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Hygroscopicity of organic compounds from biomass burning and their influence on the water uptake of mixed organic–ammonium sulfate aerosols

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Abstract

Hygroscopic behavior of organic compounds, including levoglucosan, 4-hydroxybenzoic acid and humic acid, and their effects on the hygroscopic properties of ammonium sulfate (AS) in internally mixed particles are studied by a hygroscopicity tandem differential mobility analyzer (HTDMA). The organic compounds used represent pyrolysis products of wood that are emitted from biomass burning sources. It is found that humic acid aerosol particles only slightly take up water, starting at RH above ∼ 70 %. This is contrasted by the continuous water absorption of levoglucosan aerosol particles in the range 5–90 % RH. However, no hygroscopic growth is observed for 4-hydroxybenzoic acid aerosol particles. Predicted water uptake using the ideal solution theory, the AIOMFAC model and the E-AIM (with UNIFAC) model are consistent with measured hygroscopic growth factors of levoglucosan. However, the use of these models without consideration of crystalline organic phases is not appropriate to describe the hygroscopicity of organics that do not exhibit continuous water uptake, such as 4-hydroxybenzoic acid and humic acid. Mixed aerosol particles consisting of ammonium sulfate and levoglucosan, 4-hydroxybenzoic acid, or humic acid with different organic mass fractions, take up a reduced amount of water above 80 % RH (above AS deliquescence) relative to pure ammonium sulfate aerosol particles of the same mass. Hygroscopic growth of mixtures of ammonium sulfate and levoglucosan with different organic mass fractions agree well with the predictions of the thermodynamic models. Use of the Zdanovskii–Stokes–Robinson (ZSR) relation and AIOMFAC model lead to good agreement with measured growth factors of mixtures of ammonium sulfate with 4-hydrobenxybenzoic acid assuming an insoluble organic phase. Deviations of model predictions from the HTDMA measurement are mainly due to the occurrence of a microscopical solid phase restructuring at increased humidity (morphology effects), which are not considered in the models. Hygroscopic growth factors of mixed particles containing humic acid are well reproduced by the ZSR relation. Lastly, the organic surrogate compounds represent a selection of some of the most abundant pyrolysis products of biomass burning. The hygroscopic growths of mixtures of the organic surrogate compounds with ammonium sulfate with increasing organics mass fraction representing ambient conditions from the wet to the dry seasonal period in the Amazon basin, exhibit significant water uptake prior to the deliquescence of ammonium sulfate. The measured water absorptions of mixtures of several organic surrogate compounds (including levoglucosan) with ammonium sulfate are close to those of binary mixtures of levoglucosan with ammonium sulfate, indicating that levoglucosan constitutes a major contribution to the aerosol water uptake prior to (and beyond) the deliquescence of ammonium sulfate. Hence, certain hygroscopic organic surrogate compounds can substantially affect the deliquescence point of ammonium sulfate and overall particle water uptake.

1 Introduction

The hygroscopicity of aerosol particles plays a critical role in visibility degradation, cloud formation, radiative forcing and thereby regional and global climate (Sloane and Wolff, 1985; Charlson et al., 1992; Pandis et al., 1995; Heintzenberg and Charlson, 2009; Shi et al., 2012). Also, the hygroscopic properties of aerosol determine which fraction of aerosol particles can act as cloud condensation nuclei (CCNs) and thus contribute to the aerosol indirect effect (Pilinis et al., 1995; McFiggans, 2006; Hallquist et al., 2009). Moreover, water uptake by aerosol particles influences their health effects, as reported in epidemiological studies (Pöschl, 2005). Therefore, understanding the interactions between water vapor and aerosol particles, as well as the related physicochemical processes in the atmosphere is of great significance.

Biomass burning is one of the important sources of anthropogenic atmospheric aerosols and also leads to the emission of greenhouse gases. The annual globally burned land area is in the range of 3 to 3.5 million square kilometers, resulting in emissions amounting to 2.5×10^9 kg carbon per year (van der Werf et al., 2006; Schultz et al., 2008). Particles in biomass burning smoke enriched with hygroscopic organic and inorganic constituents are suggested to act as efficient cloud condensation nuclei (Novakov and Corrigan, 1996). 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). 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). 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). Several groups have reported that a significant portion of particles in 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). For example, Andreae et al. (2002) studied the chemical composition of the WSOC fraction of particles generated by biomass burning and divided these detected WSOC into three different classes: (1) neutrals (N), (2) monocarboxylic and dicarboxylic acids (MDA), and (3) polycarboxylic acids (PA). Further, Artaxo et al. (2002) have suggested organic surrogate compounds representing size-resolved WSOC chemical composition for the dry and wet seasonal periods of their field campaign in Rondônia, Amazonia. On the basis of chemical structure, these surrogate compounds can be represented approximately by: levoglucosan, 4-hydroxybenzoic acid, and humic acid (Hoffer et al., 2006). Sampled WSOC typically contain a wide range of chemical species that are expected to show rather different water solubilities (Mochida and Kawamura, 2004). However, it is still uncertain whether those WSOC are inherently CCN active or whether they are made active through association with water-soluble inorganic species (Roberts et al., 2001, 2002; Wu et al., 2011). All these factors are of great importance in determining the CCN activity of biomass burning particles.

