Response

Response editor

General comments

You have a final opportunity to revise your manuscript with a possibility for publication in ACP after the revision. Your last round of revisions was not sufficiently responsive to the referee's comments. Please revise the manuscript again, addressing the second round of reviewer comments and taking care to thoroughly address the comments of both reviewers from the first round. Be careful to ensure that your responses in the author's response document are carried through to changes in the manuscript.

Reply: *We would like to thank the editor for the comments. We and constructive suggestions to improve our manuscript. Our responses to the comments and changes to the manuscript are included below in the order that the comments were given. We repeat the specific points raised by the reviewer in bold font, followed by our point-by-point response to the reviews in italic font. The pages numbers and lines mentioned are with respect to the revised manuscript.*

Comment 1: As one example of meaningfully modifying the text in response to the first round of reviewer comments (and there are more instances where this needs to be done), in the Responses you wrote, "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. " This text, which provides a thorough review of the literature, is the type that should be incorporated in the manuscript, rather than the abridged version that you added.

Reply: *thank you very much for the editor's conscientiousness on our present article. According to editor's suggestion, we added some discussion on referee's comments.*

Related additions and changes included in the revised manuscript.

Page 5 line 97 - 106*: the sentences "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; Dusek et al., 2011; Frosch et al., 2011; Zamora and Jacobson, 2013). Studies about the hygroscopicity of individual organic compounds characteristic to biomass burning aerosol particles were performed by Mochida and Kawamura (2004). Their results showed that the hygroscopic diameter growth factors of levoglucosan aerosol particles are 1.23 at 80 % relative humidity (RH), while 4-hydroxybenzoic acid does not show any hygroscopic growth up to 95% RH when starting with dry particles. Water uptake by humic acid and mixtures of humic materials with ammonium sulfate were determined using a HTDMA setup by Brooks et al. (2004). They showed that the presence of humic acid affects the water uptake of mixed particles containing ammonium sulfate + humic acid." ***were revised to*** *"Previous studies have been carried out to investigate 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 Zdanovski-Stokes-Robinson (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."*

Page 2 line 28 - 33*: we added some discussion after the sentence "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)."*

We add

"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 detailed chemical composition 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). Recently,"

Page 2 line 37 - 44: *we added some discussion after the sentence "several groups have reported that a significant portion of particles in biomass burning (from 11 % to as high as 99 % by mass) consist of water-soluble organic carbon (WSOC) (Ruellan et al., 1999; 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)."*

we add

"One way to handle the large number of organic compounds comprised within the water-soluble atmospheric aerosol fraction is to identify a set of model substances that may be representative in reproducing the hygroscopic behavior of the water-soluble organic fraction of the real aerosol particles (May-Bracero et al., 2002; Rissler et al., 2010; Wu et al., 2011; Zamora and Jacobson, 2013). For example, based on the identification of model compounds with the help of chromatographic chemical separation, HNMR (Proton Nuclear Magnetic Resonance) analysis， and TOC (Total Organic Carbon) measurements,"

Page 3 line 50 - 71*: then sentence "these surrogate compounds can be represented approximately by: levoglucosan,4-hydroxybenzoic acid, and humic acid (Hoffer et al., 2006)."* ***was revised to*** *"neutral compounds mainly consist of sugar-like compounds such as levoglucosan, which is the most abundant semivolatile product of the pyrolysis of cellulose (Iinuma et al., 2007; Claeys et al., 2010; Engling et al., 2013; Samburova et al., 2013). Another significant fraction of WSOC are aromatic acids like 4-hydroxybenzoic acid, which has been identified as a pyrolysis product of lignin, and 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). Water-soluble organic carbon is also linked to a class of complex poly carboxylic acids, which are denoted by the generic term "HULIS" (humic-like substances) (Decesari et al., 2001; Fuzzi et al., 2001; Dinar et al., 2006a, b, 2007; Pope et al., 2010; Fors et al., 2010；Zamora et al., 2011). Also, an aerosol population can appear as externally mixed, heterogeneously internally mixed (i.e., coated or phase-separated particles) or homogeneously internally mixed (Riziq et al., 2008; Shamjad et al., 2012; Maskey et al., 2014). The mixing structure of atmospheric aerosols has a significant effect on their hygroscopicity (Chan et al., 2006; Maskey et al., 2014). For example, Chan et al. (2006) studied the hygroscopic behavior of solid ammonium sulfate coated with glutaric acid in two consecutive cycles of hydration and dehydration using an electrodynamic balance (EDB). They concluded that the different deliquescence behavior of mixed particles observed between the two cycles of hydration and dehydration was caused by the different mixing structures of particles (most likely, core-shell phase-separated, and well-mixed particles in the first and second cycles, respectively)."*

