

We appreciate valuable comments from the reviewers. Our answers to the comments are provided below. The reviewers' comments are written in italic.

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 15–16), 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 κ_{BSOA} was as large as that of κ_{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](#): “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 8](#))

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:

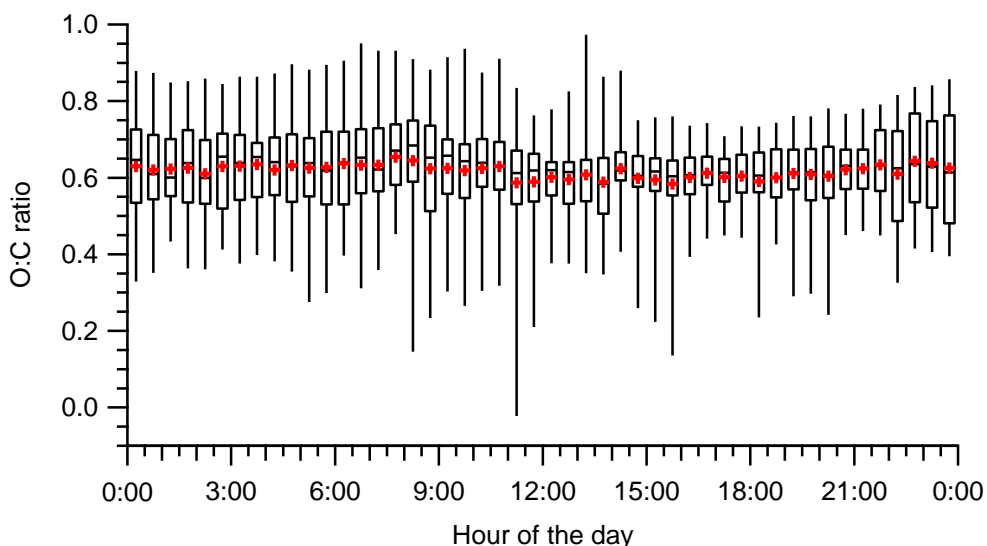


Figure S19: Box and whiskers plot of the diurnal variation of O:C ratios of bulk OA (only data with $m_{\text{org}} > 0.3 \mu\text{g m}^{-3}$ are included) for the entire study period. The horizontal line within the box indicates the median, boundaries of the box indicate the 25th- and 75th-percentile, and the whiskers indicate the highest and lowest values. The cross symbols in the box 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 $m_{\text{org}} > 0.3 \mu\text{g m}^{-3}$ were 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 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 κ_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_{dry} of 30 nm, κ_t is presented in 2-h time resolution because of the low data coverage (Fig. S12).”

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 κ_{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 κ_{BSOA}) and aged BSOA (using size-resolved κ_{ROA}).”

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 κ_{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 κ_{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 κ_{org} (page 15 lines 9–10) in the ACPD manuscript. Using stricter filters to rule out the large κ_{org} in the 360 nm panel in Fig. S14 and/or the negative κ_{org} values result in loss of data that are likely real. For example, to omit all negative κ_{org} values in Fig. S14b, data points with ε_{org} smaller than 0.89 must be excluded. In addition, although the volume additivity assumption used for the derivation of κ_{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 κ results in some negative κ_{org} as “apparent” κ 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.