Previous laboratory studies have addressed the hygroscopic behavior of internally mixed organic–inorganic particles by the hygroscopicity tandem differential mobility analyzer (HTDMA) technique (Brooks et al., 2004; Gao et al., 2008). However, 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). 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. However, actual biomass burning aerosols are typically much more complex in terms of composition. 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 (Decesari et al., 2006).

In this work, the hygroscopic properties of relevant organic compounds from biomass burning are determined by the HTDMA technique. Using this experimental technique, we also study the influence of the organic surrogate compounds on the water uptake behavior of mixed organic–inorganic aerosols containing ammonium sulfate. Moreover, mixtures of several the organic components with ammonium sulfate, mimicking more complex particles observed in the atmosphere are investigated to determine the influence of organic compounds on the overall particle hygroscopicity. In addition, we use the Zdanovskii–Stokes–Robinson (ZSR) relation (Stokes and Robinson, 1966), the Extended Aerosol Inorganic Model (E-AIM) (Clegg et al., 1992, 1998a, b, 2001; Clegg and Seinfeld, 2006; available online: http://www.aim.env.uea.ac.uk/aim/aim.php), and the Aerosol Inorganic–Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) model (Zuend et al., 2008, 2011) to predict the hygroscopic growth of mixed aerosol particles and provide comparisons to our experimental findings.

2 Experimental and modeling methods

2.1 HTDMA instrument setup and experimental protocol

A schematic of our HTDMA setup is presented in Fig. 1. The HTDMA setup is comprised of three main components: (1) the aerosol particle generation section, (2) the particles sizing and humidification system and (3) a relative humidity control system. Polydispersed sub-micrometer particles are generated using an atomizer (MSP 1500, MSP) from bulk solutions with different mass fractions of organic and inorganic species, assuming that the compositions of the mixed aerosols remain the same as that of the solution used in the atomizer. The aerosol particles pass through three silica gel diffusion dryers (SDD) and a Nafion gas dryer (Perma Pure Inc., USA), bringing the particles to a dry state ($RH_1 < 5\,\%$). The dry aerosols are subsequently charged and then enter the first differential mobility analyzer (DMA1), where a near-monodisperse distribution of particles of the desired dry diameter (D_0) of 100 ± 1 nm is selected. After size selection, aerosols are pre-humidified in a Nafion conditioner tube, and then flow into a second Nafion tube at the set relative humidity, RH_2, of a growth factor measurement. 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). 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). The relative humidity of the DMA2 sheath flow, RH_3, is measured using a dew point hygrometer (Michell, UK), with an uncertainty of ±0.08 % RH. To allow the aerosol to equilibrate at the specified RH, we ensure that RH_3 is equal to RH_2. In addition, critical orifices were used to regulate the sheath flows, which were both recirculated using closed-loop arrangements (Jokinen and Makela, 1997).

2.2 Theory and modeling methods

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, $\mathrm{GF(RH)} = D(\mathrm{RH})/D_0$, where $D(\mathrm{RH})$ is the particles diameter at a specific RH and D_0 the diameter at dry conditions (RH $= 0\,\%$), are predicted using different thermodynamic models and mixing rules. In each model, we assume that these particles are spherical. As a consequence, the predicted mobility equivalent diameter is equal to the volume equivalent diameter of a sphere.

2.2.1 GF data fit

An expression proposed by Dick et al. (2000) is used to present the relationship between water activity, a_w and GF(RH) for particles of individual compounds:

$$\mathrm{GF} = \left[1 + \left(a + b \cdot a_\mathrm{w} + c \cdot a_\mathrm{w}^2\right) \frac{a_\mathrm{w}}{1 - a_\mathrm{w}}\right]^{\frac{1}{3}} \tag{1}$$

Here it is assumed that $a_\mathrm{w} = \mathrm{RH}/100\,\%$ (i.e., assuming gas-particle equilibrium at the set RH level while neglecting a curvature effect) (Kreidenweis et al., 2005). The coefficients a, b, and c are determined by fitting Eq. (1) to measured GF data. Equation (1) is appropriate to describe continuous water uptake behavior of particles sufficiently large ($D \gtrsim 100\,\mathrm{nm}$), such that the Kelvin effect can be ignored (Brooks et al., 2004).

