

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 #2

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The manuscript by Dusek et al. (ACPD-10-29853-2010) describes laboratory experiments in which aerosol particles produced from different biomass burning experiments were examined with respect to their water uptake at sub- and supersaturated conditions. It gives a thorough examination of how different effects/parameters related to water uptake (surface tension, slight solubility, particle non-ideality, shape factor) can influence the results obtained from these kinds of measurements, before then the derived results are interpreted. This is an interesting and valuable study a) because particles originating from biomass burning certainly influence the atmospheric aerosol, at least close to the source regions, and b) because the sensitivity studies nicely show the uncertainties introduced by the different effects/parameters. Therefore, this manuscript

might deserve publication after the review process.

However, my concern about the data evaluation presented in this paper is, that artificial errors are introduced where it is not necessary. This concerns the use of epsilon(CCN) instead of using epsilon(Sm) (see my specific comments below), as well as deriving the soluble volume fraction (epsilon) related to ammonium sulfate as a proxy, where the full non-ideal behavior of ammonium sulfate is included (also more about this below), although the examined particles might not show this kind of non-ideal behavior at all. Also, epsilon is more difficult to generalize than e.g. the particle hygroscopicity parameter kappa, which is often used today. I refrain from demanding that the data evaluation and also the error/sensitivity studies should be based on kappa (instead of using epsilon), but I think this would certainly improve the paper. However, it is up to the authors to decide if they want to change this or not.

Nevertheless, there are additional specific comments that need to be addressed, and I cannot suggest publication of this manuscript before revisions will have been made.

Specific comments:

Abstract, lines 22ff: Does this last sentence relate to the 50nm particles, or to biomass burning particles in general? If it is a general value, how does $k=0.15-0.2$ compare to $k=0.07$ you give in line 10 in the abstract?

page 29856, lines 27-28: I suggest you explain this in the light of the deliquescence process (i.e. dilution at the RH where particles just form a saturated solution).

page 29857, lines 1-3: The effect you mention (i.e. that SA substances barely affect water uptake at subsaturated conditions, but can have a large effect on the critical supersaturation) is shown in detail in a paper you've cited earlier, anyway (Wex et al. 2008), so you should mention that here, too.

page 29857, line 13: Also Chang et al. (2007) did not achieve closure between $N(\text{CCN})$ as measured directly with those derived from AMS measurements during times when

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the organic content of the aerosol was high. They also relate this to solubility or surface tension effects. Please add this citation here.

page 29858, line 4: Is this the CCN counter as described in Roberts and Nenes (2005)? If yes, please say so.

page 29859, line 2: The sentence needs to be reformulated; it sounds strange that the discrepancies should be based on model calculations.

page 29862, lines 1-2: Please, for clarity, add to the text in the parenthesis, that you, however, omit a concentration dependent behavior of sigma.

page 29862, lines 14ff: I found it confusing to have this paragraph first, and then, in the next paragraph, being introduced to the example of very smooth humidified size distributions with only one mode (in Figure 1). Reverse the order of these two paragraphs, and make it clear if the problems you describe for the biomass burning aerosol relate to the broadness of the measured peaks or to multiple peaks that you observed, or to both.

page 29862, line 21: The curves you show in Figure 1 are very smooth – were they really measured and then smoothed, or are these theoretical values? Please explain in the text.

page 29863, line 9ff: You introduce an artificial error to your data by your choice of using epsilon(CCN) instead of epsilon(S). In the past, this kind of data (as in Figure 2a) has been evaluated by fitting an error-function to the data (e.g. Rose et al. (2008)). This would have been better instead of using an interpolation to get S_m , as you did. It gets worse when you derive epsilon for all your measured data and interpolate then. The deviation between epsilon(CCN) and epsilon(S_m) will depend strongly on the number of measurement points you have in the interval around $CCN/CN=0.5$. You can still show the error that is introduced by the second method you showed, but for the evaluation of your own data you use later on, I suggest following what has been established as a

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feasible way of data evaluation, i.e. the error function fit, or at least use epsilon(S_m).

page 29863, line 23: Please add to the text, if you used a shape factor for NaCl, and if yes, which one?

page 29864, line 1ff: Where do the <2% come from? Do you simply relate the 2% uncertainty in RH to 2% uncertainty in the growth factor? This cannot be done so easily, because at lower RH (i.e. where growth factor curves are less steep) an uncertainty in RH translates into a much smaller uncertainty in the growth factor than at higher RH (where the growth factor curve is steep). Anyway: This whole paragraph goes back and forth a bit. I suggest you include a Figure showing the theoretical growth factor curve for an aerosol with a GF of 1.1 at 85% RH (and maybe a further one for a GF of 1.4) (this corresponds to kappa of about 0.06 to 0.09). From this curve clearly will follow the uncertainty in the growth factors for the 2% uncertainty in RH. This saves you a lot of guessing and you can write this paragraph more straight forward.

