**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Water uptake of biomass burning aerosol at sub- and supersaturated conditions: closure studies and implications for the role of organics" *by* U. Dusek et al.

Anonymous Referee #1

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This manuscript presents a study on water uptake of biomass burning aerosol with a detailed hygroscopicity closure study which tries to link the hygroscopicity (soluble fraction) below and above saturation. The subject of the paper is highly relevant and interesting, not many studies exist in this topic. The manuscript is nicely written, contains a comprehensive discussion on the findings, however I have the feeling that sometimes not every possible explanation of the observed behavior is taken into account. Another critical point is the data handling (see the general and specific comments), here substantial improvement is needed. In summary, I suggest the paper for publication in ACP but only after a significant improvement.

General comments:

Page 29859, line 16 (and the whole manuscript): The kappa value for ammonium sulfate is RH and particle size dependent. Using kappa=0.6 for both HTDMA and CCNC measurements (and also for different particle dry sizes) introduces error in the reported kappa values (for a 100nm ammonium sulfate particle kappa=0.63 at the point of activation, and kappa=0.53 at RH=85%). This error might not be big, but it is unnecessarily introduced and can be easily avoided. Therefore I suggest to calculate directly the kappa values from the measurements (as introduced by Petters and Kreidenweis, 2007) throughout the whole manuscript. Or calculate the proper kappa value for ammonium sulfate (at the applied RH and dry diameter) using the same water activity parametrization as it was used to derived epsilon and then use this ammonium sulphate kappa to derive the kappa value of your measurement.

Section 3.3: You define your "significant" supersaturation from the CCN activation curve where 50% of the particles are activated. In order to be sure that this method is correct you have to be sure, that you got successfully rid of any multiple charged particles and you don't have any background counts in the CCNC, so that your activation curve starts from 0. And also that at full activation the CCN/CN ratio is 1 (which is often not the case because of the independent measurements of the CN and CCN concentrations and/or not sufficient counting statistics at low concentrations). Did you measure both plateaus for the activation curves (for the example scan which is shown in Figure 2, neither the full activation nor the non-activation is captured)? Using another approach to define a "significant" supersaturation helps to get rid of this problem: fitting a sigmoid or cumulative Gaussian function on the data, where the base and maximum values are allowed to vary, is a solution. Of course it is only possible if you have sufficient measurement points. Which can be critical if measurements were performed only at 5 different supersaturations.

The difference between the derived supersaturations using the two methods (CCN/CN vs. supersaturation or epsilon) originates from the low resolution of your measure-

ments as well (as you have mentioned). Searching for the 50% activation point in the different spaces (CCN/CN vs. S or CCN/CN vs. epsilon space) is equivalent to different methods how you connect the two closest measurement points that surround the 50% activation: assuming a linear relationship (linear interpolation in the CCN/CN vs. S space) or a specific non-linear relationship (the epsilon vs. S relationship multiplied with a linear relationship which is equivalent to the linear interpolation in the CCN/CN vs. epsilon space). The observed difference between epsilon_CCN and epsilon_G is simply due to the different interpolation. With higher supersaturation resolution this difference would decrease, and in ideal case with arbitrary high resolution it would even disappear. So actually this is a measurement error caused by your low resolution which is independent from the uncertainty of the single measurement points. Therefore the two errors has to be summed to get the true error, and the "interpolation" error cannot be neglected just because it is smaller than the error originating from the uncertainty of the individual measurement points.

However, probably it is still better to use S_cˆm as "significant" supersaturation (linear interpolation in the CCN/CN vs. S space) and not the roughly 20% higher value. If the aerosol is not highly externally mixed (which is suggested by figure 1) then the CCN/CN spectrum is roughly anti-symmetrical around the 50% activation point. So a linear interpolation between the measurement points around the 50% activation is a better idea.

Sections 5 and 6: During the hygroscopicity closure mainly the mean soluble fractions from the HTDMA and CCNC are compared. However, for some individual experiments, "behavior", which is clearly different from the average "behavior" can be observed (e.g. the experiment where the 150nm particles seem to have at least a factor 2 higher epsilon_G than epsilon_CCN). I would suggest to discuss those extreme cases as well.

Specific comments:

Page 29855, line 4-5: Did you really burn and measure peat and grass? You show results only on different wood types. It would be actually nice to add a summarizing table with all experiments and fuel types to the manuscript.

Page 29856, line 1-2: The insoluble part plays a role as well, since the absolute amount of insoluble and soluble material determines the particle's size, which plays a big role in hygroscopic growth and CCN activation.

Page 29856, line 19-20: This is a strong statement. Can you really objectively say that?

Page 29858, line 10-12: If I am correct, for the multiple charge correction the size distribution data is needed. Did you have this information? Then please include the description of the instrument in the experimental part as well.

Page 29858, line 2-12: Please report on the length of one CCNC scan. How stable was the sampled aerosol during this period? How many CCN scans could you do during the 1 hour burns? Please answer the same question for the HTDMA measurements as well.

Page 29858, line 21-29: At which RH was the HTDMA measuring?

Page 29860, equation 3: This is not the definition for the ideal solutions, for ideal solutions i=1, this is a general equation for non-ideal solutions as well.

Page 29860, equation 4: Please mention, that this is the Köhler equation and give reference to it.

