Response

Response to referee 1：

We would like to thank referee #1 for the comments, the constructive criticism and suggestions to improve our manuscript. We have implemented changes based on comments and suggestions in the revised manuscript of the article. Our response to the comments and changes to the manuscript are included below. We repeat the specific points raised by the reviewer in bold font, followed by our response in italic font. The pages numbers and lines mentioned are with respect to the Atmospheric Chemistry and Physics Discussions (ACPD) paper.

General comments:

(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.

Reply: *According to the reviewer's suggestion of comment (1), we have read carefully all references that this referee mentioned and cite references that are relevant to our work. The details are given in specific response below to comment (1).*

Regarding comment (2), as the referee mentions, there are several studies that have been done on the hygroscopic behavior of ammonium sulfate, levoglucosan, 4-hydroxybenzoic acid, and humic acid (Koehler et al., 2006; Svenningsson et al., 2006; Mikhailov et al. 2008, 2009; Dinar et al., 2007). However, there are good reasons why we conducted our own the HTDMA measurements for these pure components. Firstly, we made a comparison between our experimental results and different model predictions to evaluate if the measured hygroscopic diameter growth factors (GF) of the pure components agree with one or several of the models agreement is found, the model can be considered suitable to describe the *hygroscopicity of the pure components potentially of use with the Zdanovskii-Stokes-Robinson (ZSR) relation for the prediction of GF of more complex multicomponent systems. In addition, these measurements served also as a test of our laboratory setup in comparison to the previous work conducted by other groups (comparison of the measured growth factors at different RH and deliquescence RH). We also focus on differences between the models used including ideal solution theory, AIOMFAC, E-AIM, a fitted growth factor curve, and ZSR, compared to measured hygroscopic diameter growth factors of pure compounds and mixtures of these components. Secondly, the goal was to conduct experiments and model calculations for inorganic-organic mixtures of surrogate components reflecting (in a simplyfied way) mixtures of aerosol components fund during different seasons from biomass burning sources. Growth factors of mixtures with components that we studied in our HTDMA experiments have not been measured before.*

Regarding comment (3), as this referee points out, for 100 nm dry size particles, since the surface tension of many aqueous solutions is relatively close to that of pure water, neglecting the Kelvin effect can result in up to a few percent error in a_w *(Kreidenweis et al., 2005). So we have all data corrected for this effect by calculating the Kelvin factor (Ke) accounting for curvature effects. These data and related figures have been revised and are more specifically discussed below.*

Specific comments and author response:

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.

Reply: *As the referee points out, there are several previous studies on the hygroscopic properties of relevant organic components that have not been cited in our manuscript. We extend our discussion on previous studies and we will revise the manuscript accordingly.*

Levoglucosan can be a significant portion of the organic aerosol mass and can be emitted at high enough concentration that it can be detected substantial distances from the source (Simoneit et al., 1999; Fine et al., 2002). Hygroscopic behavior of levoglucosan particles has been studied by several groups (e.g., Mochida and Kawamura, 2004; Chan et al., 2005; Koehler et al., 2006; Svenningsson et al., 2006; Mikhailov et al. 2008, 2009). For example, Koehler et al (2006) reported results on hygroscopic behavior of levoglucosan compared to the data from previously published papers (Mochida and Kawamura, 2004; Chan et al., 2005; Svenningsson et al., 2006), In addition, gradual phase transition of levoglucosan particles was observed with an upper end at ~60 % RH by Mikhailov et al. (2008, 2009). Humic like substances (HULIS) are commonly found in samples of biomass burning aerosols in many locations (Mayol-Bracero et al., 2002; Decesari et al., 2006; For et al., 2010; Iinuma et al., 2007). Most studies concerning hygroscopic behavior of HULIS have employed model compounds, mainly terrestrial and aquatic humic and fulvic acids (Chan and Chan, 2003; Brooks et al., 2004; Gysel et al., 2004; Badger et al., 2006; Svenningsson et al., 2006; Dinar et al., 2007; Sjogren et al., 2007; Mikhailov et al. 2008, 2009; Hatch et al., 2009; Pope et al., 2010; Zamora et al., 2011; Zamora and Jacobson, 2013). For example, Dinar et al. (2007) have studied the hygroscopic GF of HULIS extracted from smoke and urban pollution aerosol particles and of

Suwannee River fulvic acid using HTDMA. Water uptake of two different commercially available humic acid aerosol particles has been studied by Pope et al. (2010).

Mono- and dicarboxylic acids account for a significant mass of the organic fraction of biomass burning particles (Novakon and Corrigan, 1996; Narukawa et al., 1999; Hoffer et al., 2006; Iinuma et al., 2007; Fu et al., 2009; Dusek et al., 2011; Psichoadaki and Pandis. 2013). Effects of these mono- and dicarboxylic acids on the hygroscopic behavior of mixed organic-inorganic particles have been performed by many groups (Beyer et al., 2008; Hanford et al., 2008; Zandin et al., 2008; Frosch et al., 2011). For instance, Frosch et al. (2011)investigated the hygroscopicity of internal mixtures consisting of one organic acid (oxalic acid dihydrate, succinic acid, adipic acid, citric acid, cis-pinonic acid, or Nordic reference fulvic acid) and one inorganic salt (sodium chloride or ammonium sulfate). Previous studies investigated the hygroscopicity of organic-inorganic mixtures of representative model compounds from biomass burning (Cruz and Pandis, 1998, 2000; Raymond and Pandis, 2002; Abbatt et al., 2005; Henning et al., 2005; Svenningsson et al., 2006; Carrico et al., 2008; Dusek et al., 2011). For example, water uptake of surrogate mixtures containing a representative water-soluble organic fraction and inorganic compounds were studied by Svenningsson et al. (2006). They used the ZSR relation to compare and successfully explain the observed hygroscopic growth factors for 3 out of 4 mixtures. In addition, Carrico et al. (2008) and Dusk et al. (2011) investigated CCN activity and hygroscopic growth behavior of ambient biomass burning aerosols. To provide a better overview over these previous studies, we have added additional statements and cite the relevant references in our revised manuscript version, which are given in the following.

Related additions and changes included in the revised manuscript:

Page 11628 line1-2: we added 4 references in there. "and inorganic constituents are suggested to act as efficient cloud condensation nuclei" (Novakov and Corrigan, 1996; Petters et al., 2009; Rissler et al., 2010; Dusek et al., 2011; Frosch et al., 2011).

Page 11628 line 2-4: we added 2 references in there. "In the Amazon basin, for example, the CCN concentration in the dry season is one order of magnitude higher than in the wet season due to biomass burning" (Roberts et al., 2001; Carrico et al., 2008; Hening et al., 2010).

Page 11628 line 4-7: we added 2 references. "In addition, the aerosol indirect climatic effects resulting from increased cloud condensation nuclei concentrations are expected to be very important in tropical regions, particularly in the regions with very high biomass burning emissions" (Roberts et al., 2001; Carrico et al., 2008; Hening *et al., 2010).*

Page 11628 line 7-10: we added 4 references. "Increased CCN concentrations may lead to reduced average cloud droplet radii and associated with this, likely an enhanced negative radiative forcing of affected clouds" (Roberts et al., 2003; Lohmann and Feichter, 2005; Dinar et al., 2006a, b, 2007; Carrico et al., 2008).

Page 11628 line 10-13: we added 5 references. "Several groups have reported that a significant portion of particles from biomass burning (from 11 to as high as 99% by mass) consists of water-soluble organic carbon (WSOC)" (Ruellan et al., 1996; Novakov and Corrigan, 1996; Narukawa et al.,1999; Hoffer et al., 2006; Iinuma et al., 2007; Fu et al., 2009; Claeys et al., 2010; Dusek et al., 2011; Psichoadaki and Pandis, 2013).

Page 11628 line 21-23: we added 2 references. "Sampled WSOC typically contain a wide range of chemical species that are expected to show rather distinct water solubilities" (Mochida and Kawamura, 2004; Rissler et al., 2010; Jung et al., 2011).

Page 11628 line 27 to Page 11629 line 3: sentences "Previous laboratory studies have addressed......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) were revised to "Previous laboratory studies have addressed the effects of organic surrogate compounds from biomass burning on the hygroscopic properties of mixed organic-inorganic aerosol particles containing inorganic salts (Chan and Chan, 2003; Mochida and Kawamura, 2004; Brooks et al., 2004; Gysel et al., 2004; Chan et al., 2005; Svenningsson et al., 2005, 2006; Koehler et al., 2006; Badger et al., 2006; Dinar et al., 2007; Sjogren et al., 2007; Carrico et al., 2008; Mikhailov et al. 2008, 2009; Hatch et al., 2009; Pope et al., 2010; Zamora et al., 2011; Frosch et al., 2011; Dusek et al., 2011; Zamora and Jacobson, 2013)."

Page 11637 line 5-6: we added some discussion. Sentences "These measured GF are slightly higher than the measured hygroscopic growth factors of Leonardite Standard HA by Brooks et al. (2004). However, a contrasting phenomenon was observed by Zamora and Jacobson (2013); no hygroscopic growth of humic acid particles was observed over the full range of RH in their study."

Page 11642 line 21-23: we added 4 references. Sentence "Levoglucosan, a major pyrolysis product of cellulose and hemicellulose, contributes substantially (about 16–31 % by mass) to the total organic fraction in $PM_{2.5}$ *(Mochida and Kawamura, 2004; Iinuma et al., 2007; Claeys et al., 2010; Engling et al., 2013; Samburova et al., 2013)."*

Page 11642 line 24-25: we added 6 references. Sentence "In general, MDA have been identified as pyrolysis products of lignin, which is a major constituent of woods (Mochida and Kawamura, 2004; Hoffer et al., 2006; Iinuma et al., 2007; Fu et al., 2009; Dusek et al., 2011; Psichoadaki and Pandis. 2013)."

