

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.

Anonymous Referee #2

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The paper describes the extraction of filter samples from both the dry (burning) season in Amazonia and from K-Pusztá (Hungarian urban site), and the subsequent examination of the subsaturated growth and CCN activity of various extracted fractions. The authors draw some interesting analogies between the observed behaviors of these samples, which contribute to understanding of organic aerosol components and their role in water uptake and CCN activity. The material is generally well presented and the subject matter of interest to ACP readers. I recommend the article be published after the authors consider the following proposed clarifications.

Comments:

1. One aspect that is not entirely clear to me is whether / how the Gf data are corrected for either rearrangement ($G_f < 1$) or for the Kelvin effect when water activities are derived from them using the K_R model. Equation (3) shows how Gf relates to a_w . Is equation (2) used to change the measured RH to a_w ? (In contrast to the K_R fits, it seems that equation (6) can be applied at all values of RH, from subsaturated to supersaturated, so this concern should not arise when applying the rho_ion model; however, it might be useful to clarify the RH \rightarrow a_w step in the data fitting for both models, just for completeness.)

2. I don't understand when or why equation (13) is used. Which figure has a line constructed using this equation – is it Figure 3? I was confused (both here and in the discussion on p. 26940, lines 17-18) whether the lines in Figure 3 represented actual HTDMA data taken during the study, or were constructed afterward from volume fractions of the aerosol (are those various data shown – ie, the fractions of various components and their measured hygroscopicities?). I may have missed this, but this figure and discussion seemed a bit beyond the main point of the paper, which is to look for closure between sub- and supersaturated water contents of various organic fractions extracted from filter samples.

3. I also do not understand why Equation (14) is used to fit data. Is it not the same as equation (3), except for the need to relate a_w to RH? Since equation (3) is used to fit the data in most of the text, why are those fits not shown in Figure 2 instead of introducing Equation (14)?

4. p. 26940, lines 13 - 14: For the calculation of the K_R values, it is stated that they were made in two ways. One, assuming the dissociation is the same as ammonium sulphate, and two, assuming “full” dissociation. Since the chemical structure of the HULIS is not known, what is assumed for “full” dissociation? It is called “ideal behavior” in the Tables, which means (p. 26936, line 1) $\chi_\phi=1$. Does it mean that implicitly,

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ν (number of moles of ions in each molecule) is set =3 and this is captured in the K_R best-fit variable, so that the best-fit K_R of all other compounds can be directly compared to that for ammonium sulphate?

5. Following on point (4), and this also relates to pg. 26935-6, where the fitting of K_R is initially described: It seems that the approach assumes that the quantity χ_ϕ varies with a_w for the organic mixtures in the same way as it varies with a_w for ammonium sulphate. Is there a reason to expect that this is the case for organics, or is this similar behavior simply assumed to facilitate comparison with ammonium sulphate? The fits then yield estimates of K_R which probably vary with a_w , since χ_ϕ varies with a_w . It might be helpful to clearly state here that K_R is not a constant, unlike in some single-parameter fitting approaches. (I believe the same is true for ρ_{ion} : its defining equation means it is also not a constant even for ideal solutions.)

6. Equation (4) is only valid for the determination of critical supersaturation for a subset of conditions, as shown later in the paper: when the water contents are too low, the approximations leading to equation (4) are not valid. It might be helpful to note this when the equation is first introduced. Why is it even necessary to apply equation (4)? Once representative values for K_R have been obtained, at the highest possible RHs, could not an equation analogous to equation (6) be applied to determine critical supersaturations?

7. p. 26936, line 18-19: The method does not really neglect the presence of surface active compounds. I believe it accounts for their presence (albeit in an unknown way) through the derived values of K_R . However, it is true that the conversion between RH and a_w for the fitting also requires an assumption about the surface tension. It's not clear to me this has been consistently applied through the initial data reduction and the subsequent sensitivity calculations in Section 5.3. Can you please explain this more clearly?

8. p. 26936, and following, especially pg. 26941: The adjustment of surface tension

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to bring the predictions from subsaturated growth into agreement with the direct CCN measurements is interesting. For both the K_R and ρ_{ion} approaches, it is implicitly assumed that a single aqueous phase exists and that the water activities derived apply over the full range of solution compositions, so that surface tension becomes the only variable that can be adjusted to bring the measurements and extrapolations into agreement. As discussed in the text, other researchers have also found cases where the extrapolation does not work within experimental errors, most notably for α -pinene / O₃ SOA (e.g., Duplissy et al., 2008) but also for field samples (e.g., Mochida et al., JGR, 2006). As discussed by Prenni et al. (JGR, 2007), although surface tension suppression can certainly explain this behavior, several other factors may also play a role, including gradual dissolution or the presence of salts with high deliquescence points, as discussed in the manuscript. Wex et al. (ACP, 2009) explored some of these possibilities and Petters et al. (ACP, 2009) suggested that highly nonideal thermodynamics for aqueous solutions of organic species could be responsible. To my knowledge, however, none of these prior studies could unequivocally state the reason for the lack of simple closure. It remains a very interesting phenomenon that some systems, and HULIS in particular, display this behavior.

9. p. 26943, line 4-5: it is stated that the effect of neglecting the solute volume will not be important for ambient aerosols, but I don't see why this should be the case. Certainly many measurements have been reported of low-hygroscopicity ambient aerosols? It seems more valid to state that the solute volume can be neglected provided the measured G_f is larger than (X , some derived value).

10. p. 26944, lines 11-15: I'm not sure it can be concluded for certain that one sample is more surface active than the other, unless of course the statement is qualified as valid IF the hygroscopicity model applied to both cases is in fact an accurate description of the aerosols.

11. p. 26945: Very nice and informative discussion.

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12. Section 6: This discussion, with broader context, is helpful. It appears there is a developing consensus on the water uptake at low RH by HULIS, and this section discusses nicely the potential role of surface tension suppression in ambient aerosols. It is a useful contribution to current understanding.

Minor points:

13. The discussion in the Introduction summarizing what is known about HULIS is very helpful.

14. p. 26931, line 10: Does it matter the volume of water that was used for extraction, or is it always in such excess that even slightly soluble species are expected to dissolve in the water-soluble fraction? Perhaps it would help to give the volume of water used here, for comparison with other studies, in case this factor makes a difference when comparing between them.

15. p. 26937, line 11: the symbol “phi” is missing from the sentence: “into and PHI is the...”

16. p. 26939, line 1: the symbol “rho_ion” is missing from the sentence: “calculate a new RHO_ION and the iteration...”

17. p. 26940: it is interesting that the day samples were more hygroscopic than the night samples.

18. p. 26941, line 21: Were Gf corrected for restructuring before fitting?

19. p. 26942, line 5: I believe that Figure 9 is referred to before Figures 7 and 8.

20. Figure 9 would be easier to compare with Figure 6 if it had log-log axes also. The log-log axes are more commonly used to display the CCN data.

21. Table 3: KAPPA is spelled out; I think this should be K_R

22. Figure 6: what are the straight lines that are shown? These are not explained

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either in the figure caption or the text. Why are they included?

23. Figure 7: “K-pushta winter” missing a space.

24. Figure 8: with the scales as presented it is hard to glean from this figure what the authors intend to convey, namely, that the model has incorrect limiting behavior because the curves should end at their respective horizontal lines. Is there a better way to show this, or perhaps the figure could just be removed and the results explained briefly?

25. The reference Ziese et al. (2007) is missing.

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