

Review on "Some insights into the condensing vapors driving new particle growth to CCN sizes on the basis of hygroscopicity measurements" by Z. J. Wu et al.

The authors present a case study on atmospheric new particle formation at a continental location, addressing the question of the composition of the condensing vapors in NPF growth indirectly through HTDMA and AMS measurements. While the paper discusses only three NPF events it provides an interesting view into the composition of the growth in NPF, which is still not very well characterized. I recommend the manuscript for publication after the following issues have been addressed.

The authors greatly appreciate that the reviewer spent lots of time to read this manuscript and provide these constructive suggestions. We modified the manuscript according to the comments point by point.

My main concern is that the AMS data is underutilized. The paper seems to have a general mindset that only sulfuric acid and organics can contribute to the growth (e.g. page 8413, rows 1-2). Does the AMS data support this? What is the contribution of e.g. ammonium to the growth? For instance Zhang et al. (2004) combined AMS and SMPS in order to get an insight into chemistry of new particle formation and growth. I strongly recommend applying the Zhang et al. (2004) approach in your data set. This way you could compare the AMS and hygroscopicity implications on the composition.

Response:

By following the referee's comments, we carefully read Zhang's EST paper and made a deeper analysis of size-resolved AMS data. The particle volume size distributions were calculated firstly. Based on the particle volume size distribution, the size-resolved particle mass concentrations were estimated using a particle density of 1400 kg/m^3 . The results are shown in the Fig.1. The mass concentrations of particles below 50 nm in mobility diameter are lower than $1 \mu\text{g/m}^3$. We tried to integrate the AMS size distribution data to calculate the mass concentrations of organic, sulfate, nitrate, and ammonium. However, the signals for particle size smaller than 50 nm in AMS dataset are too noisy and cannot be used to analyze the chemical composition of new particles. The mass concentrations of particles below 100 nm in mobility diameters are several $\mu\text{g/m}^3$, as displayed in the Fig.1. And, the signals for this size range are much better. Considering the accuracy of size-resolved particle mass concentration detected by AMS and the transmission efficiency of aerodynamic lenses (100 nm in Dva) (Canagaratna et al., 2007), the chemical composition of 30-100 nm particles is chosen to perform the further analysis.

In addition, the fragment m/z 44 and 57 mass concentrations of 30-100 nm particles were calculated. m/z 44 (CO_2^+ ion fragment) is a good tracer for photochemically formed secondary organic aerosol, while m/z 57 (C_4H_9^+) is generally associated with primary organics from combustion sources (Zhang et al., 2004). An analysis on both chemical composition and fragment m/z 44 and 57 was added into the manuscript.

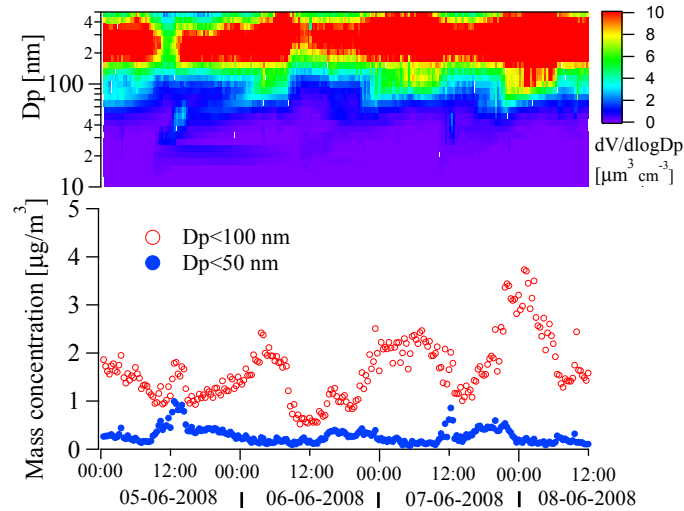


Fig.1: Particle volume size distribution and estimated mass concentration of particles smaller than 50 nm and 100 nm in mobility diameter.

Modification in the MS:

A new plot (Fig.3 in the MS) and some discussions were added into the section 4.2.

