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Atmospheric
Chemistry
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Discussions

# *Interactive comment on* "Hygroscopic properties of Amazonian biomass burning and European background HULIS and investigation of their effects on surface tension with two models linking H-TDMA to CCNC data" *by* E. O. Fors et al.

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Reply to anonymous referee no. 2.

First of all we would like to thank the referee for insightful and relevant remarks! We have tried our best to give adequate answers and we have made corrections in the manuscript according to the recommendations given. The answers are in the same order as in the referee comments.

1) Good point! The growth factors have been recalculated according to their "minimum

size” including the shrinking. This way the effect in taken into account as much as possible. We are not sure why some restructure and some not. It can be a question of the sample, but also of changes in nebulising conditions such as droplet size, solute concentration etc., as well as conditions drying the particles. Since the same H-TDMA was used for all samples, we assume that it is sample dependent. The following text has been added: “The reason for this behaviour is unknown. It cannot be determined whether this effect originates from different nebulising and drying conditions and/or if it is the sample properties that are different. The growth factors used in this work are recalculated so that the minimum growth factor equals 1, to avoid underestimating the water uptake of the samples.” Regarding the connection between aw and RH, is true that equation 2 is always used for the conversion. The text after equations 3a anb b has been changed to “where kappa_R is the number of soluble entities per volume dry unit, M_w the molecular weight of water, _w the water density, and chi_omega a correction term introduced to account for non-ideal behaviour, and aw calculated according to equation 2.”

2) Equation 14 is used to make one parameter fits in figure 2 (The K-Puszta samples) for the samples. Then these fitted humidograms were used as an input to equation 13, where we used the volume fraction of HULIS as a flexible parameter. This way we could make an estimation of the volume fraction HULIS of the total extract, and these values are presented on line 24 and 25 on page 26944. The relevance is that it gives a quantification of the actual amount of HULIS in the water soluble extract. Even though it was found to be very surface active, apparently it did not affect the full sample very much since a nice closure was achieved based on water surface tension. Regarding figure 3, the lines are max and min GFs during the filter sampling period, and are based on on-site measurements from the H-TDMA, and then weighted as an internally mixed aerosol. This can be seen as an indicator on how much of the aerosol was actually HULIS, even though it is not quantified in this case. The details on this data can be found in Rissler et al. (2006).

3) It is correct that it is basically the Köhler equation in the form represented in equation 6, but with the simplification that the Kelvin effect is not included, since aw is substituted for RH over the whole humidogram.

4) Full dissociation in this case means that chi_omega in Eq. 3 and 4 is equal to 1, i.e. the solution behaves ideally. The only way ammonium sulphate is used is to estimate chi_omega in the non-ideal case. This does not mean that we assume that the number of moles of ions in each molecule is set to 3. Kappa is ions/non-dissociating molecules and is not the number of molecules (no dissociation factor needed). The best-fit K_R is the ion density assuming that not all ions/molecules are directly reflected in the Gf (as for most salts). We try to clarify this further by changing the scentence to "The calculations were made both assuming a dissociation as that of a model salt (here using chi_omega according to Ammonium sulphate) and assuming full dissociation (chi_omega=1; values in parenthesis). In previous studies that use the model epsilon has been used representing the soluble material (Rissler et al., 2004). In this case epsilon is very related to the model salt. The advantage with kappa is that is does not refer as much to the model salt but to a "physical number".

5) We are not sure what meant in the first part of the question is. kappa_R is in the model used as a constant. For ammonium sulphate the van't Hoff factor is close to 2 at 90% RH, which means that the "full dissociation" or "ideal" way of calculating will give you a lower kappa_R value. The kappa_R value will change slightly when you use different RH values from the H-HTDMA data, but in this case, an average value was used. The parameter that changes with water activity is, like you state, chi_omega, which is in some sense represents the "non-ideality" of the model salt. In this case it is implicitly represented by the van't Hoff factor, and the values used when extrapolating into the supersaturated regime are from Low et al. (1969). The choosing of ammonium sulphate is somewhat arbitrary, and mostly chosen because it has been frequently used in the past (because it is the dominating inorganic salt in many ambient aerosols), and we want to test the model similarly as in previous studies and show the difference to the

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“ideal” case. Since the HULIS sample does not contain any inorganics, the non-ideality introduced by the salt is not likely to describe the pure HULIS very well. On the other hand, the van’t Hoff factor does not change very much between 90% and the points of activation in this case, surface activity and exclusion of the dry particle volume at the point of activation are the dominating effects in this case. In the case of _ion, it is also a “static” parameter, in the sense that it does not change when the RH changes. Just like with kappa_R, you will obtain different values of _ion depending on what data point in the humidogram you use, but once a value is set, it stays constant according to equation 6 during the extrapolation into supersaturation. In this model there is no “non-ideality” taken into account.