Page 11643 line 1-2: we added 6 references. Sentence "soluble organic carbon was identified as PA having molecular structures similar to humic materials (HMs) (Decesari et al., 2001; Fuzzi et al., 2001; Dinar et al., 2006a, b, 2007; Pope et al., 2010; Zamora et al., 2011; Fors et al., 2010).

Reply*:As this referee pointed out, Mikhailov et al, (2008, 2009) have studied effects of chemical composition, physical state, and microstructure on the hygroscopic behavior of a model smoke aerosol series containing ammonium sulfate, levoglucosan, and oxalic and humic acids. In these papers, with consideration of particle restructuring effects, they used the hygroscopic mobility diameter growth factor definition*

$$GF(RH) = D(RH) / D_0$$

Here, D(RH) is the particle diameter at a specific RH and D_0 *the reference diameter. the reference (minimum) diameter* D_0 *is obtained from different experimental protocols, e.g.:*

Hydration (h) mode minimum mobility diameter: $D_0 = D_{h,\min}$

Hydration&dehydration (h&d) mode minimum mobility diameter: $D_0 = D_{h\&d,\min}$

With these definitions from Mikhailov et al., the minimum diameter is the smallest diameter observed at any RH during a specific mode of performing an experiment. In many other studies, the reference diameter is taken to be the dry size diameter at RH ≈ 0 %, therefore neglecting any restructuring and potential shrinkage of particles at elevated relative humidity.

Related additions and changes included in the revised manuscript:
Page 11631 line 6: we added some discussion after the sentence: "The mobility-diameter growth factor is calculated as the ratio of mobility a particle established after exposure to a set RH level (mobility-diameter after humidification) to the reference mobility of the dry aerosol particles (at RH< 5 %). Hygroscopic diameter growth factors, GF(RH) = D(RH)/D0, where D(RH) is the particles diameter at a specific RH and D0 the diameter at dry conditions (RH= 0 %)"

We add:

D0 is often taken as the initial mode diameter of the aerosol ($D_{h,dry}$) *at dry conditions, RH ≈ 0 % selected by DMA1. In addition, following the definition of Mikhailov et al. (2009), a reference diameter* D_0 *can be defined as being the minimum diameter* ($D_{h,min}$) *observed while following an experimental protocol. The values of this minimum diameter and initial dry diameter are summarized in Table 2 (for set dry RH3 below 5 % RH in the HTDMA operation) and measured hygroscopic growth factor of* *compounds presented in Fig. 2. In addition, hydroscopic diameter growth factors are based on these reference minimum diameters for the pure components are predicted using different thermodynamic models and mixing rules. In each model, we assume that these particles are spherical. As a consequence, the predicated mobility equivalent diameter is equal to the volume equivalent diameter of a sphere.*

Table 2. Initial dry diameter ($D_{h,dry}$) (RH < 5 %) and minimum mobility diameter ($D_{h,min}$) in hydration (h) mode of the HTDMA experiments.

Aerosol type	$D_{h,dry}$ (nm)	$D_{h,min}$ (nm)
Ammonium sulfate	100.6	99.5
Levoglucosan	99.8	99.6
Humic acid	100.4	100.3
4-Hydroxybenzoic acid	100.2	95.0

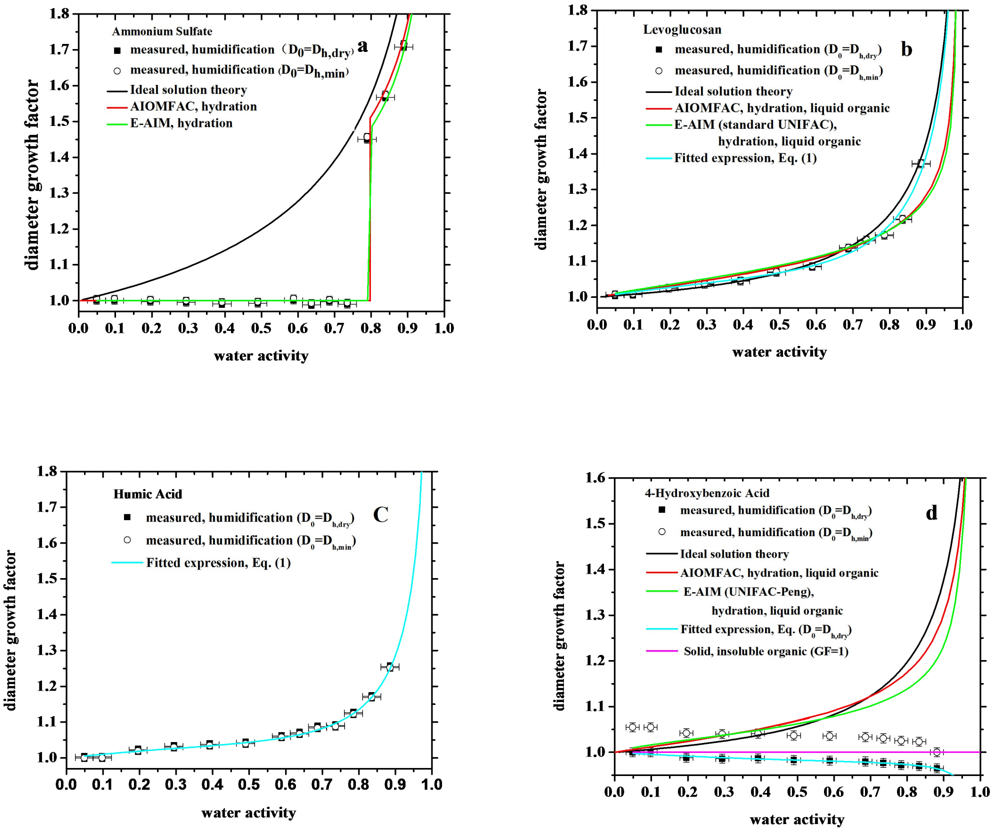


Fig. 2. Hygroscopic diameter growth factor (GF) for D_0 (initial dry diameter RH < 5 %) aerosol particles. The measurements, model calculations, and fitted expression Eq. (1) represent conditions of particle growth during a hydration experiment from 5 % to 90 % RH at 298.15 K. Measured growth factors are corrected for the Kelvin effect and and therefore shown vs. water activity. Symbols: measured GF are shown with respect to D_0 = $D_{h,\ dry}$

(black squares) or $D_0 = D_{h\&d,min}$ (open circles). Systems: **(a)** ammonium sulfate **(b)** levoglucosan, **(c)** humic acid, and **(4)** 4-hydroxybenzoic acid.

Page 11635 line 20: we add discussion in the revised manuscript. Sentence "Figure.2a presents growth factors of 100 nm (dry diameter) ammonium sulfate particles from low to high RH.......80% RH after deliquescence is 1.45 at 24.9 ℃ as measured by Wise et al. (2003)." was revised to
"Fig. 2a. presents growth factors with respect to $D_0 = D_{h,dry}$ and $D_0 = D_{h,min}$ ammonium sulfate particles from low to high RH.......80% RH after deliquescence is 1.45 at 24.9 ℃ as measured by Wise et al. (2003). In addition, the effects of particle shape/porosity restructuring on hygroscopic behavior of AS particles investigated are rather small (Mikhailov et al., 2004, 2008, 2009)."

Page 11636 line 23-25: we add discussion in the revised manuscript. Sentences "The measurements also suggest that levoglucosan absorbs a small amount of water even at 5% RH, and it is liquid over the full range of RH potentially rather viscous at lower RH)." was revised to "The measurements also suggest that levoglucosan absorbs a small amount of water even at 5% RH, and that it remains liquid over the full range of RH potentially rather viscous at lower RH. However, another possible explanation for slight water uptake of levoglucosan could be that nanoparticles produced by crystallization at very low RH contain volume and surface defects (porosity, polycrystalline state), which may facilitate water adsorption followed by absorption starting already at low relative humidity (Mikhailov et al., 2008, 2009). This possibility cannot be ruled out by our measurements, but the observation, which do not show a deliquescence step, would suggest that such an effect could only take place with a gradual deliquescence in the levoglucosan system.

Page 11637 line 5: we add discussion in the revised manuscript after the sentence "Above 70% RH, the particles start to take up increasingly more water toward high RH."
We add:
"The effects of microscopic restructuring on the water uptake of humic acid aerosol particles are relatively the same small, comparable with those of ammonium sulfate and levoglucosan aerosol particles."

Page 11637 line 14: we add discussion after sentence "The hygroscopic growth curves for 4-hydroxybenzoic acid are presented in Fig. 2d. No hygroscopic growth (within error) was observed below 90% RH."
We add:

Sentence "measured hygroscopic diameter growth factors with respect to $D_{h,min}$ nm are above 1.0, and are close to 1.0 toward high RH (the minimum diameter was found at the highest RH measured). The main reasons for the observation of smaller particles at higher RH is likely the restructuring and/or partial evaporation of particles at higher relative humidity in the hydration mode. The measured hygroscopic diameter growth factor with respect to $D_{h,dry}$ show of course the same slight decrease in particles diameter with increasing RH. with this definition of the reference diameter leading to GF smaller than 1.0 at higher RH."

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.