Page 21 line 463 - 477*: the sentences "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."* ***were revised to*** *"Note that for this model comparison (Fig. 4) no specific particle size is assumed, i.e., these are model calculations for bulk system conditions without the necessity of a correction factor accounting for droplet curvature. Deviations in predicted diameter growth factors related to the different solution density models used are therefore visualized by the comparison of the two model predictions, especially for* *water activities above deliquescence of ammonium sulfate, where the predicted mass growth factors agree very well. Fig. 4 illustrates that the two different thermodynamic models can yield different predictions of diameter growth factors because of two reasons: (i) differences in predicted activity coefficients for a given mixture composition, which is seen from deviations between the models in Fig. 4a (mass growth factors vs. water activity) particularly for* $a_w < \sim 0.6$ *and/or (ii) due to a different solution density model used, as seen from a comparison of panels (a) and (b) of Fig. 4 for* $a_w > \sim 0.6$*. Based on this comparison, slight differences between E-AIM and AIOMFAC diameter growth factor predictions are explained by the use of two different approaches for the description of solution density (and therefore volume)."*

Page 26 line 582 - 593: *the sentences "The water soluble organic carbon (WSOC) fraction in biomass burning aerosol is mainly composed of neutral compounds, a large fraction of which consisting of sugar-like compounds such as levoglucosan, mannosan and D-glucose. Levoglucosan, a major pyrolysis product of cellulose and hemicellulose, contributes substantially (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). 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). We use 4-hydroxybenzoic acid to represent as a surrogate the MDA fraction; The polyacidic (PA) fraction of organic compounds is found in all samples of biomass burning aerosols (Decesari et al., 2006). Using the H-NMR technique for aerosol analysis of samples from the Po valley in Italy more than 40% of the water soluble organic carbon* 522 *was identified as PA having molecular structures similar to humic materials (HMs) (Decesari et al., 2002; Fuzzi1 et al.,2001; Dinar et al., 2006a, b, 2007; Pope et al., 2010; Zamora et al., 2011; Fors et al., 2010). Therefore, organic surrogate compounds (levoglucosan, 4-hydroxybenzoic acid, and humic acid) have been proposed to represent the composition of WSOC on the basis of speciation methods and functional groups analysis (Decesari et al., 2006)."* ***were revised to*** *"Mixtures compounds consisting of levoglucosan, humic acid, and 4-hydroxybenzoic acid, representing WSOC chemical composition for different seasonal periods in the Amazon region, based on the chemical characterization of both individual compounds analysis and functional group analysis deployed during the field experiment by Decesari et al. (2006) and Rissler et al. (2006). Also, the mixtures present quantitatively the average chemical structure of WSOC and can be used as surrogates in microphysical models involving organic aerosol particles over tropical areas affected by biomass burning (Andreae et al., 2002; Artaxo et al., 2002; Zhu et al., 2002; Rissler et al., 2006; Decesari et al., 2006). Therefore, with the organic surrogate compounds (levoglucosan, 4-hydroxybenzoic acid, and humic acid) as example of neutral compounds, mono/di-carboxylic acids, and polyacids, respectively, it is of interest to study the interaction of water with mixed ammonium sulfate-organics particles from these main organic compound classes."*

Comment 2: A specific point regarding reviewer 2's comment in the first round: the effect of particle size on hygroscopicity should be discussed. You made a minor text change on Page 11628 line 21-23 to include the word "size distribution" but this is not a true discussion.

Reply: ***Page 4 line 71 - 84:*** *we add some discussion on size distribution "In addition, it has been reported that water-soluble organic compounds from biomass burning, i.e., mono- and carboxylic acids, levoglucosan, and humic acid were quite abundant in the find mode (D_p < 1.1 um) (Robert et al., 2003; Rissler et al., 2006; Vestin et al., 2007; Agarwal et al., 2010; Claey et al., 2010). Also, different effects of particles size (in the submicron size range) on the hygroscopic growth factors and deliquescence behavior of aerosol are reported in the literature (Hämer et al., 2000; Mirabel et al., 2000; Djikaev et al., 2001; Russell and Ming, 2002; Robert et al., 2003; Biskos et al., 2006a, b), especially for particles smaller than 100 nm in the diameter. For example, Biskos et al. (2006a, b) observed that the deliquescence and efflorescence of ammonium sulfate nanoparticles (6 - 60 nm) are similar to their larger-particle counterparts. The hygroscopic growth factors, however, decrease substantially with decreasing particles diameter from 60 to 6 nm. In this study, particles of ~ 100 nm dry diameter are used in our laboratory experiments, thus, albeit of interest, such size effects were not studied for our model mixtures."*

Response referee #1

General comments

The manuscript is improved by correction of calculated results, citations of prior work and changes to the text, however the findings of prior work are not discussed fully. My primary concern continued to be that most if not all of the systems studied here have already been studied and reported in the literature, and compared to thermodynamic models including ideal solution theory. There are numerous grammar, spelling and punctuation errors that need to be corrected if the paper is accepted for publication.