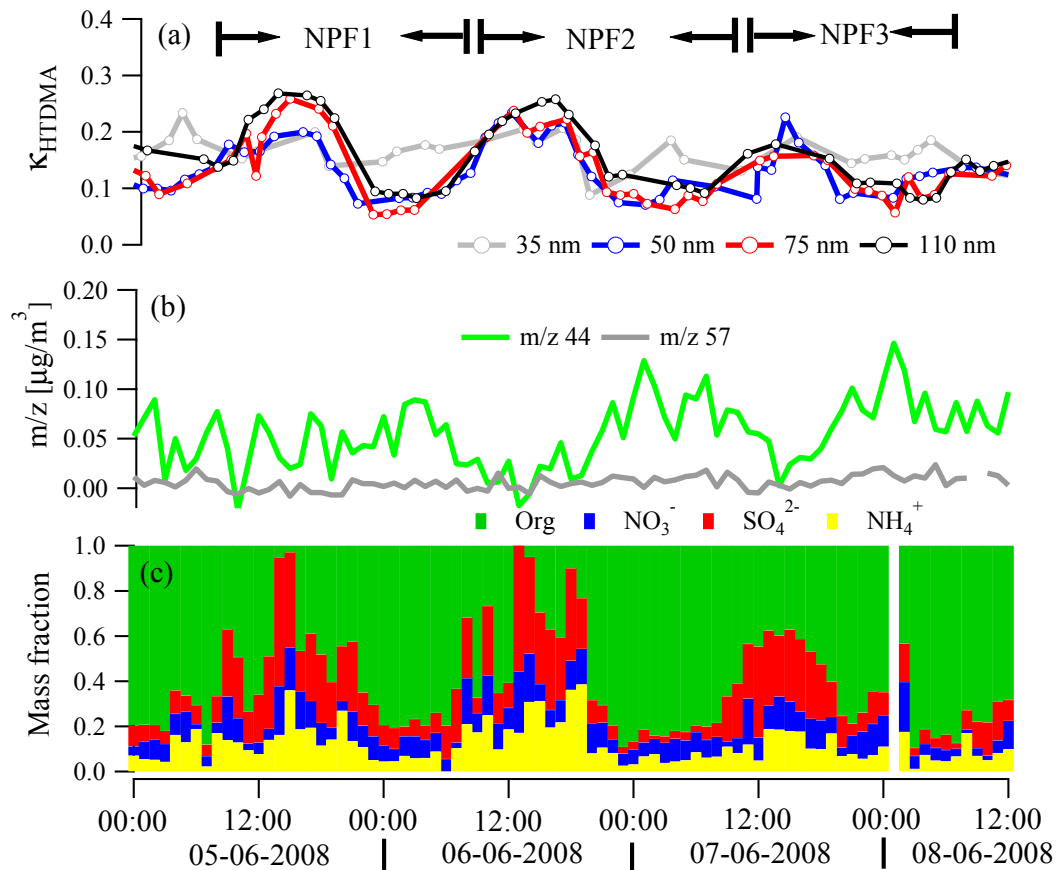


Fig.3: Size-resolved particle hygroscopicity (a), m/z 44 and 57 mass concentrations in 30-100 nm particles (b), and mass fraction of organic, sulfate, nitrate, and ammonium in 30-100 nm particles (c).

“As displayed in Fig.3 (c), the sulfate and ammonium were dominated in the inorganic mass fraction in 30-100 nm particles and obviously increased during the particle formation period (indicated by grey dashed line in Fig.1). While, the nitrate accounted for a minor fraction, which also observed by Zhang et al. in Pittsburgh (Zhang et al., 2004). They found nitrate contributed the least to the new particle growth. After 3:00pm on each day, the organic mass fraction increased and reached its maximum at midnight, indicating that organics played a key role in the particle growth at a later time of the NPF event. The mass fraction of ion fragments m/z 44 and 57 in 30-100 nm particles are shown in the Fig. 3(b). The m/z 44 (CO₂⁺ ion fragment) is a tracer for secondary organic aerosol, while m/z 57 (C₄H₉⁺) is generally associated with primary organics from combustion sources (Zhang et al., 2004). The m/z 57 mass concentration is close to zero during the events. Compared m/z 57, the m/z 44 mass concentration are considerable, indicating that the organics contributing to particle growth was mainly secondary organic species.”