***Reply**: As the referee pointed out: page 11628 line 23-24: sentence "However, it is still uncertain whether those WSOC are inherently CCN active or whether they are made active through association with water-soluble organic species (Roberts et al., 2001, 2002; Wu et al., 2011)" was revised to "However, for a variety of WSOC compounds, it is not well known what the deliquescence relative humidity (DRH) of the pure compound is, which determines if it can exhibit substantial water uptake at moderate RH or not least as long as crystallization took place at dry conditions (followed by a hydration trajectory). Some organic components that show a small* *solubility in pure water (i.e., these require a large volume of water to be extracted and labeled as a WSOC), may have a DRH close to 100 % RH, which is not accessible in our hydration experiments (RH probed up to ~ 90 % RH).”*

4-Hydroxybenzoic acid aerosol showed no water uptake up to 90 % RH in our HTDMA hydration experiments (Fig. 2d). According to the referee's suggestion, we conducted further experiments for 4-hydroxybenzoic acid particles with hydration to high RH followed by dehydration to a set RH. Dry-size 100 nm 4-hydroxybenzoic acid aerosol was exposed to an RH slightly above 100 % RH through the use of a humidifier, and then dried to a certain RH set point (90 % - 10 % RH), as shown in Fig below.

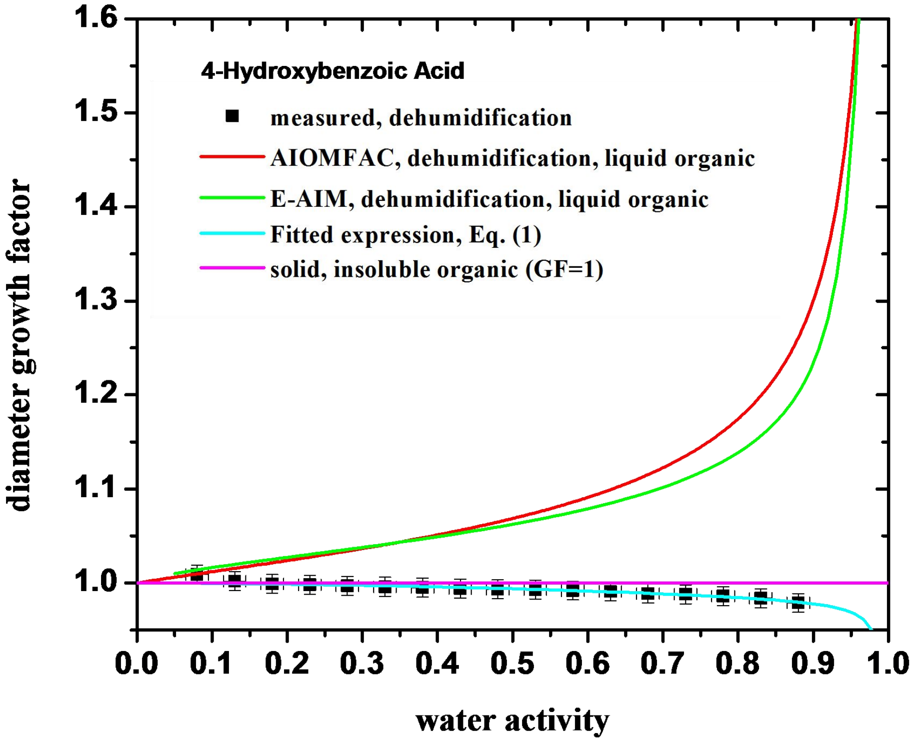


Fig. Hygroscopic diameter growth factor (GF) for D_0 = 100.2 nm (initial dry diameter RH< 5 %) 4-hydroxybenzoic acid aerosol particles. The measurements, AIOMFAC and E-AIM model calculations, and the fitted expression Eq. (1) represent growth factors for dehydration (dehumidification) conditions from 90 % RH to 10 % RH at 298.15 K systems. Measured growth factors are corrected for the Kelvin effect.

A *possible reason for no observed hygroscopic growth of 4-hydroxybenzoic acid aerosol is that it never or only briefly existed in a liquid state in the HTDMA setup. While it may have deliquesced in the supersaturation humidifier, its efflorescence may take place already above 90 % RH. Hence, the RH set points at 90 % RH and below will refer to GF of the crystallized compound (and RH-dependent restructuring effects* *of these crystallized particles). A second possible issue could be that the residence time in the humidifier (~5s) is insufficient for 4-hydroxybenzoic acid to fully deliquesce. The same phenomenon was observed by Mochida and Kawamura (2004); they performed a very similar experiment in order to seek the possible presence of supersaturated solutions of 4-hydroxybenzoic acid aerosol that would yield a meaningful growth factor for the liquid (metastable) particle state at lower RH setpoints, but they found as well no obvious change in diameter for 4-hydroxybenzoic acid aerosol up to 95 % RH under dehydration conditions.*

We add the following discussion in the revised manuscript:

Page 11637 line 27: we added some discussion after the sentence "an effect that is also known for certain volatile inorganic particles (e.g., NH_4NO_3) (Lightstone et al., 2000; Hersey et al., 2013)".

We add:

"In order to probe hysteresis effects of 4-hydroxybenzoic acid during hydration and dehydration processing of the aerosol, another experiment was conducted for 4-hydroxybenzoic acid. First, the 4-hydroxybenzoic acid aerosol particles was passed through a water supersaturation humidifier (RH of above 100 %), followed by drying to the different RH setpoints (90 % to 5 % RH). No obvious diameter changes other than potential restructuring effects were observed in this experiment. A possible reason is that the particles deliquesce in the supersaturation humidifier, but that their efflorescence occurs above 90 % RH, likely even above 97 % RH (Mochida and Kawamura, 2004). A second possible issue could be that the residence time in the humidifier section (~5 s) of our HTDMA setup is too short for 100 nm 4-hydroxybenzoic acid particles to fully deliquesce. Our observations of this very limited solubility of 4-hydroxybenzoic acid, and hence, a high DRH are in agreement with the experimental data of Mochida and Kawamura (2004) for this system".

Point (3):The authors have not corrected RH to a_w (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 a_w 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. 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"

Reply: *according to referee's comments, we used the following equation (Kreidenweis et al., 2005):*

$$s = a_w \exp\left\{\frac{4\sigma_{sol} M_w}{RT\rho_w D_p}\right\}$$

Here a_w *is the water activity of a bulk solution corresponding to the solution droplet of diameter* D_p, σ_{sol} *is the surface tension of the solution,* M_w *is the molar mass of water,* ρ_w *is the density of liquid water at T, R is the universal gas constant, T is the temperature and s is the saturation ratio equal to RH/100 %. For humic acid, we assumed that the surface tension of the droplet solution is equal to the surface tension of pure water,* σ_w *(Mikhailov et al., 2008). With these additions, we revised Page 11655* ***Table 1****.*

Table 1. Substances and their physical properties used in this work.

Chemical compound	Chemical formula	Molar Mass [g mol^{-1}]	Density in solid and liquid state [g cm^{-3}]	Solubility g/(100 cm^3 H_2O)	Solution surface Tension [J m^{-2}]	Manufacturer,purity
Ammonium sulfate	$(NH_4)_2SO_4$	132.140	1.770[a], 1.550[b]	74.400 (at 20℃)	0.072	Alfa Aesar, 99.95%
Levoglucosan	$C_6H_{10}O_5$	162.100	1.618[c] 1.512[d]		0.073[e] (0.01-10mg/mL)	Aldrich, 99%
4-Hydroxybenzoic acid	$C_7H_6O_3$	138.100	1.460 1.372[f]	0.675(at 25℃)	0.070[g]	Alfa Aesar, 99.99%
Humic acids		NA	0.800[h]	NA	0.073[i]	Aldrich, 99%

[a] Clegg and Wexler (2011a);

[b] Lienhard et al. (2012);

[c] Tuckermann and Cammenga (2004);

[d] Jedelsk´y et al. (2000);

[e] Kiss et al. (2005);

[f] Yates III and Wandruszka (1999);

[i] Mikhailov et al. (2008).

Page 11656 Table 2. Due to consideration of the Kelvin effect with the fitted expression, we revised the coefficients listed in Table 2:

Table 2. Coefficients (a, b, c) of the fitted growth curve parameterization to measured growth factor data using Eq. (1). Measured growth factors of D_0 nm particles used in Eq. (1) were first corrected for the Kelvin effect.

Chemical compounds	*a*	*b*	*c*
Levoglucosan	0.45602	-0.69869	0.44755
4-Hydroxybenzoic acid $D_0=D_{h,dry}$	-0.14061	0.22767	-0.09526
Humic acid	0.33579	-0.60172	0.40850

Page 11631 line 14-15: we added two equations and pertaining information:

$$RH/100\% = a_w \times K_e \tag{2}$$

$$Ke = \exp\left\{\frac{4\sigma_{sol} M_w}{RT\rho_w D_p}\right\} \tag{3}$$

Here a_w *is the bulk water activity (mole fraction basis) at the composition of the solution droplet corresponding to gas phase RH at equilibrium with a bulk solution,* σ_{sol} *is the surface tension of the solution,* M_w *is the molecular mass of water,* ρ_w *is the density of pure water at T, R is the universal gas constant, T is the temperature,* D_p *is the sphere-equivalent mobility particle diameter, and* K_e *is the so-called Kelvin correction factor term accounting for the droplet curvature.*

The simplest assumption is that the Kelvin factor is equal to 1 (i.e., neglecting the droplet curvature effect), applicable to large particles, however, for 100 nm diameter particles, ignoring the Kelvin effect at a given RH level and measured growth factor, leads to an error in the corresponding bulk solution equivalent water activity of about 1 - 2 % (Kreidenweis et al., 2005; Koehler et al., 2006). In this work, we have corrected all HTDMA GF data by evaluating the Kelvin term (Eq. 3) for the retrieved droplet size at a certain RH to obtain the corresponding water activity for comparison with models. The coefficients a, b, and c of Eq. (1) are determined by fitting Eq. (1) to

GF vs. a_w data obtained by using Eq. (2) with measured GF data at known experimental RH levels. Equation (1) is appropriate to describe continuous water uptake behavior of particles with a reference diameter at dry conditions (i.e., with GF = 1.0 at RH = 0 %).