2.2.2 GF predictions by ZSR

Assuming that the water uptake for each of the components of mixed particles can be treated independently at a given RH, i.e., the assumption of the Zdanovskii, Stokes, Robinson mixing rule, and that the partial volumes of individual components/phases are additive, the GF of a mixture, $\mathrm{GF_{mix}(RH)}$, can be estimated from the GF_j of the pure components j and their respective volume fractions, ε_j, in the mixture (Malm and Kreidenweis, 1997):

$$\mathrm{GF}_{\mathrm{mix}} = \left[\sum_j \varepsilon_j (\mathrm{GF}_j)^3\right]^{\frac{1}{3}} \tag{2}$$

2.2.3 GF prediction by E-AIM

E-AIM is a thermodynamic equilibrium model used for calculating gas/liquid/solid partitioning, widely used in the community. This model includes density predictions for aerosol systems containing inorganic and organic components in aqueous solutions. This allows for better consideration of non-ideal mixing effects on solution density, and hence particle diameter at different RH. The group-contribution method UNIFAC (UNIversal quasi-chemical Functional group Activity Coefficients) (Fredenslund et al., 1975; Hansen et al., 1991), can be used within the E-AIM model to predict activity coefficients in aqueous solutions of multifunctional organic compounds (Clegg et al., 2001). However, the standard UNIFAC model (Fredenslund et al., 1975; Hansen et al., 1991) is usually not appropriate for organic components in which two strongly polar groups are separated by less than four carbon atoms giving rise to intramolecular interactions, such as hydrogen bonding between certain polar groups. Some specific interaction parameters of UNIFAC were revised by Peng et al. (2001). The use of these modified UNIFAC parameters improves the prediction of the water activity of dicarboxylic acids and hydroxy-di-carboxylic and -tricarboxylic acids. These modified UNIFAC parameters can also be chosen for calculations within the E-AIM model. The use of E-AIM model for mixed organic–inorganic systems has been described in a range of papers (Hanford et al., 2003, 2008; Clegg and Seinfeld, 2006b; Pope et al., 2010a, b; Yeung and Chan, 2010).

We applied the E-AIM model to obtain the equilibrium state of aqueous mixtures and predict the GF as a function of RH. The water uptake by the organic components is estimated by choice with either the standard UNIFAC model or the modified UNIFAC model with certain interaction parameters by Peng et al. (2001) UNIFAC-Peng as part of the E-AIM model. Both flavours of UNIFAC have been applied for certain systems studied in this work.

2.2.4 GF prediction by AIOMFAC

The AIOMFAC model by Zuend et al. (2008, 2011) is a thermodynamic group-contribution model designed to calculate activity coefficient covering inorganic, organic, and organic–inorganic interactions in aqueous solutions over a wide concentration range. Like the optional choice in the E-AIM model, AIOMFAC also includes a modified UNIFAC model. In addition, AIOMFAC includes long-range and middle-range molecular interaction contributions based on a semi-empirical Pitzer-type model expression to explicitly account for interactions between inorganic ions and organic functional groups (plus water) in mixed solutions. This model has been successfully applied to a variety of thermodynamic equilibrium calculations, including the consideration of liquid–liquid phase separation and the deliquescence of ammonium sulfate (e.g., Zuend et al., 2010; Song et al., 2012; Zuend and Seinfeld, 2012; Shiraiwa et al., 2013).

In this study, we use a thermodynamic equilibrium model based on AIOMFAC (Zuend and Seinfeld, 2012; Shiraiwa et al., 2013) which assumes that all components are in a liquid or amorphous (viscous) solution, potentially exhibiting liquid–liquid phase separation in a certain RH range – except for ammoniums sulfate, which, as an option, is allowed to form a crystalline phase in equilibrium with the remaining solution (to represent the efflorescence and deliquescence hysteresis behavior of the inorganic salt depending on the mode of hydration/dehydration and starting RH in computations). Liquid–liquid phase equilibria are predicted using the algorithm of Zuend and Seinfeld (2013). However, the formation of solid (crystalline) organic phases is not generally considered at this point since in actual complex organic aerosols, the formation of crystalline organic phases is likely suppressed (Marcolli et al., 2004). Thus, in the context of this study, where solid organic phases may be present in some of the systems, the model will not be applicable – at least not to as part of the hydration branch of a humidity cycle. As an exception, we apply the model for the mixed systems of

4-hydroxybenzoic acid and ammoniums sulfate also in a mode where the assumption is made that the organic component is solid and insoluble over the whole RH range considered (this allows for better comparison with the experimental findings). Since this thermodynamic model predicts the water content (mole fraction of water) of a mixture in equilibrium with the gas phase at a given RH level, mass growth factors can be calculated directly. However, to compute diameter growth factors, assumptions about the density of different mixture components and non-ideal mixing effects on solution density need to be made. 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).

