Response

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

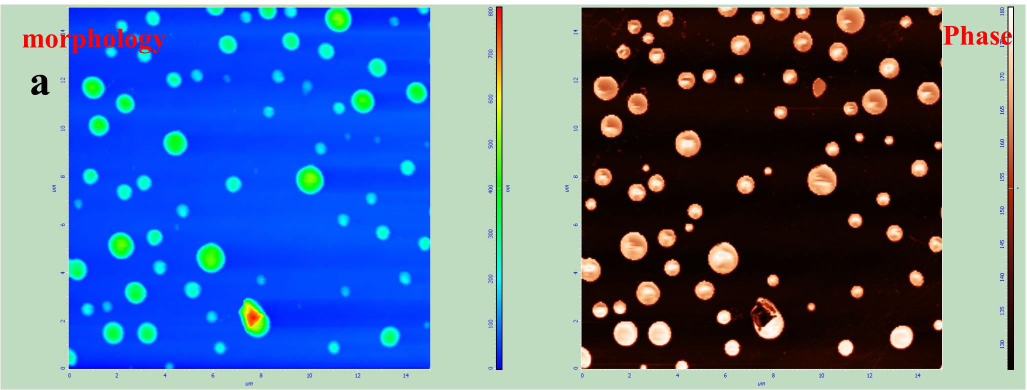
contain impurity species. Does this affect the mixed particles? It is nice to aerosolize only DI water or other solvent to look at residual particles. The well-mixed state was assumed for their mixed particles. Evidence for this should be needed by microscopic analysis or other compositional analysis.

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® Ⅱ 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:



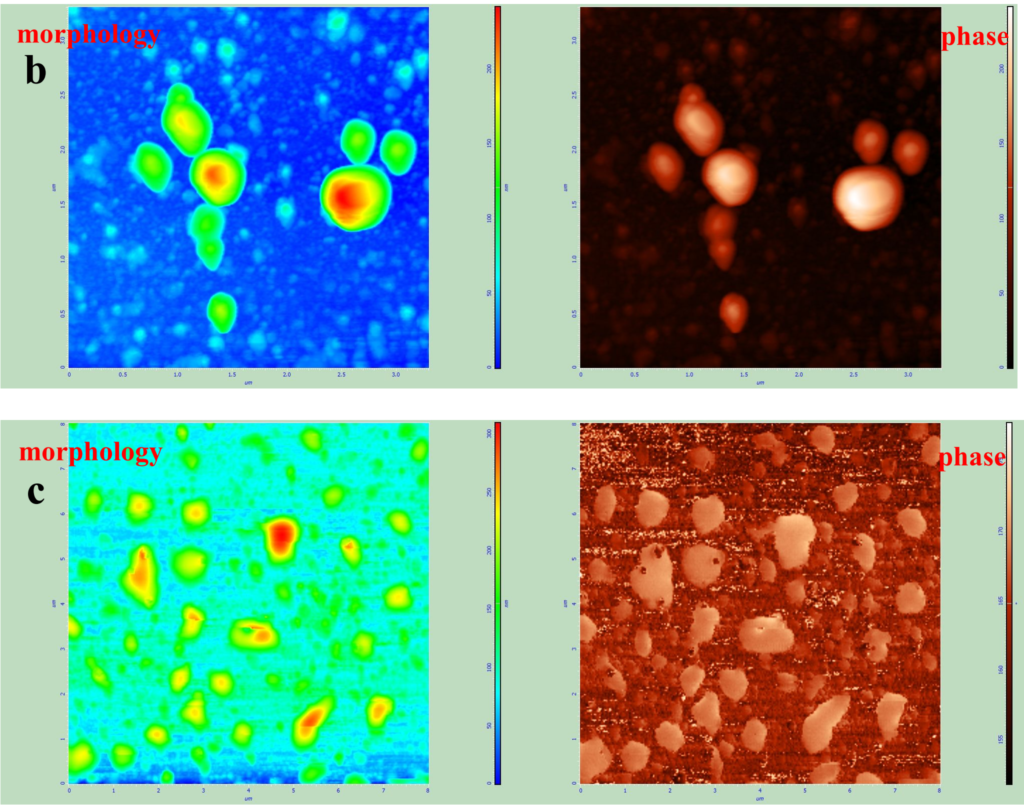


Fig. 1. AFM images of mixtures particles by mass ratio 1:1 system: **(a)** levoglucosan + AS, **(b)** humic aicd + AS, **(c)** bio-dry on SiOx/Si(100). The different color represent the height, phase of micron-particle respectively.

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."

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