Page 11632 line 3: Equation number "(2)" was revised to "(4)".
Page 11635 line 2: Equation number "(3)" was revised to "(5)".
Page 11659: we revised the panels (a), (b), (c), and (d) of Fig. 2., which are shown above in the discussion of point (1).
Page 11660 – 11663: Figures 3 to 6 will be revised accordingly to show the measured data after Kelvin effect correction and to show the ZSR predictions with the new parameterizations of the fitted expression (Eq. 1) for the corresponding mixed organic-inorganic systems.

We agree with this referee that the assumption of volume additivity is usually leading to rather small differences in predicted growth factors in comparison to more sophisticated particle density/volume estimation methods. We attribute a small effect on predicted GF curves due to different density treatment in E-AIM and the AIOMFAC-based equilibrium model based on a comparison of predicted mass growth factors and diameter growth factors for pure ammonium sulfate shown in (a new) Fig. 7. In the case of predicted mass growth factors of ammonium sulfate, both models agree very well with each other, indicating the slight differences in predicted diameter growth factors must be due to the different way the conversion from particle mass to particle volume are done in the two models. Additional difference between the predictions of E-AIM and AIOMFAC for the mixed systems (e.g., levoglucosan + ammonium sulfate, shown in Fig. 3 in the revised manuscript) arise from a liquid-liquid phase separation predicted by the AIOMFAC-based equilibrium model, while the E-AIM model predicts higher miscibility of levoglucosan and aqueous ammonium sulfate with no phase separation (which, given the experimental data, seems to be correct). These different phase predictions also affect the water uptake of the overall particles and hence the predicted growth factor.

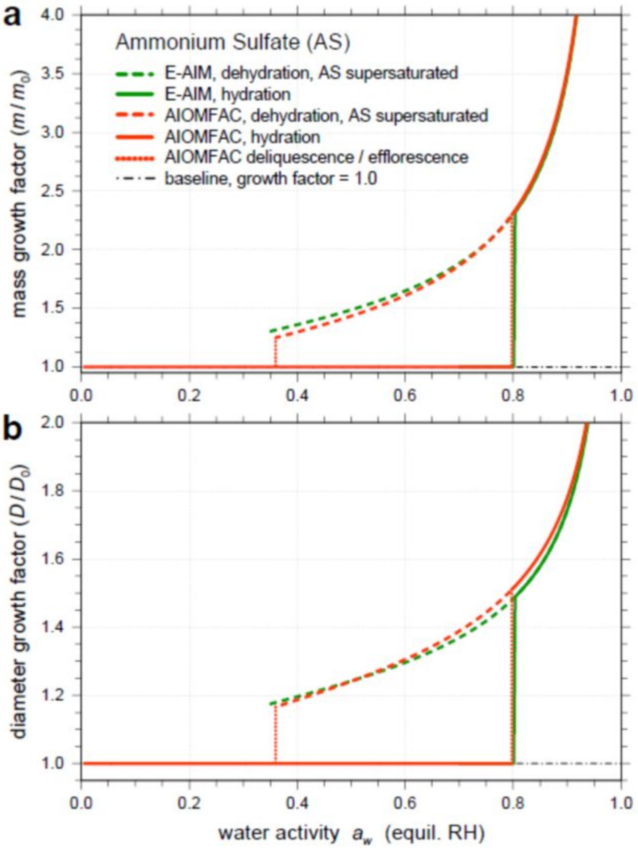


Fig. 7. Comparison of E-AIM and AIOMFAC-based mass growth factors (a) and growth diameter growth factors (b) for the binary ammonium sulfate + water system at 298.15 K.

We add the following discussion in the revised manuscript:

Page 11639, line 4-16: "A possible reason is that the E-AIM model provides droplet volume output based on density......and its prediction is a bit higher than the E-AIM model above 80 % RH" was revised to "A possible reason for small differences between the model predictions is that the E-AIM model provides droplet volume output based on density predictions of the aqueous system at different compositions (Clegg and Wexler, 2011a, b), while the other two models use a simpler volume additivity approach. We attribute a small effect on predicted GF curves due to different density treatment in E-AIM and the AIOMFAC-based model based on a comparison of E-AIM and AIOMFAC-based predicted mass growth factors and diameter growth factors for pure ammonium sulfate shown in Fig. A1. (we add Figure 7 in the appendix A of the revised paper). In the case of predicted mass growth factors of ammonium sulfate, both models agree very well with each other, indicating the slight differences in predicted diameter growth factors must be due to the different way the conversion from particle mass to particle volume is done in the two models. In addition, for the levoglucosan + AS mixtures, the AIOMFAC-based model predicts a liquid-liquid phase separation between 80 % and ~ 90 % RH for the hydration *conditions. The E-AIM model does not predict a phase separation and estimates a higher miscibility between the inorganic and organic components, which seems to be in better agreement with the experimental data. This is the major reason for the differences between the two model predictions regarding the diameter growth factors above AS deliquescence in case of the levoglucosan + AS system."*

Page 11636 line 8: sentence "The E-AIM model includes a composition dependent solution density model, while the AIOMFAC-based model does not." was revised to "The E-AIM model includes a composition dependent solution density model, while the AIOMFAC-based model simply assumes volume additivity (see discussion in Section 3.2)."

Page 11639 line 2: sentence "the E-AIM (standard UNIFAC) GF prediction is in better agreement with the measurements than the ideal solution GF curve, the AIOMFAC model as well as the ZSR relation" was revised to
"The E-AIM model includes a composition dependent solution density model, (i.e., solution density depends on water content and therefore RH), while the AIOMFAC-based model does not include such a sophisticated treatment. The AIOMFAC model assumes linear additively of pure component liquid or solid volumes/density to estimate the droplet diameter at a given RH."

Page 11635 line 23: "DGH" was revised to "DH".
Page 11646 line 21: "focus" was revised to "focuses".

References:

Abbatt, J. P. D., Broekhuizen, K., and Kumal, P. P.: Cloud condensation nucleus activity of internally mixed ammonium sulfate/organic acid aerosol particles, Atmospheric Environment, 39, 4767-4778, 10.1016/j.atmosenv.2005.04.029, 2005.

Agarwal, S., Aggarwal, S. G., Okuzawa, K., and Kawamura, K.: Size distributions of dicarboxylic acids, ketoacids, α-dicarbonyls, sugars, WSOC, OC, EC and inorganic ions in atmospheric particles over Northern Japan: implication for long-range transport of Siberian biomass burning and East Asian polluted aerosols, Atmospheric Chemistry and Physics, 10, 5839-5858, 10.5194/acp-10-5839-2010, 2010.

Beyer, K. D., Friesen, K., Bothe, J. R., and Palet, B.: Phase Diagrams and Water Activities of Aqueous Dicarboxylic Acid Systems of Atmospheric Importance, Journal of Physical Chemistry A, 112, 11704-11713, 10.1021/jp805985t, 2008.

Carrico, C. M., Petters, M. D., Kreidenweis, S. M., Collett, J. L., Engling, G., and Malm, W. C.: Aerosol hygroscopicity and cloud droplet activation of extracts of filters from biomass burning experiments, Journal of Geophysical Research, 113, 10.1029/2007jd009274, 2008.

Chan, M. N., and Chan, C. K.: Hygroscopic properties of two model humic-like substances and their mixtures with inorganics of atmospheric importance, Environmental science & technology, 37, 5109-5115, 10.1021/es034272o, 2003.

Chan, M. N., Choi, M. Y., Ng, N. L., and Chan, C. K.: Hygroscopicity of water-soluble organic compounds in atmospheric aerosols: Amino acids and biomass burning derived organic species, Environmental science & technology, 39, 1555-1562, 10.1021/es049584l, 2005.

Claeys, M., Kourtchev, I., Pashynska, V., Vas, G., Vermeylen, R., Wang, W., Cafmeyer, J., Chi, X., Artaxo, P., Andreae, M. O., and Maenhaut, W.: Polar organic marker compounds in atmospheric aerosols during the LBA-SMOCC 2002 biomass burning experiment in Rondônia, Brazil: sources and source processes, time series, diel variations and size distributions, Atmospheric Chemistry and Physics, 10, 9319-9331, 10.5194/acp-10-9319-2010, 2010.

Clegg, S. L., and Seinfeld, J. H.: Thermodynamic models of aqueous solutions containing inorganic electrolytes and dicarboxylic acids at 298.15 K. 2. Systems including dissociation equilibria, Journal of Physical Chemistry A, 110, 5718-5734, 10.1021/jp056150j, 2006a.

Clegg, S. L., and Seinfeld, J. H.: Thermodynamic models of aqueous solutions containing inorganic electrolytes and dicarboxylic acids at 298.15 K. 1. The acids as nondissociating components, Journal of Physical Chemistry A, 110, 5692-5717, 10.1021/jp056149k, 2006b.