2.2.5 Ideal solution growth factor

The water activity of an ideal solution containing a nonvolatile, non-electrolyte component is equal to the mole fraction of water (x_w) (activity coefficients of unity). Thus, in the case of an ideal solution, we can estimate the water activity of liquid particles directly from the knowledge of water content in term of x_w. Solutions comprising electrolyte components, such as ammonium sulfate or sulfuric acid, are usually strongly deviating from an ideal solution due to substantial dissolution (dissociation) of the electrolytes and non-ideal interaction between ions, water, and organic compounds. Therefore, water activities of mixed organic–inorganic systems may substantially differ from a prediction by an ideal solution assumption (e.g., Zuend et al., 2011).

In this study, the ideal solution growth factor is used to explore its use as a simple approach to describe the hygroscopic diameter growth factor of pure components and mixtures, e.g. for ammonium sulfate and mixed particles. Since hygroscopic diameter growth factor measurements using the HTDMA are on volume basis, the ideal solution

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GF is calculated using mole fractions by the equation:

$$\mathrm{GF}=\left[\frac{\sum_j\left(x_jM_j\frac{1}{\rho_j}\right)}{\sum_{j,j\neq w}\left(x_jM_j\frac{1}{\rho_j}\right)}\right]^{\frac{1}{3}} \tag{3}$$

Here, x_j, M_j, and ρ_j are mole fraction, molar mass and mass density of component j, respectively. The sum in the numerator of Eq. (3) goes over all components including water, while the sum in the denominator goes over all components except for water ($j \neq w$; "dry" conditions). Note that when dissociated electrolyte components are present in the liquid mixtures, the mole fractions in Eq. (3) have to be calculated as mole fractions with respect to completely dissociated electrolytes (or an applicable degree of dissociation). Equation (3) is more likely applicable when water and the solute components are in a liquid solution, i.e., no solid/phases present. In addition, it is assumed that the partial molar volumes of organics and water in solution are equal to those of the respective pure liquid components.

3 Results and discussion

3.1 GF of single solute systems

The hygroscopic behavior of ammonium sulfate aerosol close to room temperature is well understood and has been characterized by several groups (Gysel et al., 2002; Kreidenweis et al., 2005; Biskos et al., 2006a, b). We can use it as a reference substance to calibrate the HTDMA setup because of its well-known deliquescence point (80 % RH at 294.8 K) (Onasch et al., 1999).

Figure 2a presents growth factors of 100 nm (dry diameter) ammonium sulfate particles from low to high RH. The measured growth factor of ammonium sulfate is 1.45 ± 0.01 at 80 % RH after full deliquescence. The data agree well with values measured by Gysel et al. (2002) and Wise et al. (2003), for example, the DRH of AS at

80 % RH after deliquescence is 1.45 at 24.9° as measured by Wise et al. (2003). The hygroscopic growth experiments for pure AS are also in good agreement with the prediction from the E-AIM model and the AIOMFAC model. Here, both models correctly account for the solid, crystalline state of AS in the RH range before the deliquescence at ~ 80 % RH for the conditions of a hydration experiment. Slight differences between these two thermodynamic models, which both account very well for the non-ideal solution behavior of AS, are due to different conversions of mass growth to diameter growth factors by the models. The E-AIM model includes a composition dependent solution density model, while the AIOMFAC-based model does not. However, assuming an ideal solution, without consideration of the solid state and mixing effects on solution density, its prediction for AS results in higher than measured hygroscopic growth, also for RH > 80 %. Therefore, aside from the solid-to-liquid phase transition, the water activity in concentrated solution also deviates from ideality.

As shown in Fig. 2b, levoglucosan aerosol particles show continuous water uptake from low to high RH, and no deliquescence phase transition is observed, in excellent agreement with the behavior reported by Mochida and Kawamura et al. (2004) and Svenningsson et al., 2006. The measured GF at 80 % RH is 1.17 ± 0.01, which is similar to a result from the literature (Mochida and Kawamura, 2004), which report a growth factor of levoglucosan of 1.18 at 80 % RH. Also, the measured hygroscopic growth factors are reasonably consistent with those estimated from the standard UNIFAC model within the E-AIM model, the AIOMFAC model, ideal solution theory, and the fitted expression Eq. (1). At higher RH, deviations between the different models become more significant for a good estimate of the actual GF. 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). Zuend et al. (2011) discuss the case of AIOMFAC predictions for levoglucosan and its mixtures with different inorganic electrolytes. They state that the molecular structure of levoglucosan with several polar functional groups in close vicinity leads to less accurate model predictions for solutions containing this compound. The same is true for UNIFAC model predictions and is therefore a well-known limitation of these models for this particular system, explaining the observed deviations between model curves and measurements.