Page 29861, equation 5: This is again the Köhler equation, almost equivalent to equation 4 just using the mathematical approximation of $\exp(x) \sim 1+x$. It would make it easier for the reader to understand the equations if this was mentioned. Below and above saturation you are using the same equations to derive epsilon_G and epsilon_CCN just in the latter case you look for the maximum of the saturation curve. Therefore I suggest to merge 3.1 and 3.2 together: explain your water activity parametrization, derive the

Köhler equation (use consistent formulation e.g. RH=S) and then show first what is the difference between the derivation of epsilon_G and epsilon_CCN.

Page 29863, line 25 to page 29864, line 1: The RH measurement has an uncertainty of +-2%. This causes roughly +-3.5% uncertainty in the GF for sodium chloride measurements. You argue that since the measured biomass burning aerosol is much less hygroscopic, the uncertainty originating from the not precise RH measurement will be less than +-2%. From my point of view this argument is not correct. The propagation of the relative error on the RH is solely dependent on the first derivative of the GF(RH) function and has nothing to do with the GF(RH) value itself. So it is not a correct argument that the biomass burning aerosol is much less hygroscopic. If you have information on the first derivative of the GF(RH) function at the RH where the measurements were done (85%?) for both sodium chloride and the biomass burning aerosol then you can determine the propagated error on the GF. Otherwise, if the needed data is not available, I suggest to calculate epsilon_G for your individual measurement points assuming 2% lower and 2% higher RH as well to get the correct uncertainty of epsilon.

Page 29864, line 14 and 15: the CCN/CN term in the formulas after the delta sign has to be in brackets.

Page 29864, section 3.5: This section belongs more to the sensitivity studies, since as you show, the non-sphericity of the particles can lead to significant differences between epsilon_G and epsilon_CCN. I would move this section under section 4.

Page 29866, line 8: Change "We can deduce from his example" to "We can deduce from this example"

Page 29867, line 1-2: How "roughly" can levoglucosan be approximated to be an ideal solution? Is the non-ideality of levoglucosan neglectable when one compares it to the non-ideality of ammonium sulfate?

Page 29867, equations 11 and 12: Repetition of the equations. Could be easily refer-

enced if a good theory section existed.

Page 29867, line 12: Why did you solve it for RH=90%? It was not clearly stated but it seems to me that the GF measurements were performed at 85%. Please do the calculations at the RH where the measurements were done.

Page 29867, line 18-21: Here, you only test the effect of the non-ideality of your model salt. The effect of the non-ideality of the biomass burning aerosol has to be added to this. Can you be sure, that that is not much higher than for ammonium sulphate (e.g. if there are, give references where biomass burning aerosol seems to behave ideally, or close to that)?

Page 29868, 1st 2 sentences: Please emphasize here as well, that epsilon_G and epsilon_CCN are calculated using the surface tension of pure water

Page 29868, line 7: When you used levoglucosan as a model substance, did you assume again its ideal behavior?

Page 29868, line 17: "Epsilon_G (or kappa_G) is not influenced by a change in surface tension" Please reformulate this sentence, they are influenced but only slightly.

Page 29868, line 17-23: Please state at which RH did you do the calculations

Page 29868, line 24-27: Why is it a problem if the hygroscopicity parameter exceeds 1? It simply means that you have something, which is more hygroscopic than pure levoglucosan, or has lower surface tension. If you prefer ammonium sulfate as a model substance, just use it (it is your free choice, section 4.1 shows that ammonium sulfate is a usable model salt).

Page 29869, line 7: at which temperature does succinic acid has this solubility?

Page 29869, 2nd paragraph: Please mention already before the equations that succinic acid is treated as an ideal solution.

Page 29869, line 17-18: if the solubility is used in g/l, then the density of water has to

be also in g/l in equation 13. Please confirm that you used the correct units.

Page 29870, line 4: Again, why 90%?

Page 29870, line 18: Was something different during those pre-experiments?

Page 29870, line 27: Janhäll et al., 2010 is not in the reference list! Do you mean this paper: Biomass burning aerosol emissions from vegetation fires: particle number and mass emission factors and size distributions in ACP? In that paper I did not find anything about the hygroscopicity.

Page 29871, 10-18: Can you give an estimate to what extent should the slightly soluble material be enriched?

Page 29871, 18-25: I don't see, why the lowered surface tension is the most likely explanation. You have shown in section 3.5 that a relative small deviation from the sphericity could cause the observed phenomenon as well. Why is this less likely? Smaller parcticles -> less condensed organics and therefore higher soot fraction -> less spherical particles. For me this explanation seems as reasonable as the lowered surface tension.

Page 29871, 18-25: And could you also give here an estimate what surface tension would be needed to explain the observed discrepancy between the GF and CCN measurements.

Page 29872, 22-26: As you state: both effects reduce epsilon_G compared to epsilon_CCN. But the epsilon_G values are symmetrically distributed around the mean epsilon_CCN values. So if this was the real reason for the scatter, something else should be responsible for the higher epsilon_G average. What could that be?

Table 2: Last column should read epsilon_G. Please mention in the caption that you used the levoglucosan as model substance as well. The growth factor has a symbol of G here, in the other tables it is GF. Please be consistent.

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Table 3: Please include the values for epsilon_G as well

Table 4: In the first column you write "succ." in the others "succ"

Table 5: "succinic", please be consistent with table 4

Figure 2: The legend in panel (a) says "Data" for the black symbols, panel (b) says "Mean". Please be consistent. Still the legend: what is Sm?

Figure 3: Please add the standard deviations as error bars to see the variability of the individual measurements

Figure 5: Please add to the caption as well that at which diameters were the measurements performed. Please add also to which experiment number what kind of fuel belongs.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 29853, 2010.