Clegg, S. L., and Wexler, A. S.: Densities and apparent molar volumes of atmospherically important electrolyte solutions. 2. The systems H^+-HSO_4^--$SO4^{2-}$-H_2O *from 0 to 3 mol kg(-1) as a function of temperature and* H^+-NH_4^+-HSO_4^--$SO_4)^{2-})$-H_2O *from 0 to 6 mol kg(-1) at 25 degrees C using a Pitzer ion interaction model, and* NH_4HSO_4-H_2O *and* $(NH_4)_3H(SO_4)_2$-H_2O *over the entire concentration range, The journal of physical chemistry. A, 115, 3461-3474, 10.1021/jp1089933, 2011a.*

Clegg, S. L., and Wexler, A. S.: Densities and Apparent Molar Volumes of Atmospherically Important Electrolyte Solutions. 1. The Solutes H_2SO_4, HNO_3, *HCl,* Na_2SO_4, $NaNO_3$, *NaCl,* $(NH4)_2SO_4$, NH_4NO_3, *and* NH_4Cl *from 0 to 50 degrees C, Including Extrapolations to Very Low Temperature and to the Pure Liquid State, and* $NaHSO_4$, *NaOH, and* NH_3 *at 25 degrees C, Journal of Physical Chemistry A, 115, 3393-3460, 10.1021/jp108992a, 2011b.*

Cruz, C. N., and Pandis, S. N.: The effect of organic coatings on the cloud condensation nuclei activation of inorganic atmospheric aerosol, Journal of Geophysical Research-Atmospheres, 103, 13111-13123, 10.1029/98jd00979, 1998.

Dinar, E., Mentel, T. F., and Rudich, Y.: The density of humic acids and humic like substances (HULIS) from fresh and aged wood burning and pollution aerosol particles, Atmospheric Chemistry and Physics, 6, 5213-5224, 2006a.

Dinar, E., Taraniuk, I., Graber, E. R., Katsman, S., Moise, T., Anttila, T., Mentel, T. F., and Rudich, Y.: Cloud Condensation Nuclei properties of model and atmospheric HULIS, Atmospheric Chemistry and Physics, 6, 2465-2481, 2006b.

Dinar, E., Taraniuk, I., Graber, E. R., Anttila, T., Mentel, T. F., and Rudich, Y.: Hygroscopic growth of atmospheric and model humic-like substances, Journal of Geophysical Research, 112, 10.1029/2006jd007442, 2007.

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, Atmospheric Chemistry and Physics, 11, 9519-9532, 10.5194/acp-11-9519-2011, 2011.

Engling, G., Lee, J. J., Sie, H.-J., Wu, Y.-C., and I, Y.-P.: Anhydrosugar characteristics in biomass smoke aerosol—case study of environmental influence on particle-size of rice straw burning aerosol, Journal of Aerosol Science, 56, 2-14, 10.1016/j.jaerosci.2012.10.001, 2013.

Fine, P. M., Cass, G. R., and Simoneit, B. R. T.: Organic compounds in biomass smoke from residential wood combustion: Emissions characterization at a continental scale, Journal of Geophysical Research-Atmospheres, 107, 10.1029/2001jd000661, 2002.

Fors, E. O., Rissler, J., Massling, A., Svenningsson, B., Andreae, M. O., Dusek, U., Frank, G. P., Hoffer, A., Bilde, M., Kiss, G., Janitsek, S., Henning, S., Facchini, M. C., Decesari, S., and Swietlicki, E.: 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, Atmospheric Chemistry and Physics, 10, 5625-5639, 10.5194/acp-10-5625-2010, 2010.

Frosch, M., Prisle, N. L., Bilde, M., Varga, Z., and Kiss, G.: Joint effect of organic acids and inorganic salts on cloud droplet activation, Atmospheric Chemistry and Physics, 11, 3895-3911, 10.5194/acp-11-3895-2011, 2011.

Fu, P. Q., Kawamura, K., and Barrie, L. A.: Photochemical and Other Sources of Organic Compounds in the Canadian High Arctic Aerosol Pollution during Winter-Spring, Environmental science & technology, 43, 286-292, 10.1021/es803046q, 2009.

Hanford, K. L., Mitchem, L., Reid, J. P., Clegg, S. L., Topping, D. O., and McFiggans, G. B.: Comparative thermodynamic studies of aqueous glutaric acid, ammonium sulfate and sodium chloride aerosol at high humidity, Journal of Physical Chemistry A, 112, 9413-9422, 10.1021/jp802520d, 2008.

Hatch, C. D., Gierlus, K. M., Zahardis, J., Schuttlefield, J., and Grassian, V. H.: Water uptake of humic and fulvic acid: measurements and modelling using single parameter Köhler theory, Environmental Chemistry, 6, 380, 10.1071/en09083, 2009.

Henning, S., Rosenorn, T., D'Anna, B., Gola, A. A., Svenningsson, B., and Bilde, M.: Cloud droplet activation and surface tension of mixtures of slightly soluble organics and inorganic salt, Atmospheric Chemistry and Physics, 5, 575-582, 2005.

Henning, S., Wex, H., Hennig, T., Kiselev, A., Snider, J. R., Rose, D., Dusek, U., Frank, G. P., Pöschl, U., Kristensson, A., Bilde, M., Tillmann, R., Kiendler-Scharr, A., Mentel, T. F., Walter, S., Schneider, J., Wennrich, C., and Stratmann, F.: Soluble mass, hygroscopic growth, and droplet activation of coated soot particles during LACIS Experiment in November (LExNo), Journal of Geophysical Research, 115, 10.1029/2009jd012626, 2010.

Holmes, B. J., and Petrucci, G. A.: Oligomerization of levoglucosan by Fenton chemistry in proxies of biomass burning aerosols, Journal of Atmospheric Chemistry, 58, 151-166, 10.1007/s10874-007-9084-8, 2007.

Iinuma, Y., Brüggemann, E., Gnauk, T., Müller, K., Andreae, M. O., Helas, G., Parmar, R., and Herrmann, H.: Source characterization of biomass burning particles: The combustion of selected European conifers, African hardwood, savanna grass, and German and Indonesian peat, Journal of Geophysical Research, 112, 10.1029/2006jd007120, 2007.

Jung, J., and Kim, Y. J.: Tracking sources of severe haze episodes and their physicochemical and hygroscopic properties under Asian continental outflow: Long-range transport pollution, postharvest biomass burning, and Asian dust, Journal of Geophysical Research, 116, 10.1029/2010jd014555, 2011.

Jung, J., Kim, Y. J., Aggarwal, S. G., and Kawamura, K.: Hygroscopic property of water-soluble organic-enriched aerosols in Ulaanbaatar, Mongolia during the cold winter of 2007, Atmospheric Environment, 45, 2722-2729, 10.1016/j.atmosenv.2011.02.055, 2011.

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

Martin, S. T., Andreae, M. O., Artaxo, P., Baumgardner, D., Chen, Q., Goldstein, A. H., Guenther, A., Heald, C. L., Mayol-Bracero, O. L., McMurry, P. H., Pauliquevis, T., Pöschl, U., Prather, K. A., Roberts, G. C., Saleska, S. R., Silva Dias, M. A., Spracklen, D. V., Swietlicki, E., and Trebs, I.: Sources and properties of Amazonian aerosol particles, Reviews of Geophysics, 48, 10.1029/2008rg000280, 2010.

Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Poschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, Atmospheric Chemistry and Physics, 9, 9491-9522, 2009.

Mikhailov, E. F., Vlasenko, S. S., and Ryshkevich, T. I.: Influence of chemical composition and microstructure on the hygroscopic growth of pyrogenic aerosol, Izvestiya, Atmospheric and Oceanic Physics, 44, 416-431, 10.1134/s0001433808040038, 2008.

Petters, M. D., Carrico, C. M., Kreidenweis, S. M., Prenni, A. J., DeMott, P. J., Collett, J. L., and Moosmüller, H.: Cloud condensation nucleation activity of biomass burning aerosol, Journal of Geophysical Research, 114, 10.1029/2009jd012353, 2009.

Pope, F. D., Harper, L., Dennis-Smither, B. J., Griffiths, P. T., Clegg, S. L., and Cox, R. A.: Laboratory and modelling study of the hygroscopic properties of two model humic acid aerosol particles, Journal of Aerosol Science, 41, 457-467, 10.1016/j.jaerosci.2010.02.012, 2010.

Psichoudaki, M., and Pandis, S. N.: Atmospheric aerosol water-soluble organic carbon measurement: a theoretical analysis, Environmental science & technology, 47, 9791-9798, 10.1021/es402270y, 2013.

Raymond, T. M., and Pandis, S. N.: Cloud activation of single-component organic aerosol particles, Journal of Geophysical Research-Atmospheres, 107, 10.1029/2002jd002159, 2002.

Rissler, J., Svenningsson, B., Fors, E. O., Bilde, M., and Swietlicki, E.: An evaluation and comparison of cloud condensation nucleus activity models: Predicting particle critical saturation from growth at subsaturation, Journal of Geophysical Research, 115, 10.1029/2010jd014391, 2010.

Samburova, V., Hallar, A. G., Mazzoleni, L. R., Saranjampour, P., Lowenthal, D., Kohl, S. D., and Zielinska, B.: Composition of water-soluble organic carbon in non-urban atmospheric aerosol collected at the Storm Peak Laboratory, Environmental Chemistry, 10, 370, 10.1071/en13079, 2013.

Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., Rogge, W. F., and Cass, G. R.: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, Atmospheric Environment, 33, 173-182, 10.1016/s1352-2310(98)00145-9, 1999.

Vestin, A., Rissler, J., Swietlicki, E., Frank, G. P., and Andreae, M. O.: Cloud-nucleating properties of the Amazonian biomass burning aerosol: Cloud condensation nuclei measurements and modeling, Journal of Geophysical Research, 112, 10.1029/2006jd008104, 2007.

Zamora, I. R., Tabazadeh, A., Golden, D. M., and Jacobson, M. Z.: Hygroscopic growth of common organic aerosol solutes, including humic substances, as derived from water activity measurements, Journal of Geophysical Research: Atmospheres, 116, n/a-n/a, 10.1029/2011jd016067, 2011.

Zamora, I. R., and Jacobson, M. Z.: Measuring and modeling the hygroscopic growth of two humic substances in mixed aerosol particles of atmospheric relevance, Atmospheric Chemistry and Physics, 13, 8973-8989, 10.5194/acp-13-8973-2013, 2013.