Minor comments

page 8405, row 14 “Freshly formed particles are about several nanometers in diameter” Can you give more precise size, maybe with a reference? “About several nanometers” sound quite large for a freshly formed particle to me.

Response:

Freshly formed particles are about 1 nanometer in diameter (Kulmala et al., 2012). It was corrected in the MS.

Page 8405, row 27-29 Please clarify the last sentence.

Response:

The sentence is deleted from the manuscript.

page 8408 The methods for aerosol particle formation and growth rate analysis are not described at all. Please add a section in Chapter 3 on these.

Response

One section (3.4) was added in the texts to describe the method.

Modification in the MS:

3.4 Calculation of particle formation and growth rate

Assuming a constant particle source during a time period of t, the particle formation rate (J_{nuc}) can be expressed as (Dal Maso et al., 2005):

$$J_{nuc} = \frac{dN_{nuc}}{dt} + F_{coag} + F_{growth} \quad [10]$$

In this study, N_{nuc} is the number concentration of nucleation mode particles ranging from 3 nm to 25 nm. F_{growth} is the flux of particles out of the specified size range (3-25 nm). The newly formed particles rarely grew beyond 25 nm before formation

ended, and F_{growth} can be neglected. F_{coag} represents a loss of formed particles due to coagulation to the preexisting particle population. It can be calculated from the following equation:

$$F_{\text{coag}} = \text{Coag} S_{\text{nuc}} N_{\text{nuc}} \quad [11]$$

where $\text{Coag} S_{\text{nuc}}$ is the coagulation sink of particles in the nucleation mode. The detailed calculation of coagulation sink is given in Deal Maso et al. (2005).

The observed particle growth rate (GR) can be expressed as:

$$\text{GR} = \frac{\Delta D_m}{\Delta t} \quad [12]$$

where D_m is a mean geometric diameter of log-normal ultrafine particle mode, which has been fitted to the number size distribution (Heintzenberg, 1994). GR means evolution of the mean diameter within a time period Δt .

page 8411, row 16-17 Please give a reference (or a detailed description) for the hygroscopic growth parameterization.

Response:

The method of hygroscopic growth parameterization originates from Laakso et al., 2004.

Modification in the MS:

One reference was added into the MS “For this adjustment, an empirical growth law based on one year of hygroscopicity measurements at Melpitz was used (Refer to Laakso et al., 2004).”

page 8412, row 1-2 Please include a short discussion on the accuracy of the H₂SO₄ estimate.

Response:

The accuracy of simulated H₂SO₄ concentration is estimated as follow: Percentage error = abs ([H₂SO₄]_{measured} - [H₂SO₄]_{simulated}) * 100 / [H₂SO₄]_{simulated}. Here, [H₂SO₄]_{measured} is the sulfuric acid concentration measured during 9-day measurements for EUCAARI-2008. The percentage error is around 40%.

These sentences were added into the MS.

page 8412, row 19 “where [H₂SO₄]_{det} is the median value from the measured sulfuric acid concentration” Do you mean the estimated H₂SO₄ or did you have direct measurements as well?

Response:

[H₂SO₄]_{det} is wrong. The H₂SO₄ concentration is estimated one. It was corrected in the MS.

Modification in the MS:

[H₂SO₄]_{det} is modified to [H₂SO₄]_{meas}.

page 8413, row 13 Please indicate GR size range.

Response:

The observed particle growth rate (GR) can be expressed as:

$$GR = \frac{\Delta D_m}{\Delta t}$$

where D_m is a mean geometric diameter of log-normal ultrafine particle mode, which has been fitted to the number size distribution (Heintzenberg, 1994). GR means evolution of the mean diameter within a time period Δt . The evolution of mean geometric diameter during NPF event is displayed in the following Fig.1 (a) (in the MS) as white circles. The period during which the observed GR is calculated is marked by NPF1, NPF2, and NPF3.