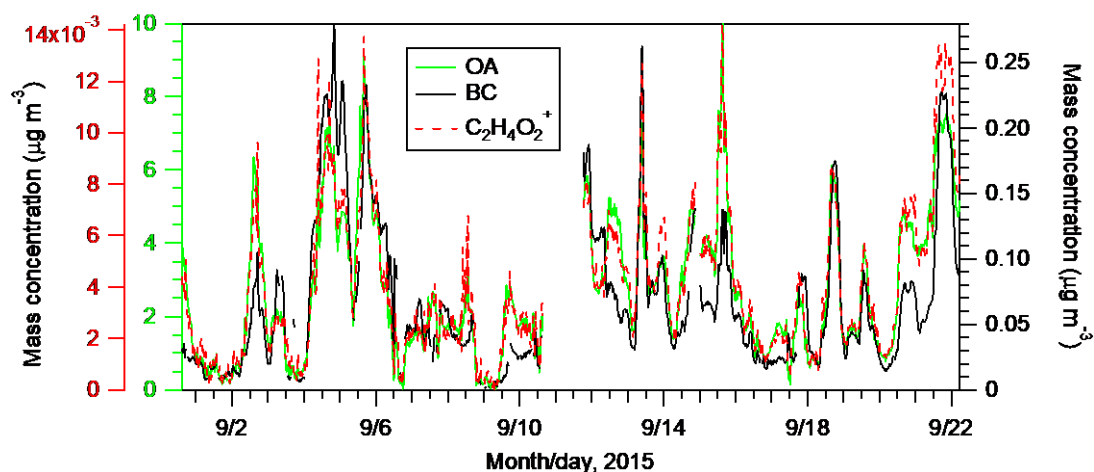


Figure R1: Time series of the mass concentrations of BC, OA, and fragment $C_2H_4O_2^+$.

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 15–16)

The correlation between κ_{org} and $v\text{LOOA}/(v\text{LOOA}+v\text{MOOA})$ is not high, and you used this relation to derive κ_{LOOA} and κ_{MOOA} , which may introduce even higher uncertainties. I think your analysis should start from the closure between measured κ and ZSR-derived κ . You can replace κ_{org} with κ_{LOOA} and κ_{MOOA} , and ask your computer to find the best solution for κ_{LOOA} and κ_{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 κ_{LOOA} and κ_{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 κ_{BSOA} and κ_{ROA} (Table R1) and $F_{\text{CCN,BSOA}}$ (Table R2), the resulting differences are: the κ_{BSOA} value for 100 nm particles (0.094) is 5.9% higher, whereas the changes for larger particles are negligible; κ_{ROA} are 11–13% lower; using size-averaged κ_{BSOA} overestimated $F_{\text{CCN,BSOA}}$ by 8–13% if compared to those using size-resolved κ_{BSOA} (12–19% using the ORIG method (page 23 line 25)); $F_{\text{CCN,BSOA}}$ 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 κ_{LOOA} and κ_{MOOA} in the manuscript is not modified.

Table R1: Size-resolved κ_{BSOA} and κ_{ROA} calculated from κ_{LOOA} and κ_{MOOA} derived using ALT method

d_{dry} (nm)	κ_{BSOA}	κ_{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 κ_{BSOA} , size-averaged κ_{BSOA} , and size-resolved aged κ_{BSOA} to that derived using size-resolved κ_{BSOA} ¹

Hour of day	Ratios of $F_{\text{CCN,BSOA}}$ from different assumptions		
	Size-resolved	Size-averaged	Aged, Size-resolved
	κ_{BSOA}	κ_{BSOA}	κ_{BSOA} ²
0000–0200 JST	1	1.13	1.56
0200–0400 JST	1	1.12	1.57
0400–0600 JST ³	1	0.922	1.31
0600–0800 JST ³	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

¹Both κ_{BSOA} and κ_{ROA} are from Table R1;

²The condition of size-resolved aged κ_{BSOA} assumes that the value of κ_{BSOA} equals that of κ_{ROA} ;

³The 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 κ_{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 κ_{org} during 1200–2000 JST and 2000–1200 JST are indicated as filled circles and diamond markers, respectively. The standard deviations of the mean κ_{org} are indicated by the whiskers. The standard deviations of the mean $v_{\text{LOOA}}/(v_{\text{LOOA}}+v_{\text{MOOA}})$ are presented in Table S6. The size-resolved κ values of BSOA and ROA are indicated by the three-pointed stars and triangles, respectively. The diameters of κ_{org} , κ_{BSOA} , and κ_{ROA} are differentiated by colors. ...”

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 κ , 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 1 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 κ_{ROA} at 100 nm was erroneously used as κ_{BSOA} for all the four diameters with the assumption of size-resolved aged BSOA. The size-resolved κ_{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.

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.

Han, Y. M., Iwamoto, Y., Nakayama, T., Kawamura, K., and Mochida, M.: Formation and evolution of biogenic secondary organic aerosol over a forest site in Japan, *Journal of Geophysical Research-Atmospheres*, 119, 259-273, 10.1002/2013jd020390, 2014.

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.