As can be seen from Fig. 2c, humic acid aerosol particles show a slight increase in GF from 10 % RH to 70 %. Above 70 % RH, the particles start to take up increasingly more water toward high RH. These measured GF are slightly higher than the measured hygroscopic growth factors of Leonardite Standard HA by Brooks et al. (2004), perhaps due to different origin and composition of the humic acid samples. Due to the lack of detailed physical and chemical information about the used humic acid, the GF of humic acid particles are only presented with a data fit based on Eq. (1). The determined fit parameters are listed in Table 2. For model calculations with E-AIM and AIOMFAC, the chemical structure or at least the type and relative abundance of functional groups needs to be known, which is not the case for the humic acid particles.

The hygroscopic growth curves for 4-hydroxybenzoic acid are presented in Fig. 2d. No hygroscopic growth (within error) was observed below 90 % RH. On the contrary, the measured growth factors show a slight decrease in particles diameter with increasing RH, which is consistent with previous experiments by another group (Mochida and Kawamura, 2004). The reasons for the decrease in particle diameter are not fully understood, but the same behavior is reported by Shi et al. (2012) for particles consisting of ammonium sulfate + benzoic acid. On the basis of Transmission electron microscopy (TEM) image analysis, they attribute the diameter decrease to the microscopic restructuring of solid particles with increasing RH, which may affect the particle mobility diameter. Therefore, a similar effect could be responsible for the observations from our experiments. Another potential reason for a decrease in apparent diameter could be the partial evaporation of semivolatile organics from the aerosol particles in the HT-DMA (here: 4-hydroxybenzoic acid, pure liquid vapour pressure $p^{0,L} = 8.11 \times 10^{-4}$ Pa at 298.15 K, Booth et al., 2012), an effect that is also known for certain volatile inorganic particles (e.g., NH_4NO_3) (Lightstone et al., 2000; Hersey et al., 2013). Obviously, the observed results are different from the GF curves predicted by the ideal solution theory, the AIOMFAC model, and the UNIFAC-Peng (within E-AIM) model. For these predictions hydration mode, starting with particles at 0 % RH, the applied models assume that the organic component is present in the liquid state and that solid organic phases are not present. However, the experimental data indicate that 4-hydroxybenzoic acid is solid and remains solid in the range from 5 to 90 % RH for a hydration experiment. Hence, the shown model predictions clearly deviate from the measurements due to the unfavourable assumption of a liquid solution and not because of a general limitation of the models for describing growth factors of the aqueous 4-hydroxybenzoic acid. Would the models account for a solid organic phases, the predicted GF would be 1.0 throughout the showed experimental RH range with deliquescence of the organic crystal expected to occur at an RH value greater than 90 %. Indeed, the model curves may well capture the water uptake/loss behavior prior to crystallization for the case of a dehydration experiment starting at very high RH (∼ 100 %) with liquid particles becoming supersaturated, metastable solution as RH is decreased below the deliquescence point).

3.2 Mixed systems: ammonium sulfate + levoglucosan

The measured water uptake by 100 nm particles consisting of different mixtures of ammonium sulfate + levoglucosan with dry mass ratios of 3 : 1, 1 : 1, and 1 : 3, shown in Fig. 3, present a reduction in the GF at RH > 80 % with increasing levoglucosan mass fraction and therefore decreasing AS content. For example, the growth factors are 1.30, 1.30, and 1.28 at 80 % RH, respectively, relative to the GF of 1.45 of pure AS particles at 80 % RH. Particles start to take up water well before the full deliquescence of AS at RH = ∼ 80 %. Similar behavior is observed by Qiu and Zhang (2013) for particles containing 10 wt% monomethylaminium sulfate (MMAS) or dimethyllaminium sulfate (DMAS) and ammonium sulfate. Those particles also exhibit a moderate growth by water uptake in the RH range of 40–70 %.