Modification in the MS:

“These events are the best cases which showed clear particle bursts and subsequent growth process during the entire field campaign. The starting and ending time for each event were marked in the Fig.1 (a) as NPF1, NPF2, and NPF3.”

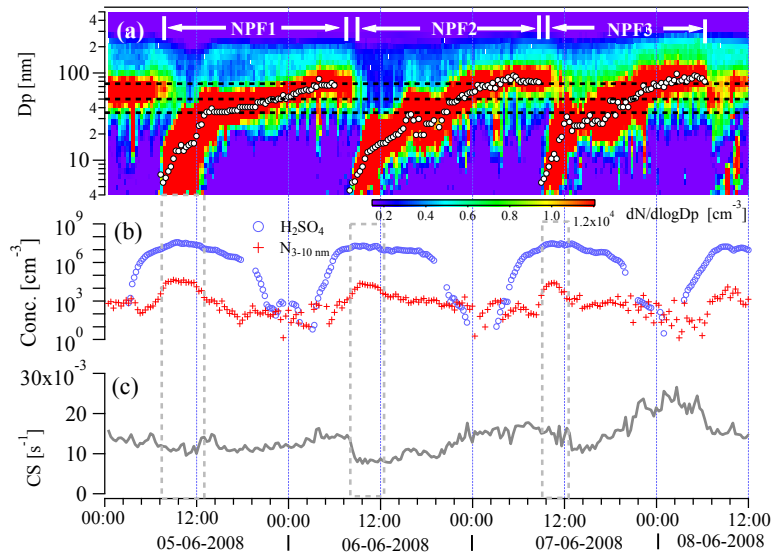


Fig. 1: Particle number size distribution, 3-10 nm particle number concentration, H_2SO_4 concentration, condensation sink (CS) during the NPF events. The starting and ending time of the events were marked in the upper place of panel (a) by NPF1, NPF2, and NPF3. The grey dashed lines indicated the time period of particle formation.

“As indicated by the white circle in the Fig.1 (a), the mean geometric diameter (D_m) of log-normal ultrafine particle mode increased to around 100 nm within 24 hours. Over the time period from the beginning to the end of the NPF events as marked in Fig.1 (a), the average GR_{obs} were respectively 2.8, 3.6, and 4.4 $nm\ h^{-1}$ for NPF events on June 5th, 6th, and 7th, 2008.”

page 8415, row 7-8 “This was consistent with the variations in particle hygroscopic growth at RH= 90% above-mentioned.” Please clarify this sentence.

Modification in the MS:

This was consistent with the variations in particle hygroscopic growth at RH= 90% displayed

in the Fig. 3 (a))

page 8416, row 22-24 “At Melpitz, biological activities produced a lot of biogenic volatile organic compounds (BVOCs) and lead to an organic-rich environment during summertime.”
Can you give a reference to support this statement?

Response:

The VOCs measurements performed at Melpitz research station showed that VOCs are mainly biogenic volatile organic compounds. The following figure copied from a supplementary material of a recent publication (Mutzel et al., 2015) displayed the VOCs concentration during summertime at Melpitz station. It is very clear that the BVOCs are dominated in the atmosphere of Melpitz.

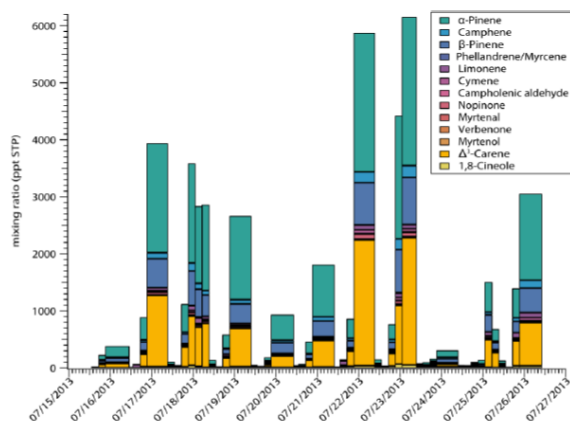


Figure S5. Time variation of the different VOC compounds sampled by TENAX cartridges. The width of each bar is covering the complete sampling period of each cartridge.