Reply: *We would like to thank referee #1 for the comments, the constructive criticism and suggestions to improve our manuscript. We extend our discussion on findings of previous works in detail, and correct all grammar, spelling and punctuation errors. We repeat the specific points raised by the reviewer in bold font, followed by our point-by-point response to the reviews in italic font. The pages numbers and lines mentioned are with respect to the revised manuscript.*

Comment 1: A new figure was added as Fig. 7. But is actually discussed prior to

Fig. 4.

Reply: *we have revised the order of figures.*

Page 21 line 463: "Fig. 7." was revised to "Fig. 4."
Page 23 line 503: "Fig. 4." was revised to "Fig. 5."
Page 24 line 532: "Fig. 5." was revised to "Fig. 6."
Page 25 line 553: "Fig. 5." was revised to "Fig. 6."
Page 25 line 558: "Fig. 5." was revised to "Fig. 6."
Page 27 line 603: "Fig. 6a." was revised to "Fig. 7a."
Page 28 line 622: "Fig. 6b." was revised to "Fig. 7b."

Comment 2: The inversion method (the authors state they used the method of Stolzenburg and McMurry) is not mentioned.

***Reply*:** *Page 7 line 152 - 155, we added some discussion after the sentence "Finally, the number size distributions for the humidified aerosols are measured using the second DMA (DMA2) coupled with a condensation particle counter CPC (Model 1500, MSP)."*

We add:

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

Comment 3: Line 286-287: this is all very well known. Ammonium sulfate solutions are used for calibration purposes and it is well understood they deviate from identity.

Reply: *thank you for suggestion. according to referee's comments, we deleted this sentence.*

Page 15 line 337: "Therefore, aside from the solid-to-liquid phase transition, the water activity in concentrated solution also deviates from ideality."

Comment 4: Line 306: It appears Zuend et al. (2011) already studied levolucosan-salt mixtures and compared with existing thermodynamic models. What is new here?

Reply: *As discussed on line 306, Zuend et al. (2011) compared water activity predictions of the AIOMFAC model with electrodynamic balance measurements by Lienhard et al. (2011) for the binary system of levoglucosan + water system and three ternary systems consisting of levoglucosan, water and an ammonium salt (either ammonium sulfate, ammonium nitrate or ammonium bisulfate). In this study, we compare the binary levoglucosan system in terms of our measured HTDMA data and the different models (including AIOMFAC, E-AIM, and the fitted expression). This model comparison is not discussed in Zuend et al. (2011). In addition, the discussion of the binary levoglucosan + water system (Fig. 2) serves the purpose of the comparison with, and discussion of, the levoglucosan + water + ammonium sulfate systems with different levoglucosan mass fractions (Fig. 3). Thus, we believe that it is reasonable to show and briefly discuss the levoglucosan + water system (on lines 306 - 312), even though previous studies have looked at that system already.*

Comment 6: Line 323-325: there are literature values for humic acids. Why not compare here?

Reply: *We greatly thanks the referee's comments. We added some discussion about humic acids. Page 17 line 367-373, the sentences "A similar tendency had been observed 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." was revised to "these measured GF are slight higher than the measured hygroscopic growth factors of Leonardite Standard HA by Brook et al，(2004), for example, the measured GF at 80 % is 1.13 ± 0.01 while report from literature (Brook et al., 2004）a growth factor of humic acid of 1.0 ± 0.01 at 80 % RH. 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, perhaps due to different origin and composition of the humic acid samples."*

Comment 7: Line 407 and following, and Fig. 7: the mass growth factors above deliquescence are identical. How were diameter growth factors derived? These are not standard output for E-AIM, so the authors must have computed them. At the least it should be obvious what densities were assumed for the solutions, as E-AIM will provide this output. I don't understand why the authors cannot more fully address the differences if they are going to make comparison of these two models a major focus of this work. Further, what size dry particle is assumed? The surface tension can then play a role as well, whether one assumes pure water or a solution surface tension in computing the Kelvin term. All of these factors have been studied thoroughly and reported in the literature, for ammonium sulfate and other salts. Below deliquescence, the properties of the supersaturated solutions do appear to be estimated differently; again, the precise differences should be discernable from model output.