6) The following sentence has been added after equation 3: “It should be noted that equation 4 is only valid under the assumption that the dry particle volume is negligible, a fact which which will be further analysed later in this paper.” It is true that it is quite possible to use a version of equation 6 to determine the critical supersaturation also with kappa_R. In fact, _ion and kappa_R have the same physical meaning, namely the number of soluble entities per dry volume unit. The reason for using equation 4 is that it is a widespread equation and has traditionally been used to predict the point of activation, and still is. Possibly because it is simpler, as one does not have to find the maximum of the Köhler curve since equation 4 presents a simple analytical solution.

7) It is true that the surface tension is somehow taken into account when kappa_R is calculated from subsaturation. The kappa_R value includes both solubility and surface activity. However, it is important that the sensitivity of kappa_R on the surface tension at subsaturation is not as high as the dependence of the critical supersaturation on the surface tension. In other words, the surface tension plays a bigger role at activation than at subsaturation. Regarding the connection between aw and RH, water surface tension is used for the Kelvin effect at subsaturation. Of course it would be possible to use a combination of the two models, and use both non-ideality of a model salt and a parameterized surface tension according to Szyskowsi-Langmuir, but in this

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work we chose to evaluate already established methods rather than to suggest a new one. The sentence “the presence of surface active compounds Is neglected” has been changed to “the presence of surface active compounds is to a large extent neglected. While a surface active compound would in fact influence the kappa_R value in one way, via the molality and density parameterisations of ammonium sulphate from Tang and Munkelwitz (1994) and Potokuchy and Wexler (1995), the conversion from RH to aw assumes water surface tension already at subsaturation, and again the surface tension reappears as a parameter in equation 4.”

8) We can only agree with this point! Even though there are now numerous studies on this matter, there are simply too many free parameters to come to a definite conclusion. It would be easier if the H-TDMA data was complemented with surface tension measurements and ideally also with some quantification of molecular weight for different types of sample. But even then, since HULIS is quite a wide concept, different samples will have widely different properties even though the same principle of extraction is applied (as in this work). We feel that it is somehow practical to bulk all these unknown properties together, by e.g. attributing any deviation from an ideal solution with water surface tension solely to surface tension effects and ignore surface-to-bulk partitioning, limited solubility, non-idealities etc.

9) This is true, there is often a less hygroscopic or near hydrophobic mode present in the ambient aerosol. The sentence has been changed to the following: “Under normal circumstances, such as measurements of ambient aerosols, there are often both more hygroscopic and less hygroscopic particles present, as well as near hydrophobic particles (Swietlickiet al. 2008). When performing e.g. CCN closure studies or parameterisations of CCN concentrations based on H-TDMA data it can therefore be important to take this fact under consideration as well as when dealing with isolated compounds of low solubility such as HULIS, as can be seen from the difference in critical supersaturation predicted by the two models used in this paper.” Later in the same page the following was added: “Based on the results from this work, equation 4 should

only be applied for GF > 1.1, which gives an overestimation of the sc value of 2% for 50 nm particles. However, for smaller particles, larger growth factors should be used as threshold values for the same relative error."

10) Good point. As previously discussed in this reply, for practical reasons we have attributed all deviations from ideal solution with water surface tension to surface activity. The text has been changed to the following for clarification: ". In any case, assuming that the ion is a valid representation of the particle-water interaction, these results indicate that the rural HULIS discussed in this work is more surface active than the urban HULIS previously investigated by Ziese et al. (2007), which gave $\sigma$ values for HULIS between 52.1 mN/m (dry diameter 40.6 nm) and 70.3 mN/m (dry diameter 125 nm). The reason for this behaviour remains unknown, but since the HULIS is defined solely by the method of extraction, it can be expected that different particle sources will present different kinds of HULIS. It should also be noted that the apparent difference in surface tension also could be attributed to differences in e.g. increasing solubility with water activity. "

11) Thank you!

12) Thank you again!

13) See question 12.

14) We have studied the extraction efficiency by extracting pieces of hi-volume filters with different amount of water and measuring the DOC content of the extract. We have concluded that 2 ml of water for 1 cm2 of filter was adequate with the carbon load present in our samples. So, the assumption is correct, water is in such excess that even slightly soluble species are expected to dissolve in the water-soluble fraction.

15) This somehow disappeared in the publication; we will make sure it is included in the final printing.

16) Same as 15).

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17) The following has been added as a hypothesis: “This is possibly due to the aging process of the aerosol. During night the boundary layer collapses and the sampling is more dominated by fresh particles from smouldering. During daytime, the boundary layer height increases and aged particles are mixed down (Rissler et al., 2006). As has been recently shown recently by Jimenez et al. (2009), aged SOA tend to be more oxidized and more soluble than fresh SOA, which would support these results.”

18) See the answer to 1).

19) This is correct; the numbering of the figures has been changed.

20) This will be corrected for.

21) This is now corrected

22) The figure text has been changed to the following for clarification: “Measured critical supersaturations for the K-puszta samples. The lines represent the supersaturation ratios of three different arbitrary ideal compunds as a function of dry diameter, Dp., and are intended solely to guide the eye on the ideal dependence of sc on Dp. The sc values are calculated according to equation 4.”

23) This is now corrected.

24) After discussions we have decided that we will keep the figure, as we feel it is vital to the discussions regarding the modeling errors.

25) This is now corrected.

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