Zardini, A. A., Sjogren, S., Marcolli, C., Krieger, U. K., Gysel, M., Weingartner, E., Baltensperger, U., and Peter, T.: A combined particle trap/HTDMA hygroscopicity study of mixed inorganic/organic aerosol particles, Atmospheric Chemistry and Physics, 8, 5589-5601, 2008.

Response to referee 2:

We are grateful to Referee #2 for the comments and the constructive suggestions to improve our manuscript. We have implemented all the comments and suggestions in the revised manuscript. Our point-to-point responses to the individual comments are as follows, we repeat the specific points raised by the reviewer in bold font, followed by our responses in italic font. The numbers of pages and lines are with respect to the ACPD.

Comment 1: As the authors stated, actual biomass burning aerosols are typically much more complex in terms of composition, and the hygroscopicity of biomass burning aerosols likely depends on the mixing of a diversity of organic compounds with inorganic constituents during different time periods in the field. I am not certain where this paper can appropriately answer this question based on data using internally mixed particles of organic surrogate compounds and ammonium sulfate. Rather than drawing conclusions on the hygroscopicity of biomass burning aerosols, it would be better to focus on hygroscopicity of specific organic –ammonium sulfate mixture with well-mixed mixing structure. Discussion on the effect of mixing-structure of mixed particles on hygroscopicity should be included. In this paper, all particles would be well-mixed particles. Is this the typical case for biomass burning aerosols? How about hygroscopicity of core-shell particles having the same mass fraction of the well-mixed particles?

Reply*:Because of the complex chemical composition of biomass burning aerosols (Decesari et al., 2000, 2006; Shimmo et al., 2004), there is lack of qualitative as well as quantitative information on the detail chemical composition and and mixing state (i.e., internally or externally mixed aerosol populations and/or whether individual particles consist of a single, homogeneously mixed phase or multiple liquid/solid phases). Consequently, following Fuzzi et al. (2001) approach, it is of interest to study the interaction of water with mixed particles consisting of compounds from these main classes. Mixtures containing levoglucosan, humic acid, and 4-hydroxybenzoic acid represent a example of neutral compounds, mono/di-carboxylic acids, and polyacids, respectively (Andrece et al., 2002; Artaxo et al., 2002; Zhu et al., 2002; Decesari et al., 2006; Rissler et al., 2006; Jung et al., 2011). To represent the inorganic component that can attribute to water uptake of mixed biomass burning aerosol, ammonium sulfate is used in there due to it is ubiquitous in the atmosphere. Therefore, in this paper, we focus on the hygroscopic behavior of mixed organic component and ammonium sulfate. The investigation of the hygroscopic behavior of single organic component is to further study their influences on hygroscopic behavior for the specific organic+AS particles. for example, mixtures of levoglucosan with AS. With increasing* *mass fraction of levoglucosan, a clear shift of the onset of AS deliquescence to lower RH is occurring, which also leads to an overall more smooth looking hygroscopic growth factor curve, this indicates levoglucosan aerosol has a significant influence on mixed AS + levoglucosan compared with 4-hydroxybenzoic acid and hunmic acid.*

We added some discussion about the hygroscopic behavior of mixed AS+organics in the revised manuscript (the detail has been presented in the comment (7)).

Aerosol can appear as externally mixed, heterogeneously internally mixed (i.e., coated particles) or homogeneously internally mixed (Riziq et al., 2008; Lang-Yona et al., 2009; shamjad et al., 2012; Maskey et al., 2014). The assumption of homogeneously internally mixtures may be not valid, for example, atmospheric particles undergo different aging processes, such as heterogeneous reactions, condensation, coagulation, and oxidation, they may exist in various mixing structures that include multiple chemical species. However, for externally or heterogeneously internally mixed with other aerosol constituents, it is complicate to the qualitative as well as quantitative analysis all particles, and the hygroscopic growth factors are not comparable with that of those of the biomass burning (Andrece et al., 2002; Artaxo et al., 2002; Zhu et al., 2002; Decesari et al., 2006; Rissler et al., 2006; Jung et al., 2011). Correspondingly, in the case of homogeneously internally mixtures, we choose threes organic components representing WSOC as experimental stimulation object to study their mixture's hygroscopicity. And further made comparison with different model predictions and other results studied by several group (Svenning et al., 2006; Rissler et al., 2010; Wu et al., 2011; Zamora and Jacobson, 2013). In addition, The measured GF values of our biomass burning model systems are similar to the results reported by Jung et al. (2011) for biomass burning aerosols sampled collected in Ulaanbaatar, Mongolia, for which the GF were found to be between 1.30 and 1.35 at 80% RH during hydration.

The mixing structure of atmospheric aerosols has a significant effect on their hygroscopicity. The hygroscopic behavior of mixed aerosol containing core -shell has been studied by several group (Chan et al., 2006; Maskey et al., 2014). For example, the hygroscopicity of internal mixtures of ammonium sulfate aerosol and organics such as succinic acid, levoglucosan with core-shell and well-mixed mixing structures were performed by Maskey et al. (2014) using HTDMA technique. They showed that the GF of the well-mixed particles was higher than that of the core-shell particles with the same fraction volume, and for core-shell particles consisting ammonium sulfate and succinic acid, the particles size remained unchanged until a slow increase occurred at 79 % RH, which a clear shift of deliquescence was observed at 72 % RH for the well-mixed particles (ammonium sulfate and succinic acid) during the *hydration process. This suggested that mixing structure of the particles were determined to better understanding of the hygroscopic behavior of the internally mixed particles. And we have added some discussion on the effect of mixing-structure of mixed particles on hygroscopicity in the ACPD. And we will study and compare the hygroscopic behavior between core-shell particles and well-mixed particles with the same mass fraction in the future.*

Related additions and changes included in the revised manuscript:
Page 11638 line 21-25: Sentence "Particles start to take up water well before the full deliquescence of AS at RH= ~ 80 %....those particles also exhibit a moderate growth by water uptake in the RH range of 40 - 70 %." was revised to "there is a clear shift in the full deliquescence of AS at RH= ~ 80 % RH to lower RH with increasing levoglucosan mass fraction, which indicates the levoglucosan aerosol particles have significant effect on the deliquescence of ammonium sulfate. And with increasing levoglucosan mass fraction, the smoothing of hygroscopic behavior is obvious. this phenomenon was observed for mixtures of ammonium sulfate and succinic acid, malonic acid, monomethylaminium sulfate (MMAS), dimethylaminium sulfate (DMAS) by previous studies (e.g., Zaedini et al., 2008; Hämer et al., 2002; Qiu and Zhang, 2013). Qiu and Zhang (2013) observed that particles consisting of 10 wt % MMAS, or DMAS and ammonium sulfate exhibit a moderate growth by water uptake in the RH range of 40 - 70 % RH. In addition, the hygroscopicity of internal mixtures of ammonium sulfate aerosol and levoglucosan with core-shell and well-mixed mixing structures were performed by Maskey et al. (2014) using HTDMA technique. They showed that the GF of the well-mixed particles was higher than that of the core-shell particles with the same fraction volume"

Comment 2: Authors stated that "the residence time of particles before entering into DMA2 is about 2.5 s in the second Nafion tube. This particle residence time may be insufficient for some organic compounds to reach equilibrium at the high RH (Chan, 2005; Sjogren et al., 2007; J. Duplissy et al., 2009) and that to allow the aerosol to equilibrate at the specified RH, we ensure that RH3 is equal to RH2". How to ensure that all organic compounds tested here reached equilibrium?

Reply: *As referee mention, an important concern about hygroscopic behavior of these organic components is if the particles have achieved equilibrium state in measurement. In order to ensure that all organic components attained equilibrium during this residence time, firstly, we used a double Nafion arrangement in the HTDMA system, in this experiment the 100 nm aerosol is humidified by two-step* *process. In the first step, the dry aerosol particles are pre-humidified in the first Nafion tube by the excess air from the HTDMA, which means that aerosol can come close to the humidity of the excess air but cannot excess it. And the second humidification step brings aerosol humidity rapidly to the desired sheath humidity in a second Nafion conditioner tube. Furthermore, because the aerosol flow has been pre-humidified somewhat in the first Nafion tube, the transfer of water vapour from the sheath flow which envelops the second Nafion is small, thereby enhancing the equilibration of these aerosol flow (Duplissy et al., 2009). Secondly, in this experiment, the total of residence of time of aerosol equilibration before entering DMA2 is about 5s during the hydration process. Kerminen (1997) estimated the residence time for achievement of water equilibrium to be between 8 ×10^{-6}s and 0.1s for 100 nm and 500 nm particles. Therefore, the typical residence time of a few seconds in the humidification section in DMA measurement is sufficient for most equilibrium hygroscopic measurements (Brooks et al., 2004; Gysel et al., 2004, Johnson et al., 2004; Mikhailor et al., 2004; Wu et al., 2013). Chan and Chan (2005) have recommended that the residence time of particles in the humidification region may indicate whether kinetic limitations to mass transfer.*

For example, Zhang and Chan. (2000) found that there is a significant retardation of water evaporation and growth rate of magnesium sulfate droplets at high concentration at low RH using Raman spectroscopy. However, residence time may not be adequate for those coated with organic layers, MgSO4, sodium pyruvate, arginine, glutaric acid and asparagine because of mass transfer (Ha and Chan, 2001; Zhang and Chan, 2000; Peng and Chan, 2001; Chan et al., 2005). To avid misunderstanding, our results for hygroscopicity of three organic components at a residence time of 5s are compared with that of Mochida and Kawamura, 2004, Koehler et al., 2006 and Brooks et al., 2004, respectively at more than 5s residence time. The measured GF at 80 % RH is 1.17 ± 0.01, which similar to a results from Mochida and Kawamura, 2004. In addition, Biskos et al. (2006) observed that significant difference between the RH of aerosol flow and sheath flow (≧3 % RH), can be lead to erroneous results for components. Therefore, in this experiment, it must keep the RH difference between aerosol flow and sheath air as small as possible (≤ ± 2 % RH) (Biskos et al., 2006). To avoid confusing, we have revised the discussion in the ACPD.