The experimental hygroscopic growth results for AS + levoglucosan mixtures are compared with four models predictions. The E-AIM model with standard UNIFAC is in relatively good agreement with the measured hygroscopic growth factors, but slightly overestimating the water uptake at RH < ~ 70 %. Especially in the case of the 1 : 1 mixtures of AS: levoglucosan (by mass), 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. A possible reason 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 approach. For example, in the equilibrium calculations with AIOMFAC, although solid and liquid phase partitioning is considered, the densities of both AS and levoglucosan are kept constant at their respective pure molar liquid density values at different aqueous solution compositions with increasing RH, the density of the solid fraction of AS is considered separately as well. Hence, when we convert mass growths to diameter growths factors, aqueous phase density of mixed aerosol particles in the AIOMFAC-based equilibrium model is between the solution density at as low as 5 % RH and the density at as high as 99 % RH predicted by the E-AIM model. Therefore, the AIOMFAC model prediction is a bit lower than that of the E-AIM model in the range from 5 to 80 %, and its prediction is a bit higher than the E-AIM model above 80 % RH. In addition, the E-AIM model predicts a slightly higher mutual solubility of AS and levoglucosan at RH < 80 % in comparison to AIOMFAC, which leads to more dissolution of AS and associated with that, to a large water uptake at RH below full deliquescence. Regarding the ideal solution curve without consideration of a solid AS phase, the ideal curve approaches better with the measured GFs with increasing mass fraction of levoglucosan, which is a consequence of a reduced effect and less abrupt deliquescence transition of ammonium sulfate in the mixtures with higher levoglucosan mass fraction. The ZSR model is based on hygroscopic growth factors of ammonium sulfate and levoglucosan derived from E-AIM predictions for AS and fitted GF curve (Eq. 1) for levoglucosan. At RH above 80 %, the ZSR model is in relatively good agreement with the measured particle hygroscopicities when accounting for measurement error. However, due to the nature of the classical ZSR model used, the mutual solubility of AS in aqueous levoglucosan solution at RH < 80 % below full AS deliquescence is not considered, i.e., the water uptake of organic and inorganic components is treated separately and no dissolution effects are accounted for. At those lower RH conditions, this leads to the largest deviations from experimental data for the ZSR predictions in comparison to the two other models.

3.3 Mixed systems: ammonium sulfate + humic acid

Hygroscopic behavior of 100 nm particles containing ammonium sulfate + humic acid with dry mass ratios of 3 : 1, 1 : 1, 1 : 3, shown in Fig. 4, present a reduction in GF at RH > 80 % with increasing mass fraction of HA (decreasing AS content). 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. A similar tendency had been observed by Brooks et al. (2004) for mixtures containing HA and AS, which exhibit a size growth prior to 80 % RH. Hygroscopic growth factors referring to the water uptake contribution by HA in the ZSR relation are obtained from the fitted growth curve of pure HA particles (Eq. 1). As for the levoglucosan + AS system, E-AIM predictions of the growth factors of pure AS are used in the ZSR relation here. The resulting ZSR prediction agrees relatively well with the measured hygroscopic growth of the different mixtures. Also qualitatively, when comparing the three mixtures, the ZSR prediction reproduces the lower GF of the 3 : 1 AS : HA particles at RH < 80 % least amount of HA and then by contrast the higher GF for RH > 80 % due to a large water uptake contribution from AS after deliquescence. Model predictions using the E-AIM and AIOMFAC could not be performed for this system because of the lack of knowledge about the actual molecular structure of the humic acid samples used.

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3.4 Mixed systems: ammonium sulfate + 4-hydroxybenzoic acid

Figure 5 shows the measurement and model predictions for particles consisting of ammonium sulfate + 4-hydroxybenzoic acid with dry mass ratios of 3 : 1, 1 : 1, 1 : 3, A GF reduction from Fig. 5a–c at high relative humidity is mainly due to an increasing mass fraction of 4-hydroxybenzoic acid. For example, the measured growth factors are 1.31, 1.26, and 1.10 at 80 % RH after full AS deliquescence for the particles containing 25 wt%, 50 wt%, and 75 wt% 4-hydroxybenzoic acid (dry mass percentages), respectively. Hygroscopic behavior of mixed 4-hydroxybenzoic acid–AS particles is found to be essentially unaffected by the presence of 4-hydroxybenzoic acid. However, the GF of such particles differ from pure AS particles due to the different basis of normalization dry diameter includes insoluble organic phase for the same dry size particles class. The ZSR relation agrees very well with the measured hygroscopic growth for mixed particles within measurement error due to fitted hygroscopic growth factors for 4-hydroxybenzoic acid are used as input for the ZSR relation (Eq. 2). For the case of particles containing AS and 4-hydroxybenzoic acid, the ideal solution curves shows a large deviation from measured GFs, partly because of the solid organic phase, but it is also obvious that such mixtures deviate from ideal behavior. As in the case of binary 4-hydroxybenzoic acid + water system (Fig. 2d), for the mixed systems with ammonium sulfate (Fig. 5), E-AIM model predictions are referring to a system where the organic component remains liquid at all RH, i.e., without consideration of a solid organic phase that is most likely present during these hydration experiments. However, the crystallization and dissolution of ammonium sulfate is considered by the two thermodynamic models. Hence, the systematic offset observed when comparing model results and measurements in Fig. 5 is mainly due to incorrect model assumptions for these organic–inorganic mixtures. In the case of the AIOMFAC model prediction a solid organic phase is assumed, i.e., it is assumed that the organic growth factor contribution GF (4-hydroxybenzoic acid) = 1.0 for the whole RH range, the resulting particle growth prediction is still a bit higher than the measured hygroscopic particle growths above 80 % RH.This is largely explained by the fact that the measurement indicate GF < 1.0 at RH $\approx 80\,\%$ and above, potentially due to particles morphology effects, which then presents a systematic offset between measurements and model prediction. Microscopical particle morphology restructuring and associated size changes of solid particles at moderate to high RH levels have been found in other experiments too. An interesting, yet contrasting phenomenon was observed by Sjogren et al. (2007). They investigated different mixtures of ammonium sulfate + adipic acid in the RH range from ~ 5 % to ~ 95 % using HTDMA instruments and an electrodynamic balance (EDB). In addition, Sjogren et al. (2007) studied the morphology of samples of their mixed aerosols containing solid (insoluble) adipic acid using scanning electron microscopy (SEM). Growth factors indicating significant water uptake at RH below the full deliquescence of AS and systematic deviations from ZSR predictions observed are explained by Sjogren et al. (2007) as a result of morphological effects, including an inverse Kelvin effect, leading to enhanced particle growth factors due to water uptake into cracks, veins and pores of polycrystalline solids. In contrast, our observations indicate a shrinking of 4-hydroxybenzoic acid containing particles with increasing RH or at least a decrease of their mobility-equivalent diameters.