Modification in the MS:

At Melpitz, biogenic volatile organic compounds (BVOCs) emitted from biological activities are dominate volatile organic compounds (Mutzel et al., 2015) and lead to an organic-rich environment during summertime. The oxidation products of BVOCs may be responsible for the new particle growth.

page 8417, row 14-15 “The observation showed that sulfuric acid is a key species of atmospheric nucleation.” In my opinion this has not been shown. For instance analysis similar to Sihito et al. (2006) could be used to back up this statement.

Response:

Nucleation mechanism is not concerned in this work. This sentence is deleted from the MS.

page 8417, row 16 “CC” should probably be CCN?

Response:

It was corrected.

page 8417, row 26 “decline” do you mean increase?

Response:

Yes, it was corrected.

page 8418, row 1-4 “Our results implied that the CCN production associated with atmospheric nucleation may be overestimated if assuming that new particles can serve as CCN in case they grow to a fixed particle size, which was used in some previous studies, especially for organic-rich environments.” Please quantify the error of the fixed size approach in your case for a few typical threshold sizes. This would be valuable information for evaluating the uncertainty in other studies that did not have hygroscopicity measurements available.

Response:

In our case, the mean critical diameter is around 50 nm at SS=0.6%. Assuming a constant critical diameter of 50 nm at SS=0.6%, the CCN number concentration is averagely 1.13 times of that with varied critical diameters during the NPF events. Under similar conditions, the CCN number concentration at SS=0.4% with a constant critical diameter of 70 nm is 1.15 times of that with varied critical diameters. These results will be added into the MS.

Modification in the MS:

“In our case, the mean critical diameter is around 50 nm at SS=0.6%. Assuming a constant critical diameter of 50 nm at SS=0.6%, the CCN number concentration is averagely 1.13 times of that with varied critical diameters during the NPF events. Under similar conditions, the CCN number concentration at SS=0.4% with a constant critical diameter of 70 nm is 1.15 times of that with varied critical diameters.”

page 8425, Table 1 Please include GR_{obs} for each size range.

Response:

In table 1, $F_{GRH_2SO_4} = GR_{H_2SO_4} / GR_{obs}$ is the ratio of H_2SO_4 condensational growth to the observed particle growth rate. Here, GR_{obs} for 35, 50, and 75 nm were calculated over the time period during which mean geometric diameter of log-normal ultrafine particle mode grew to 35, 50, and 75 nm, respectively, as indicated by the white circles in the Fig.1 (a).

Modification in the MS:

One sentence is added into the MS

“Here, GR_{obs} for 35, 50, and 75 nm were calculated over the time period during which mean geometric diameter of log-normal ultrafine particle mode grew to 35, 50, and 75 nm, respectively, as indicated by the white circles in the Fig.1 (a).”

page 8426, Fig. 1 There are so many parameters in this graph that it is getting difficult to read. Please

1. plot H_2SO_4 and N3-10 on logarithmic axis (see e.g. Sihto et al., 2006)
2. plot CS in its own panel
3. plot OA mass fraction in its own panel, or preferably prepare a new figure showing the AMS data for the study period (cf. Zhang et al., 2004)

Response:

Figures are replotted and added into the MS:

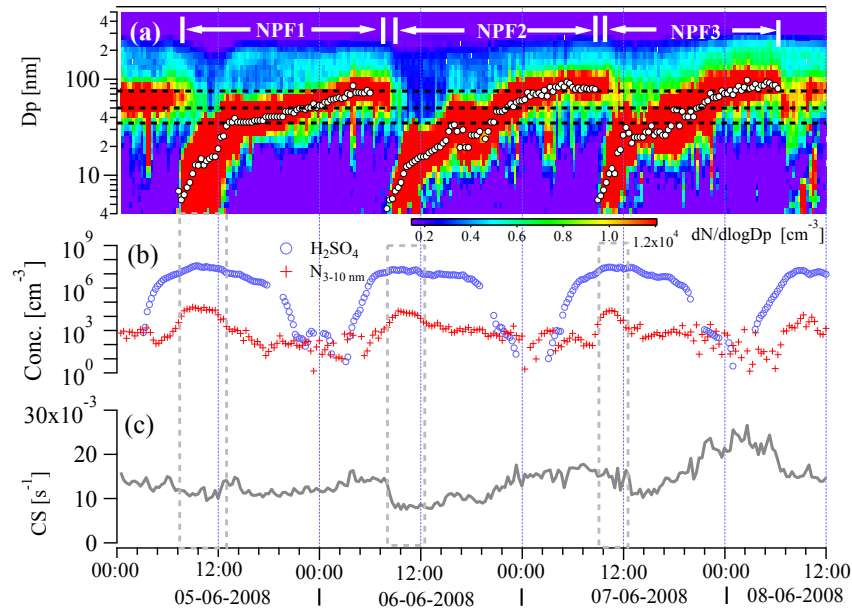


Fig. 1: Particle number size distribution (a), 3-10 nm particle number concentration and H_2SO_4 concentration (b), condensation sink (CS) (c) during the NPF events. The starting and ending time of the events were marked in the upper place of panel (a) by NPF1, NPF2, and NPF3. The white circles in the panel (a) are the D_m of new particles modes. The grey dashed lines indicated the time period of particle formation.

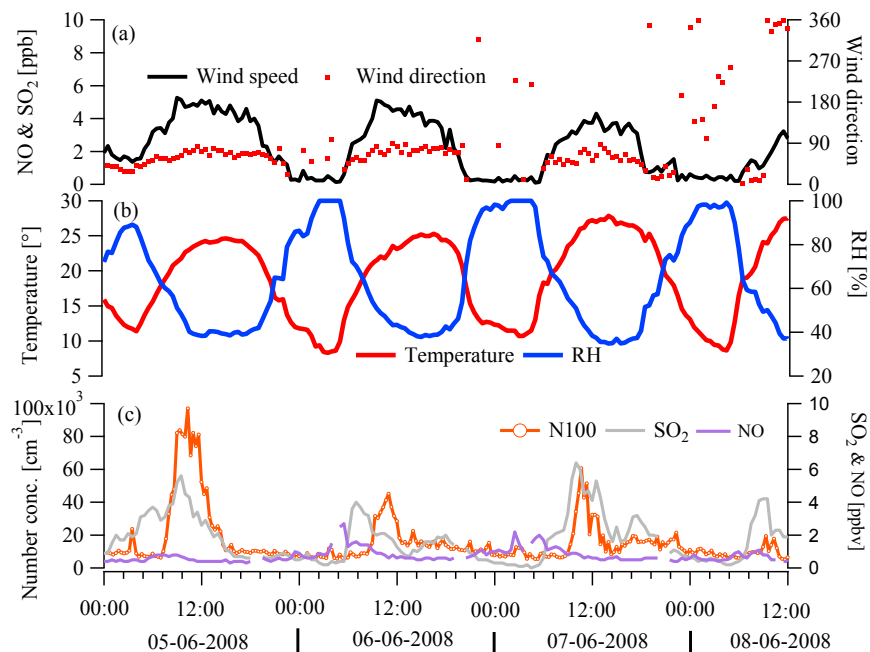


Fig. 2: The time series of wind speed and wind direction (a), ambient temperature and RH (b), and SO_2 & NO concentrations and number concentrations of particles in diameters of 3-100 nm (b).

