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Interactive comment on "Hygroscopicity of organic compounds from biomass burning and their influence on the water uptake of mixed organic–ammonium sulfate aerosols" *by* T. Lei et al.

Anonymous Referee #1

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Review of ACPD Lei et al. Hygroscopicity of organic compounds from biomass burning. . .

The paper reports the results of laboratory HTDMA studies of particles composed of species that are proxies for the organic compounds detected in biomass burning (BB) particle-phase emissions, as well as mixed inorganic-organic particles. The authors also conducted extensive comparisons with available thermodynamic models, including a simple idealized water uptake scenario + ZSR assumption. A main conclusion drawn from the study is that water uptake in BB particles can occur beginning at low relative humidity due to the presence of the organics, and that this initial water uptake can begin to dissolve inorganic components such as ammonium sulfate, lowering the apparent deliquescence humidity.

The experimental methodology appears to be sound and the manuscript is generally well-written. However, there are three main issues with this paper that result in my inability to recommend it for publication in its present form, as follows.

(1) The authors have failed to cite a large body of literature that has addressed the same questions as presented here. This includes uncited studies of levoglucosan water uptake, HULIs water uptake, and BB-surrogate mixed particle water uptake.

(2) As a result of (1), the results from this work are largely well-known and thus unsurprising. There are few original ideas or new insights contributed by this study, with the possible exception of 4-hydroxybenzoic acid, which as far as I can tell has only been investigated in one prior HTDMA study. Unfortunately, because of the way the HTDMA experiments were conducted, this is largely a negative result because this compound showed no water uptake up to the RHs that were achieved.

(3) The curve fits that are provided by the authors to summarize their data, for use in future water uptake calculations, are not accurate because they have not been corrected for Kelvin effects. Thus, this main product from this work requires revision before it can be used by the community.

Below I elaborate on each of these points in detail.

Point (1):

Regarding levoglucosan water uptake, in the Introduction the authors cite only Mochida and Kawamura (2004): “Studies about the hygroscopicity of individual organic compounds characteristic to biomass burning aerosol particles were performed by Mochida and Kawamura (2004).” Svenningsson et al. (2006), whose work is cited later in the paper, also studied levoglucosan and other BB surrogates, as well as mixtures with inorganics (see next point). Koehler et al. (2006), a paper not cited in this manuscript, studied levoglucosan particles with an HTDMA and curve-fit GF similarly to the method presented here. They also checked against idealized solution theory (which is discussed in section 2.2.5 as if this was a unique feature of this work, but has been examined in Koehler et al for the levoglucosan system and in many other papers for other compounds). Furthermore Koehler et al. showed that levoglucosan, glucose and fructose were all similar in water uptake, which demonstrates that molecular size and structure (i.e., idealized treatment) are sufficient to capture hygroscopic behaviors. They also summarized relevant experimental data on sugars available up to that point, many of which papers are not referenced here. Koehler et al. (2006) has been cited 40 times and Svenningsson et al. (2006) has been cited 125 times. In all of these citing papers there are certainly several that are relevant to this manuscript and have not been included in the literature survey presented here.

The authors state (p.11629, lines 1-3) that “published results on the effects of organic surrogate compounds from biomass burning on the hygroscopic properties of otherwise inorganic aerosol are sparse (Brooks et al., 2004; Gysel et al., 2004; Mochida and Kawamura, 2004; Badger et al., 2006).” There are many studies that have been missed in this list, including a number on mixed HULIs / inorganics (see Dinar et al., 2007, for example), dicarboxylic acid / inorganics (e.g., Frosch et al., 2011, among others), surrogate mixtures (Svenningsson et al., 2006), and BB particles directly (e.g., Carrico et al., 2008; Dusek et al., 2011).

Finally, one highly relevant uncited paper is Mikhailov et al. (2008), Influence of chemical composition and microstructure on the hygroscopic growth of pyrogenic aerosol. They created model smoke particles and studied GF, and discuss findings with regard to particle restructuring, a phenomenon alluded to in the manuscript.