3.5 Mixtures of biomass burning organic surrogate compounds with ammonium sulfate

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 (16.6–30.9 % by mass) to the total organic fraction in $PM_{2.5}$ (Mochida and Kawamura, 2004). In general, MDA have been identified as pyrolysis products of lignin, which is a major constituent of woods. 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 was identified as PA having molecular structures similar to humic materials (HMs) (Decesari et al., 2001; Fuzzi et al., 2001). 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). The effects of such organic surrogate compounds on the hygroscopic behavior of mixed organic–inorganic particles containing also ammonium sulfate are measured and discussed in following. We use the relative abundances of the three model compound classes based on the chemical composition analysis of atmospheric particles reported by the Decesari et al. (2006). The chemical compositions of two distinct mixtures are given in Table 2. Mix-bio-dry and mix-bio-wet are compositions typical of biomass burning aerosols in the two different seasons (dry and wet) in the Amazon basin near Rondônia, Brazil (Decesari et al., 2006).

3.5.1 Water uptake of mix-bio-dry and mix-bio-wet particles

The hygroscopic behavior of mix-bio-dry particles in terms of GF is presented in Fig. 6a. Mixtures of organic surrogate compounds and AS in these dry season model particles do not show any growth below 65 % RH. However, mix-bio-dry particles begin to take up water at 65 % RH and show steep growth between 75 and 80 % RH, where the partial deliquescence of AS contributes increasingly to the water uptake and, hence, the overall growth factor. Similar water uptake behavior prior to full AS deliquescence has been reported by Zardini et al. (2008) and Wu et al. (2011) for different organic + ammonium sulfate mixed aerosol systems. The E-AIM model prediction for mixtures consisting of ammonium sulfate + levoglucosan with a comparable dry mass percentage ratio of 68 wt%: 26 wt% is in relatively good agreement with the measured growth factors above 75 % RH, this reveals that levoglucosan, as part of the mixture of organic biomass burning organic surrogate compounds, largely contributes to the water uptake of mixtures containing organic surrogate compounds and ammonium sulfate before the deliquescence of AS. The ZSR model curve is calculated on the basis of the growth factors of the pure components: for AS using E-AIM, for levoglucosan, 4-hydroxybenzoic acid and humic acid using the fitted expression (Eq. 1). The ZSR prediction tends to agree well with the water uptake investigated at RH above 80 % RH, while large deviations are found for the range between 0 and 80 % RH, for similar reasons as discussed for the AS + levoglucosan systems (Fig. 3 and related text).

The hygroscopic behavior of mix-bio-wet particles is shown in Fig. 6b. In contrast to mix-bio-dry particles, mix-bio-wet aerosols show little water uptake below 80 % RH. This result is expected given the lower mass fraction of hygroscopic organics (e.g., only 9.2 wt % levoglucosan) in the mix-bio-wet particles. The observed hygroscopic behavior of mixed organic–inorganic aerosols of other HTDMA studies on biomass burning aerosols published in the literature, e.g, Wu et al. (2011), cannot be compared directly to our measurements, because the samples and organic: inorganic rations are different. However, the work by Wu et al. (2011) shows that other mixtures containing AS and organic acids found in biomass burning aerosol from Brazil, show significant water uptake at relative humidities below 80 %, similar to our mix-bio-dry case. In addition, the E-AIM model prediction for mixtures consisting of AS and levoglucosan by mass percentage ratio of 87 wt%: 9.2 wt% is in good agreement with the measured growth curve, which indicates that levoglucosan mainly contributes to the hygroscopic behavior of the organic aerosol fraction of the mixtures consisting of biomass burning model organics and AS. Also, due to the limited water uptake prior to AS deliquescence in the mix-bio-wet case, the ZSR prediction results in a good description of the measured growth curve.