Related additions and changes included in the revised manuscript:

Page 11630 line 16-19: the sentence "The residence time of particles before entering into DMA2 is about 2.5 s in the second Nafion tube. This particle residence time may be insufficient for some organic compounds to reach equilibrium at the high RH (Chan and Chan, 2005; Sjogren et al., 2007; J. Duplissy et al., 2009)." was revised to "the residence time of aerosol flow before entering into DMA2 is about 5 s in the *humidification section. This residence time may be insufficient for some organic compounds to reach equilibrium at the high RH because of the very low accommodation coefficient (Kerminen, 1997; Ha and Chan, 2001; Zhang and Chan, 2000; Peng and Chan, 2001; Chan et al., 2005). For example, for those coated with organic layers, MgSO4, sodium pyruvate, glutaric acid and asparagine. They need more long residence time to reach equilibrium."*

Comment 3: Effect of particle size on hygroscopicity should be discussed. Some biomass burning particles observed in the ambient atmosphere are less than 100 nm.

Reply: A*s referee's comment, variations in the size distribution can strongly influence the activation and growth of CCN. It has been reported that water-soluble organic compounds from biomass burning, i.e., mono/di- acids, levoglucosan, humic acid were in find mode (Dp < 1.1 um) (Robert et al., 2003; Rissler et al., 2006; Agarwal et al., 2010; Claey et al., 2010; Vestin et al., 2007). We focus on hygroscopic behavior of mixtures (100 nm) and make a comparison between our results and literatures' results for mixtures (100 nm) AS and organics from biomass burning (Artaxo et al., 2002; May-Bracero et al., 2002; Svenning et al., 2006; Rissler et al., 2010; Wu et al., 2011; Jung et al., 2011; Zamora and Jacobson, 2013). Literatures reported have different effect of particles size on the hygroscopicity of compounds in the atmosphere (Hämer et al., 2000; Mirabel et al., 2000; Djikaev et al., 2001; Russell and Ming, 2002; Robert et al., 2003; Biskos et al., 2006), especially for the less than 100 nm particles in the ambient atmosphere. For example, Biskos et al, (2006) observed that the deliquescence and efflorescence of ammonium sulfate nanoparticles (6-60 nm) are similar to their large-particle counterparts. The hygroscopic growth factors, however, decrease with decreasing particles diameter from 60 to 6 nm. The decrease is quantitatively predicted by a model that includes the Kelvin effect and a size-dependent shape factor. To express more clearly, we revised the discussion and added some references.*

Related additions and changes included in the revised manuscript:
Page 11628 line 21-23: sentence "Sampled WSOC typically contain a wide range of chemical species that are expected to show rather different water solubilities (Mochida and Kawamura, 2004)." was revised to "Sampled WSOC typically contain the size distribution and a wide range of chemical species that are expected to show rather different water solubilities, and different effect on the hygroscopic growth factors of aerosol particles from biomass burning (Mochida and Kawamura, 2004; Biokos et al., 2006; Rissler et al., 2010; Jung et al., 2011)."

Mention 4: Can the hygroscopic growth factors of 100 nm (dry diameter) particles consisting of mixtures of organic surrogate compounds with ammonium sulfate appropriately represent particles of (a) dry and (b) wet seasonal periods in the Amazon ? Chemical compositional data would be obtained from filter samples without information on externally-mixed /internally mixed particles. Each organic species can exist independently (externally-mixed) or mixed with sulfate. How about aging process?

Reply: *According to Decsari et al, (2006) and Fuzz et al., (2001), sampling of aerosol particles was conducted from 9 September to 14 November 2002, the sampling period was subdivided into different period. In spite of the significant changes in the chemical composition of tracer compounds from the dry to the wet period, the functional groups and the general chemical classes of WSOC changed only to a small extent in the Amazon basin near Rondônia, Brazil. Model compounds consisting of levoglucosan, humic acid, and 4-hydroxybenzoic acid representing WSOC chemical composition for different periods of the campaign are then proposed based on the chemical characterization by both individual compounds analysis and functional group analysis deployed during the experiment. Model compounds present quantitatively the average chemical structure of WSOC and can be used as surrogates in microphysical models involving organic aerosol particles over tropical areas affects by biomass burning (Andrece et al., 2002; Artaxo et al., 2002; Zhu et al., 2002; Rissler et al., 2006; Decesari et al., 2006). In this paper, the goal was to experimentally simulated the hygroscopic behavior of mixtures on basis of different organic and inorganic component fractions observed for the dry and the wet period in the Amazon basin ((Andrece et al., 2002; Artaxo et al., 2002; Zhu et al., 2002; Rissler et al., 2006; Decesari et al., 2006). And we also focus on conduct experiments and model calculations for inorganic-organic mixtures of surrogate components reflecting (in a simply way) mixtures of aerosol components fund during different seasons from biomass burning resources.*

Chemical composition from biomass burning undergo different aging processes in the different process, such as heterogeneous reactions, condensation, coagulation, and oxidation, we next will focus on these problems in the future.

Comment 5: The aerosol generation part should include more information. What are the solvents for the mixed particles? The DI water or other solvents can contain impurity species. Does this affect the mixed particles? It is nice to aerosolize only DI water or other solvent to look at residual particles. The

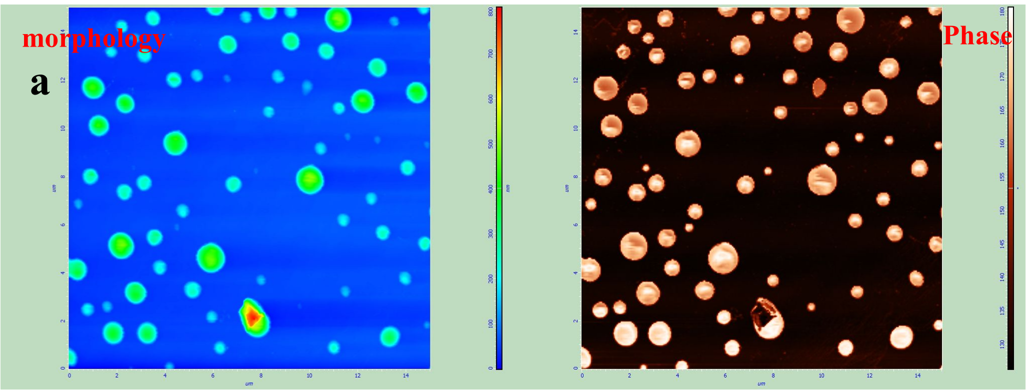
well-mixed state was assumed for their mixed particles. Evidence for this should be needed by microscopic analysis or other compositional analysis.

Reply: *We are sorry for making the referee confused. To express more clearly, we revised the discussion.*

Related additions and changes included in the revised manuscript:

Page 11630 line 6-7: sentence "Polydispersed sub-micrometer particles are generated using an atomizer (MSP 1500, MSP) from bulk solutions with different mass fractions of organic and inorganic species" was revised to "Polydispersed sub-micrometer particles are generated using an atomizer (MSP 1500, MSP) from bulk solutions (0.1 wt %) with different mass fractions of organic and inorganic species with deionised water (EASY Pure® ‖ UF ultrapure water system, 18.2 MΩ cm)"

To observe mixtures aerosol morphology, we used the tapping-mode atomic force microscopy (TM-AFM) to characterize mixtures aerosol structure. Micron-particles were generated using an atomizer from bulk solutions with different mass fractions of organic and inorganic species (deionised water: 18.2 MΩ cm), and passed through three silica gel diffusion dryers and a nafion gas dryer. Mixed particles states were presented in the following pictures:



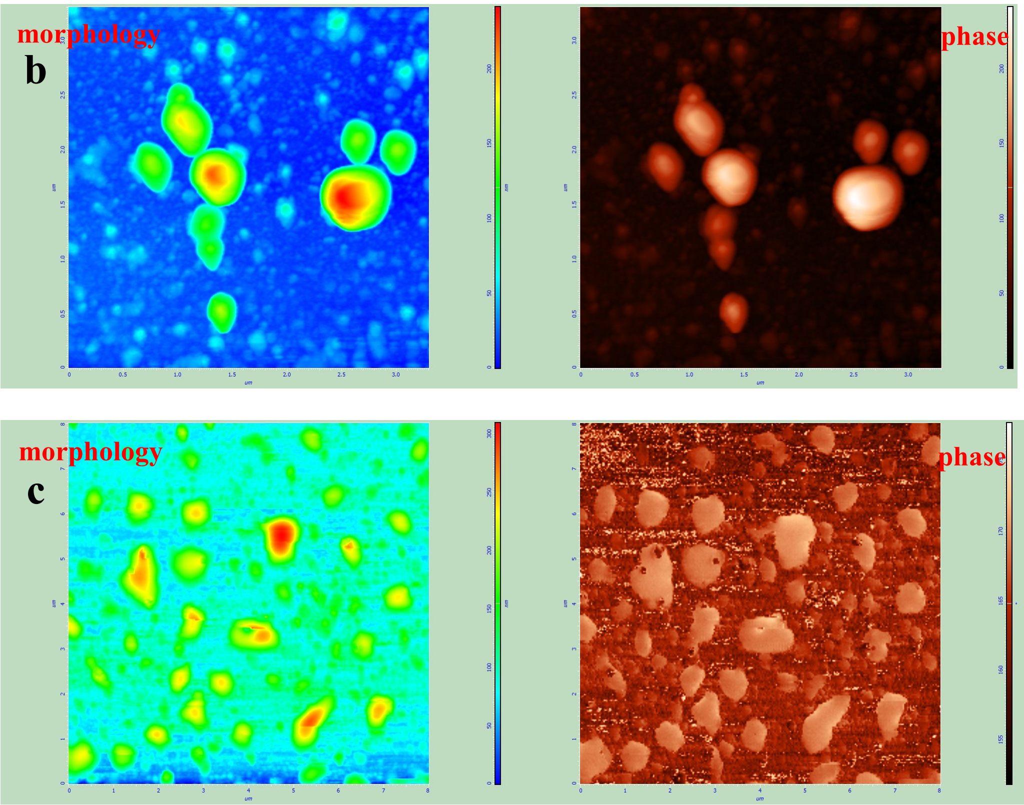


Fig. 1. AFM images of mixtures particles by mass ratio 1:1 system: **(a)** levoglucosan + AS, **(b)** humic aicd + AS, **(c)** bio-dry on SiOx/Si(100). The different color represent the height, phase of micron-particle respectively.