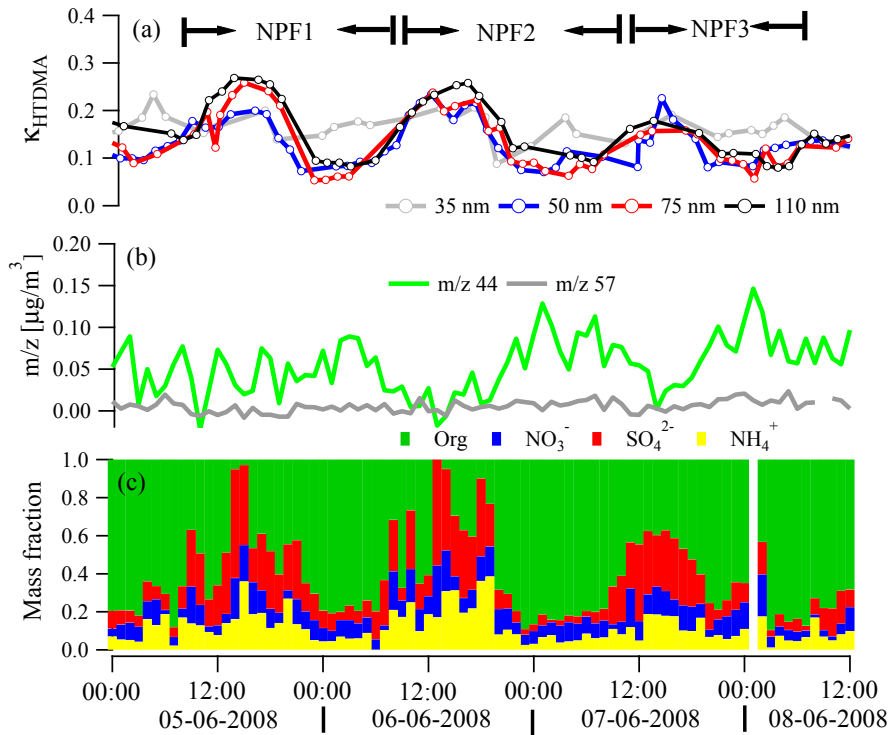
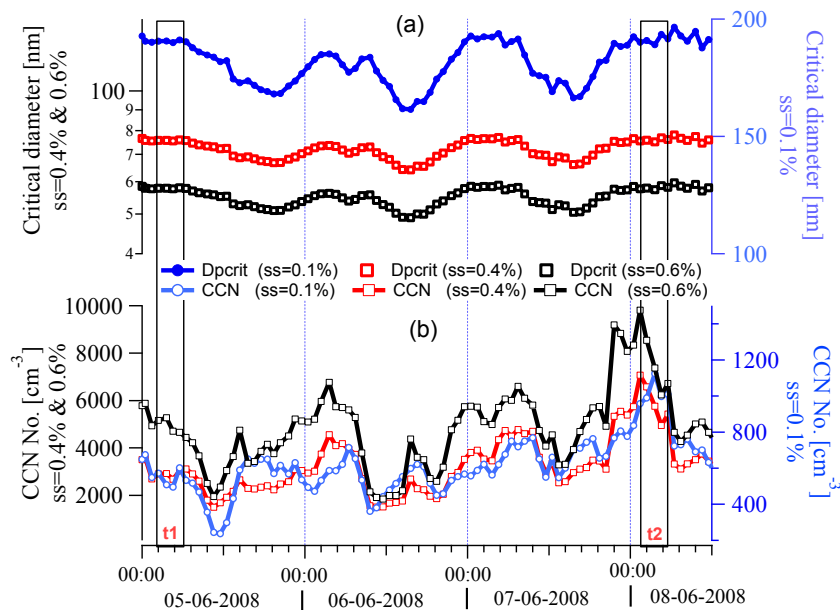


Fig.3: Size-resolved particle hygroscopicity (a), m/z 44 and 57 mass concentrations in 30-100 nm particles (b), and mass fraction of organic, sulfate, nitrate, and ammonium in 30-100 nm particles (c).

 page 8427, Fig. 2 $ss=0.1\%$ seems to be on the right axis. Please indicate if both $ss=0.4\%$ and $ss=0.6\%$ are on the left axis.

Response:

It was corrected.



References

- Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer, *Mass Spectrometry Reviews*, 26, 185-222, 10.1002/mas.20115, 2007.
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- Laakso, L., Petäjä, T., Lehtinen, K. E. J., Kulmala, M., Paatero, J., Hörrak, U., Tammet, H., and Joutsensaari, J.: Ion production rate in a boreal forest based on ion, particle and radiation measurements, *Atmos. Chem. Phys.*, 4, 1933-1943, 10.5194/acp-4-1933-2004, 2004.
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