}/(v_{LOOA}+v_{MOOA})$  between particles with different  $d_{dry}$**

$d_{dry}$ of particles to compare (nm)	1200–2000 JST				2000–1200 JST			
	$\kappa_{org}$		$v_{LOOA}/(v_{LOOA}+v_{MOOA})$		$\kappa_{org}$		$v_{LOOA}/(v_{LOOA}+v_{MOOA})$	
	Diff <sup>a</sup>	p-value <sup>c</sup>	Diff <sup>b</sup>	p-value <sup>c</sup>	Diff <sup>a</sup>	p-value <sup>c</sup>	Diff <sup>b</sup>	p-value <sup>c</sup>
<b>200 vs 100</b>	0.06	<0.01	-0.06	0.02	0.04	<0.01	-0.01	0.65
<b>300 vs 200</b>	<0.01	0.71	-0.08	<0.01	<0.01	0.31	-0.06	<0.01
<b>360 vs 300</b>	0.02	0.15	-0.04	<0.01	-0.02	0.02	-0.05	<0.01
<b>360 vs 200</b>	0.02	0.07	-0.11	<0.01	-0.02	0.07	-0.11	<0.01

<sup>a</sup> The mean of (the  $\kappa_{org}$  of particles with relatively large  $d_{dry}$  – the  $\kappa_{org}$  of particles with relatively small  $d_{dry}$ ).

<sup>b</sup> The mean of (the  $v_{LOOA}/(v_{LOOA}+v_{MOOA})$  of particles with relatively large  $d_{dry}$  – the  $v_{LOOA}/(v_{LOOA}+v_{MOOA})$  of particles with relatively small  $d_{dry}$ ).

<sup>c</sup> From 10 % two-sided t-test for the significance of the difference of Diff from zero. Low values indicate significant differences.

**Table S8: Diurnal variation of  $\kappa$  and  $\kappa_{org}$  at 2 h resolution, and their mean and SD for the entire period**

$d_{dry}$ (nm)	$\kappa$							$\kappa_{org}$			
	30	50	70	100	200	300	360	100	200	300	360
<b>0000–0200 JST</b>	0.16	0.20	0.22	0.24	0.34	0.37	0.36	0.16	0.23	0.25	0.21
<b>0200–0400 JST</b>	0.22	0.21	0.22	0.24	0.34	0.37	0.35	0.16	0.20	0.21	0.18

<b>0400–0600 JST</b>	0.18	0.21	0.22	0.25	0.34	0.38	0.39	0.16	0.21	0.24	0.23
<b>0600–0800 JST</b>	0.21	0.22	0.21	0.25	0.35	0.38	0.36	0.18	0.22	0.24	0.19
<b>0800–1000 JST</b>	0.15	0.18	0.21	0.22	0.32	0.33	0.37	0.16	0.19	0.16	0.18
<b>1000–1200 JST</b>	0.13	0.16	0.16	0.19	0.29	0.33	0.34	0.12	0.17	0.15	0.12
<b>1200–1400 JST</b>	0.090	0.14	0.14	0.16	0.26	0.32	0.34	0.11	0.16	0.19	0.18
<b>1400–1600 JST</b>	0.083	0.13	0.13	0.16	0.24	0.28	0.33	0.10	0.15	0.16	0.20
<b>1600–1800 JST</b>	0.10	0.14	0.14	0.17	0.25	0.28	0.32	0.089	0.18	0.16	0.19
<b>1800–2000 JST</b>	0.13	0.15	0.16	0.19	0.27	0.31	0.32	0.12	0.18	0.18	0.19
<b>2000–2200 JST</b>	0.14	0.18	0.18	0.21	0.29	0.33	0.34	0.14	0.19	0.20	0.17
<b>2200–0000 JST</b>	0.12	0.19	0.20	0.23	0.31	0.35	0.36	0.16	0.19	0.20	0.17
<b>Mean for entire period</b>	0.12	0.18	0.18	0.21	0.30	0.34	0.35	0.13	0.18	0.19	0.19
<b>SD for entire period</b>	0.079	0.090	0.089	0.094	0.10	0.087	0.086	0.11	0.085	0.084	0.11

Table S9: Data in Fig. 6 of the main manuscript.