To summarize, mixture consisting of ammonium sulfate and levoglucosan by mass ratio 1:1 exhibits homogeneously mixed single liquid phase, this suggest particles absorb a small amount of water even at 5 % RH. According to phase imaging, mixing state of AS+4-hydroxybenzoic acid particles phase is similar to that of AS+humic acid phase. AFM shows these particles phases are homogeneous internally mixed depending on the same of the phases. Particles in dry period show these particles are also homogeneous internally mixed state on basic of AFM phase graph.

Comment 6: Did authors use the HTDMA inversion program to derive the HGF?

Reply*: these distributions are generated from measured data by an inversion program that base on lognormal approximation (Stolzenburg and McMurry, 2008).*

Comment 7: The change of the DRH based on mixing having different mass fraction should be discussed in details.

Reply*: As referee point out, we have added the discussion about change of DRH based on mixing having mass fraction.*

Related additions and changes included in the revised manuscript:

Page 11638 line 21-25: sentence "Particles start to take up water well before the full deliquescence of AS at RH= ~ 80 %." was revised to "there is a clear shift in the full deliquescence of AS at RH= ~ 80 % RH to lower RH with increasing levoglucosan mass fraction, which indicates the levoglucosan aerosol particles have significant effect on the deliquescence of ammonium sulfate. And with increasing levoglucosan mass fraction, the smoothing of hygroscopic behavior is obvious. this phenomenon was observed for mixtures of ammonium sulfate and succinic acid, malonic acid, monomethylaminium sulfate (MMAS), dimethylaminium sulfate (DMAS) by previous studies (e.g., Zaedini et al., 2008; Hämer et al., 2002; Qiu and Zhang, 2013). Qiu and Zhang (2013) observed that particles consisting of 10 wt % MMAS, or DMAS and ammonium sulfate exhibit a moderate growth by water uptake in the RH range of 40 - 70 % RH. In addition, the hygroscopicity of internal mixtures of ammonium sulfate aerosol and levoglucosan with core-shell and well-mixed mixing structures were performed by Maskey et al. (2014) using HTDMA technique. They showed that the GF of the well-mixed particles was higher than that of the core-shell particles with the same fraction volume"

Page 11640 line 12 - 13: sentence "Adding HA causes the mixed particles to start to take up a small amount of water before the complete deliquescence of AS." was revised to "Adding HA causes the mixed particles to start to take up a small amount of water before the complete deliquescence of AS, indicating HA aerosol particles have a litter effect on the deliquescence of AS."

Page 11641 line 8 - 9: sentence "Hygroscopic behavior of mixed 4-hydroxybenzoic acid–AS particles is found to be essentially unaffected by the presence of 4-hydroxybenzoic acid." was revised to "Hygroscopic behavior of mixed 4-hydroxybenzoic acid–AS particles is found to be essentially unaffected by the presence of 4-hydroxybenzoic acid. 4-hydroxybenzoic acid aerosol particles have no influence on the deliquescence point of ammonium sulfate with the low water solubility. Similar phenomenon was observed for mixtures of ammonium sulfate and organics containing glutaric, pinonic acid, and phthalic acid with low water solubility by Cruz and Pandis, 2000 and Hamer et al, 2002."

References:

Agarwal, S., Aggarwal, S. G., Okuzawa, K., and Kawamura, K.: Size distributions of dicarboxylic acids, ketoacids, α-dicarbonyls, sugars, WSOC, OC, EC and inorganic ions in atmospheric particles over Northern Japan: implication for long-range transport of Siberian biomass burning and East Asian polluted aerosols, Atmospheric Chemistry and Physics, 10, 5839-5858, 10.5194/acp-10-5839-2010, 2010.

Chan, M. N., Lee, A. K. Y., and Chan, C. K.: Responses of ammonium sulfate particles coated with glutaric acid to cyclic changes in relative humidity: Hygroscopicity and Raman characterization, Environmental science & technology, 40, 6983-6989, 10.1021/es060928c, 2006.

Decesari, S., Facchini, M. C., Matta, E., Mircea, M., Fuzzi, S., Chughtai, A. R., and Smith, D. M.: Water soluble organic compounds formed by oxidation of soot, Atmospheric Environment, 36, 1827-1832, 10.1016/s1352-2310(02)00141-3, 2002.

Djikaev, Y. S., Bowles, R., Reiss, H., Hameri, K., Laaksonen, A., and Vakeva, M.: Theory of size dependent deliquescence of nanoparticles: Relation to heterogeneous nucleation and comparison with experiments, Journal of Physical Chemistry B, 105, 7708-7722, 10.1021/jp010537e, 2001.

Freedman, M. A., Baustian, K. J., Wise, M. E., and Tolbert, M. A.: Characterizing the Morphology of Organic Aerosols at Ambient Temperature and Pressure, Analytical Chemistry, 82, 7965-7972, 10.1021/ac101437w, 2010.

Fuzzi, S., Decesari, S., Facchini, M. C., Matta, E., Mircea, M., and Tagliavini, E.: A simplified model of the water soluble organic component of atmospheric aerosols, Geophysical Research Letters, 28, 4079-4082, 10.1029/2001gl013418, 2001.

Ha, Z. Y., and Chan, C. K.: The water activities of MgCl2, Mg(NO3)(2), MgSO4, and their mixtures, Aerosol Science and Technology, 31, 154-169, 10.1080/027868299304219, 1999.

Hameri, K., Vakeva, M., Hansson, H. C., and Laaksonen, A.: Hygroscopic growth of ultrafine ammonium sulphate aerosol measured using an ultrafine tandem differential mobility analyzer, Journal of Geophysical Research-Atmospheres, 105, 22231-22242, 10.1029/2000jd900220, 2000.

Hameri, K., Charlson, R., and Hansson, H. C.: Hygroscopic properties of mixed ammonium sulfate and carboxylic acids particles, Aiche Journal, 48, 1309-1316, 10.1002/aic.690480617, 2002.

Kerminen, V. M.: The effects of particle chemical character and atmospheric processes on particle hygroscopic properties, Journal of Aerosol Science, 28, 121-132, 10.1016/s0021-8502(96)00069-9, 1997.

Maskey, S., Chong, K. Y., Kim, G., Kim, J.-S., Ali, A., and Park, K.: Effect of mixing *structure on the hygroscopic behavior of ultrafine ammonium sulfate particles mixed with succinic acid and levoglucosan, Particuology, 13, 27-34, 10.1016/j.partic.2013.08.004, 2014.*

Mikhailov, E., Vlasenko, S., Niessner, R., and Poschl, U.: Interaction of aerosol particles composed of protein and salts with water vapor: hygroscopic growth and microstructural rearrangement, Atmospheric Chemistry and Physics, 4, 323-350, 2004.

Mirabel, P., Reiss, H., and Bowles, R. K.: A theory for the deliquescence of small particles, Journal of Chemical Physics, 113, 8200-8205, 10.1063/1.1315993, 2000.

Russell, L. M., and Ming, Y.: Deliquescence of small particles, Journal of Chemical Physics, 116, 311-321, 10.1063/1.1420727, 2002.

Shimmo, M., Anttila, P., Hartonen, K., Hyotylainen, T., Paatero, J., Kulmala, M., and Riekkola, M. L.: Identification of organic compounds in atmospheric aerosol particles by on-line supercritical fluid extraction-liquid chromatography-gas chromatography-mass spectrometry, Journal of Chromatography A, 1022, 151-159, 10.1016/j.chroma.2003.09.024, 2004.

Stolzenburg, M. R., and McMurry, P. H.: Equations governing single and tandem DMA configurations and a new lognormal approximation to the transfer function, Aerosol Science and Technology, 42, 421-432, 10.1080/02786820802157823, 2008.

Vestin, A., Rissler, J., Swietlicki, E., Frank, G. P., and Andreae, M. O.: Cloud-nucleating properties of the Amazonian biomass burning aerosol: Cloud condensation nuclei measurements and modeling, Journal of Geophysical Research, 112, 10.1029/2006jd008104, 2007.

Zhang, Y. H., and Chan, C. K.: Study of contact ion pairs of supersaturated magnesium sulfate solutions using raman scattering of levitated single droplets, Journal of Physical Chemistry A, 104, 9191-9196, 10.1021/jp0013659, 2000.

Zhou, J. C., Swietlicki, E., Hansson, H. C., and Artaxo, P.: Submicrometer aerosol particle size distribution and hygroscopic growth measured in the Amazon rain forest during the wet season, Journal of Geophysical Research-Atmospheres, 107, 10.1029/2000jd000203, 2002.