Point (2):

In the Introduction, line 23 on p. 11628, the authors state, “it is still uncertain whether these WSOC are inherently CCN active or whether they are made active through association with water-soluble inorganic species.” This statement is not true. First, we know a lot about hygroscopicity of organic compounds from work that has been done over the last 15 years. Indeed, it seems strange to ask whether the WSOC fraction of an aerosol is hygroscopic. If a compound is water soluble and thus in the WSOC fraction, it will surely exhibit water uptake, the main question being what its deliquescence RH is, which determines if it can exhibit water uptake at low RH or not. Further, the statement is not well-posed since “CCN active” is imprecise. It depends not only on composition, but on the particle size and on the supersaturation. Finally, this work does not address CCN activity, because the RH remains below about 90%. Some organic species have relatively low solubility and thus a high DRH, yet in an activating cloud drop can contribute to the total water uptake when this DRH is exceeded.

Which brings me to a shortcoming of this work. It is too bad the experimental protocol did not include first raising the particles to very high RH, then drying to the RH setpoint. In this way the authors could probe hysteresis effects that are alluded to in the discussion; for example, the 4-hydroxybenzoic acid may have dissolved under such conditions and the supersaturated solution persisted until the GF measurement. This well-known approach could address one of the main open-ended findings from this work.

Point (3):

The authors have not corrected RH to aw (section 2.2.1). In fact Kreidenweis et al. (2005) point out that for 100 nm particles as used in this study, neglecting this correction makes several % difference in the results. All of the data should be corrected to aw before being curve fit; otherwise the curve fits cannot properly represent solution behavior. It is unclear whether some of the minor discrepancies between theory and experiment that are discussed later in the paper are actually attributable to this error.

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The discussion in section 3.1 and later seems to attribute some experiment-to-model differences to assumptions about particle density. This assertion surprised me. In general when this question has been looked at before, small errors in density propagate only slightly into errors in water activity (not true for large restructuring, however). My impression has been that volume additivity is often an accurate-enough assumption for interpretation of water uptake. Are the authors suggesting otherwise? If so and if they can support this argument, it would be helpful and of interest. Please clarify the discussion of this point to state more clearly the differences between ideal density and actual solution densities and how this impacts water activity estimates.

Minor comments:

Page 11635: “DRH” should read “GF”

Page 11646, line 21: “focus” should be “focuses”

âĂČ References (not cited in manuscript)

Carrico, C.M., Petters, M.D., Kreidenweis, S.M., Collett, Jr., J.L., Engling, G. and Malm, W.C., Aerosol hygroscopicity and cloud droplet activation of extracts of filters from biomass burning experiments, J. Geophys. Res, 113, D08206, doi:10.1029/2007JD009274, 2008.

Dinar, E., I. Taraniuk, E. R. Graber, T. Anttila, T. F. Mentel, and Y. Rudich (2007), Hygroscopic growth of atmospheric and model humic-like substances, J. Geophys. Res., 112, D05211, doi:10.1029/2006JD007442.

Dusek, U., Frank, G. P., Massling, A., Zeromskiene, K., Iinuma, Y., Schmid, O., Helas, G., Hennig, T., Wiedensohler, A., and Andreae, M. O.: Water uptake by biomass burning aerosol at sub- and supersaturated conditions: closure studies and implications for the role of organics, Atmos. Chem. Phys., 11, 9519-9532, doi:10.5194/acp-11-9519-2011, 2011.

Frosch, M., Prisle, N. L., Bilde, M., Varga, Z., and Kiss, G.: Joint effect of organic acids

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and inorganic salts on cloud droplet activation, Atmos. Chem. Phys., 11, 3895-3911, doi:10.5194/acp-11-3895-2011, 2011.

Koehler, K., S. Kreidenweis, P. DeMott, A. Prenni, C. Carrico, B. Ervens and G. Feingold, “Water activity and activation diameters from hygroscopicity data. Part II: Application to organic species,” Atmospheric Chemistry and Physics, 6, 795-809, 2006.

Mikhailov, E. F.; Vlasenko, S. S.; Ryshkevich, T. I., Influence of chemical composition and microstructure on the hygroscopic growth of pyrogenic aerosol, IZVESTIYA ATMOSPHERIC AND OCEANIC PHYSICS Volume: 44 Issue: 4 Pages: 416-431, 2008.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 11625, 2014.

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