Reply: *As is discussed on lines 399 – 407, the E-AIM model includes a composition-dependent solution density prediction based on the work of Clegg and Wexler (2011a,b) alongside the activity coefficient predictions. For a given system, the E-AIM output therefore lists directly droplet volume as a function of water activity. This predicted volume, converted to a droplet diameter is used for the comparisons of diameter growth factors in the figures. We also mention that the AIOMFAC-based prediction uses a simpler approach, since it assumes linear additivity of the volumes from the different system components. On lines 230 – 233 we describe that for the AIOMFAC-based GF predictions, molar volume data is used. As suggested by the referee, we revise the manuscript to state the specific density values for all the components used (which can be converted to molar volumes of the different components). We will list this information at line 233, where the AIOMFAC-based model is described.*

We do not know the exact values of the density or molar volume values used in the

E-AIM model for the pure components (but assume that they are quite similar to ours). However, the main difference when going from mass growth factor to diameter growth factor (as compared in Fig. 4), is therefore attributed to the deviations between the non-linear solution density model used in E-AIM and the volume additivity approach in AIOMFAC. This is visualized by the comparison of the two model predictions for water activities above deliquescence of ammonium sulfate, where the predicted mass growth factors agree very well. In the model comparison (discussion of Fig. 4), no specific particle size is assumed, i.e., these are model calculations for bulk system conditions, so a curvature correction is not applied. The purpose of Fig. 4 is to illustrate that the two different thermodynamic models can yield different predictions of diameter GF because of (i) differences in predicted activity coefficients for a given mixture composition, which is seen from deviations between the models in Fig. 4a (mass growth factors vs. water activity) particularly for aw < ~0.6 – and/or (ii) due to a different solution density model used, as seen from a comparison of panels (a) and (b) of Fig. 4 for aw > ~0.6. We add part of this discussion in the revised manuscript (see additions below).

Page 12 line 273 - 285: we revised the sentence "Here we use the simplified assumption of additive component volumes, while accounting for differences between the density of solid ammonium sulfate and dissolved aqueous ammonium sulfate using pure component molar volume data reported by Lienhard et al. (2012)." was revise to "Here we use the simplified assumption of additive component volumes, while accounting for differences between the densities of solid ammonium sulfate and dissolved aqueous ammonium sulfate. In the case of water and the organic components, the physical state is assumed to be liquid (potentially a supercooled liquid) at room temperature for the purpose of defining density values. The following density values of the pure components are used (which can be converted to specific or molar volumes): ρ (water) = 0.9971 g cm-3 (Lienhard et al., 2012), ρ (levoglucosan) = 1.512 g cm-3 (Lienhard et al., 2012), ρ (4-hydroxybenzoic acid) = 1.3723 g cm-3 (Jedelský et al., 2000), ρ (ammonium sulfate, liquid) = 1.55 g cm-3 (Clegg and Wexler, 2011b), ρ (ammonium sulfate, solid) = 1.77 g cm-3 (Clegg and Wexler, 2011b). All model calculations are performed for bulk solution properties, i.e., sufficiently large particles, where no curvature correction is necessary. For comparisons with measurements, the experimental data were corrected, as discussed in Section 2.2.1. "

Comment 8: Lines 438 and following: The authors should be careful about stating that GFs are decreased due to the presence of organic. As they later note, this is to be expected since one has a lower hygroscopicity. They should make this point sooner so that readers are not confused by the idea that organics somehow suppress ammonium sulfate hygroscopicity.

***Reply**: We agree your point. To express more clearly, Page 26 line 582 - 593: we revised some the sentence "For instance, the measured growth factors are 1.30, 1.21, and 1.18 at 80 % RH after full AS deliquescence for the particles containing 25 wt%, 50 wt% and 75 wt% HA (dry composition) compared to a growth factor of 1.45 for pure, deliquesced AS particles at 80 % RH. 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." was revised to "For instance, the measured growth factors are 1.30, 1.21, and 1.18 at 80 % RH after full AS deliquescence for the particles containing 25 wt%, 50 wt% and 75 wt% HA (dry composition) compared to a growth factor of 1.45 for pure, deliquesced AS particles at 80 % RH. The HA has a lower hygroscopicity which leads the mixed particles to take up a smaller amount of water before the complete deliquescence of AS. Based on a ZSR relation assumption of (approximate) additivity of water uptake by the different mixture components according to their individual hygroscopicity, the observed reduction in GF is expected for the mixed systems. It is expected because of the lower mass fraction of the most hygroscopic component (ammonium sulfate) in these mixed systems in comparison to pure ammonium sulfate particles of the same dry size. Thus, the observed reduction in GF does not indicate a dramatic suppression of ammonium sulfate hygroscopicity by the organic components. However, present molecular interactions among organic components and dissolved ammonium sulfate may slightly affect the hygroscopicities of the individual components in comparison to pure component hygroscopicities."*