page 29865, lines 1-2: What do you mean by “The critical supersaturations ... do not depend on the equivalent particle diameter”? You measure a pair, consisting of “supersaturation” vs. “critical dry diameter”, so there is a dependency. I guess I do not understand what you want to say -> please clarify.

page 29865, lines 6-7: This is only true if the dry particle is non-spherical – please clarify in the text!

page 29866, line 4: Please mention that Eqs. 11-12 will follow in 4.1.

page 29866, lines 4-5: Add / replace text, starting at the beginning of the sentence in the middle of line 4: “To derive epsilon(g) we then use the calculated $d(\text{wet})$ and $d(\text{m})$ of 100nm, as it were done to evaluate the data if the shape factor were not known. [The measured hygroscopic growth factor ... strongly with increasing X], i.e. the derived epsilon(g) will be too small, and increasingly so with increasing shape factor. Also, the critical supersaturations were determined as described in 4.1. [Since the ...]”

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page 29867, lines 1ff: As you say, water uptake of levoglucosan can be approximated by that of an ideal solution with a van't Hof factor of 1. This touches one of my main concerns with your way of evaluating the data: by the use of ammonium sulfate as the proxy, from which you derive epsilon, you will get an artificial error for any substance that has a different concentration dependency in its non-ideal behavior than ammonium sulfate. If one wants to be able to disentangle these kinds of effects at all, it would be of advantage to first assume as little as needed when deriving epsilon (or kappa, for that means), and go on from there. You show correctly that assuming a non-ideal behavior that might not be there introduces an error. If you examined a substance that has a non-ideal behavior different than that of ammonium sulfate, these two different non-idealities start to be entangled so much that information is really lost. Therefore, as mentioned above, it might be advantageous to use kappa throughout your work. If, however, you decide to continue using epsilon, please add to the text how large the error introduced here is, compared to the errors introduced by the shape factor, SA and SS.

page 29868, 4.2: Start the chapter with a description of how you obtained the values in Table 3, e.g.: Values that would be measured for Sc if the surface tension was reduced were calculated, and from these values epsilon was derived while using the surface tension of water!

page 29868, lines 5-6: Please explain how you know that the increase in epsilon(CCN) is independent of particle diameter.

page 29868, lines 10-11: It is exactly this sentence that made me suggest do change your way of data evaluation, because this is absolutely correct!

page 29868, lines 24ff: Table 3 does not show that levoglucosan is not the model substance of choice. The surface tension reduction you assume here is pretty large, already, compared to what is generally observed (a lowering of 30% might be as low as it was observed for atmospherically relevant substances). So you do not really

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observe that epsilon exceeds 1. Also, if epsilon exceeds 1, this only means that the hygroscopicity of the particle is larger than that of levoglucosan. These large epsilon values >1 could, however, still be used. (Similarly it could be argued that the water uptake of e.g. NaCl particles cannot be described by using epsilon and ammonium sulfate as a proxy, and with this discard also ammonium sulfate as a suitable proxy.)

page 29870, lines 5ff: You showed earlier, that at least the shape effect can introduce a similar error, and the use of ammonium sulfate as a proxy acts similar. These effects cannot be disentangled from the effect of SS, therefore your conclusion here is too strong.

page 29872, line 1: Why do you show these additional data, if they were done for different burning conditions? Show at least which of your data originated from that earlier campaign, e.g. through the use of different symbols.

Figure 3: Add error bars to the epsilon values.

Literature: Chang, R. Y.-W., P. S. K. Liu, W. R. Leitch, and J. P. D. Abbatt (2007), Comparison between measured and predicted CCN concentrations at Egbert, Ontario: Focus on the organic aerosol fraction at a semi-rural site, *Atmos. Environ.*, 41, 8172-8182.

Roberts, G., and A. Nenes (2005), A continuous-flow streamwise thermal-gradient CCN chamber for atmospheric measurements, *Aerosol Sci. Technol.*, 39, 206-221.

Rose, D., S. S. Gunthe, E. Mikhailov, G. P. Frank, U. Dusek, M. O. Andreae, and U. Pöschl (2008), Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNc): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment, *Atmos. Chem. Phys.*, 8, 1153-1179.

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