Hour of the day	$F_{CCN,OA}$ (%)	$F_{CCN,BSOA}$ (%; fresh BSOA)	$F_{CCN,BSOA}$ (%; aged BSOA)
0000–0200 JST	44.5	5.85	10.6
0200–0400 JST	44.9	2.66	4.88
0400–0600 JST	40.1	0.238	0.338
0600–0800 JST	42.8	$-6.41 \times 10^{-3}$	-0.0373
0800–1000 JST	44.5	5.62	10.3
1000–1200 JST	42.7	12.7	21.3
1200–1400 JST	53.0	26.2	39.8
1400–1600 JST	52.7	28.4	42.6
1600–1800 JST	47.3	24.9	38.5
1800–2000 JST	45.7	19.8	31.9
2000–2200 JST	49.4	16.6	27.5
2200–0000 JST	45.3	4.99	9.10

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**Table S10: Different assumptions of  $\kappa_{\text{org}}$  for the prediction of  $F_{\text{CCN,OA}}$**

$d_{\text{dry}}$ (nm)	TimeSize $\kappa_{\text{org}}^{\text{a}}$				SizeReso $\kappa_{\text{org}}^{\text{b}}$				TimeReso $\kappa_{\text{org}}^{\text{c}}$				Single $\kappa_{\text{org}}^{\text{d}}$			
	100	200	300	360	100	200	300	360	100	200	300	360	100	200	300	360
<b>0000–0200 JST</b>	0.16	0.23	0.25	0.21							0.21					
<b>0200–0400 JST</b>	0.16	0.20	0.21	0.18							0.19					
<b>0400–0600 JST</b>	0.16	0.21	0.24	0.23							0.21					
<b>0600–0800 JST</b>	0.18	0.22	0.24	0.19							0.21					
<b>0800–1000 JST</b>	0.16	0.19	0.16	0.18							0.17					
<b>1000–1200 JST</b>	0.12	0.17	0.15	0.12							0.14					
<b>1200–1400 JST</b>	0.11	0.16	0.19	0.18	0.14	0.19	0.19	0.19			0.16			0.18		
<b>1400–1600 JST</b>	0.10	0.15	0.16	0.20							0.15					
<b>1600–1800 JST</b>	0.089	0.18	0.16	0.19							0.15					
<b>1800–2000 JST</b>	0.12	0.18	0.18	0.19							0.17					
<b>2000–2200 JST</b>	0.14	0.19	0.20	0.17							0.17					
<b>2200–0000 JST</b>	0.16	0.19	0.20	0.17							0.18					

<sup>a</sup> Time- and size-resolved  $\kappa_{\text{org}}$ .

<sup>b</sup> Time-averaged, size-resolved  $\kappa_{\text{org}}$ .

<sup>c</sup> Time-resolved, size-averaged  $\kappa_{\text{org}}$ .

<sup>d</sup> Time- and size-averaged  $\kappa_{\text{org}}$ .

**Table S11: Different assumptions of  $\kappa_{\text{BSOA}}$  for the prediction of  $F_{\text{CCN,BSOA}}$**

$d_{\text{dry}}$ (nm)	Size-resolved $\kappa_{\text{BSOA}}$	Size-averaged $\kappa_{\text{BSOA}}$	Aged, size-resolved $\kappa_{\text{BSOA}}$
<b>100</b>	0.089		0.18
<b>200</b>	0.11		0.18
<b>300</b>	0.12	0.11	0.18
<b>360</b>	0.12		0.19

Table S12: Data in Fig. 7 of the main manuscript.

Hour of day	Ratios of different $F_{CCN,OA}$				Ratios of different $F_{CCN,BSOA}$		
	TimeSize	SizeReso	TimeReso	Single	Size-resolved	Size-averaged	Aged, Size-resolved
	$\kappa_{org}^a$	$\kappa_{org}^b$	$\kappa_{org}^c$	$\kappa_{org}^d$	$\kappa_{BSOA}$	$\kappa_{BSOA}$	$\kappa_{BSOA}$
0000–0200 JST	1	0.913	1.09	0.993	1	1.19	1.81
0200–0400 JST	1	0.932	1.04	1.01	1	1.17	1.84
0400–0600 JST	1	0.920	1.10	1.00	1	0.899	1.42
0600–0800 JST	1	0.876	1.04	0.951	1	3.61	5.82
0800–1000 JST	1	0.964	1.02	1.04	1	1.19	1.82
1000–1200 JST	1	1.10	1.05	1.18	1	1.14	1.68
1200–1400 JST	1	1.08	1.10	1.14	1	1.12	1.52
1400–1600 JST	1	1.13	1.13	1.19	1	1.13	1.50
1600–1800 JST	1	1.18	1.19	1.26	1	1.14	1.55
1800–2000 JST	1	1.06	1.13	1.15	1	1.15	1.61
2000–2200 JST	1	0.983	1.06	1.06	1	1.16	1.65
2200–0000 JST	1	0.950	1.04	1.03	1	1.18	1.82

<sup>a</sup> Time- and size-resolved  $\kappa_{org}$ .

<sup>b</sup> Time-averaged, size-resolved  $\kappa_{org}$ .

<sup>c</sup> Time-resolved, size-averaged  $\kappa_{org}$ .

<sup>d</sup> Time- and size-averaged  $\kappa_{org}$ .

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