To summarize, the hygroscopic growth factor of mixed organic + ammonium sulfate particles is affected by the presence and relative composition of organic surrogate compounds from biomass burning. For example, the growth factors during humidification of mixed particles composed of model organics and AS at 80 % RH are 1.35 for representative dry season aerosols and 1.37 for wet season aerosols. These growth factors are lower than the GF of 1.45 for pure AS particles, which is of course expected given the lower hygroscopicity of the organic components and the general finding that water uptake contributions according to Eq. (2) usually describes a mixture's GF quite well. The measured GF values of our biomass burning model systems are similar to the ones reported by Jung et al. (2011) for biomass burning aerosols sampled in Ulaanbaatar, Mongolia, for which the GF were found to be between 1.30 and 1.35 at 80 % RH during hydration. Effects of organic surrogate compounds on the deliquescence behavior of AS are found with increasing mass fraction of hygroscopic organic surrogate compounds, particularly levoglucosan, from aerosol mixtures representing the wet and dry seasons in the Amazon basin. In the case of dry period aerosols with an enhanced mass fraction of organic surrogate compounds, a smoothing of the hygroscopic behavior is observed, likely due to the continuous water uptake by levoglucosan and partial dissolution and additional water uptake by ammonium sulfate. This result is similar to the observed behavior in simple, binary mixtures of levoglucosan + AS, suggesting that 4-hydroxybenzoic acid and HA show little to no effect on the hygroscopic behavior of mixed particles during a hydration experiment starting at dry conditions.

4 Conclusions

According to field studies reported in the literature, aerosol particles from biomass burning events always contain a variety of inorganic and organic compounds. Different compositions of these aerosol particles have a significant influence on their physicochemical properties, in particular hygroscopic behavior. Differences regarding aerosol number concentration and particle composition were observed for the dry and wet seasons in the Amazon and other regions (Artaxo et al., 2002; Decesari et al., 2006; Rissler et al., 2006). In this work, we focused on three organic compounds (levoglucosan, 4-hydroxybenzoic acid, and humic acid) to represent common compound classes from biomass burning. These organics are also representative of three different water uptake characteristics. Hygroscopic growth measurement for the two-component organic + AS particles show that certain organic compounds can have an important influence on the overall particle diameter growth factor and the partial deliquescence of

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AS, e.g., 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. In contrast, 4-hydroxybenzoic acid and humic acid show no obvious effect on the deliquescence RH of AS. Also, due to the limited solubility of these two organic compounds, the hygroscopic growth factors at RH below 95 %, as measured, are reduced relative to that of pure AS particles.

Mixtures of organic surrogate compounds with AS, representing atmospheric aerosols from biomass burning were made, with chemical compositions determined on the basis of different organic and inorganic component fractions observed for the dry and the wet period in the Amazon basin. The most striking difference in measured hygroscopic growth curves comparing the two seasons is due to presence of different amounts of levoglucosan as surrogate compound, implying that highly oxidized organic compounds like levoglucosan may play an important role in controlling the hygroscopic behavior of atmospheric particles at RH below the full deliquescence of inorganic salts, such as AS. Therefore, a main advantage of using organic surrogate compounds representing the complex WSOC fraction of biomass burning, aerosol is their use for laboratory experiments and associated evaluation and improvement of thermodynamic mixing models and parameterization for the predictions of hygroscopic behavior and CCN activity in atmospheric models.

This work focus on the water uptake and deliquescence behavior of organic compounds from biomass burning sources and their influence on the water uptake of mixed organic–ammonium sulfate aerosol particles. Ambient biomass burning aerosol particles may undergo the humidity cycles depending on the RH history of an air parcel. Humidity cycles may possible lead to solid-liquid phase transition hysteresis with distinct deliquescence and efflorescence behavior of the organic components and organic–inorganic-mixtures. Associated changes of aerosol hygroscopicity of mixed particles similar to the multicomponent systems studies in this work will be a topic of studies in the future.

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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}]	Manufacture
Ammonium sulfate	$(NH_4)_2SO_4$	132.140	1.770[a], 1.550[a]	74.400 (at 20 °C)	0.072	Alfa Aesar, 99.95 %
Levoglucosan	$C_6H_{10}O_5$	126.100	1.618[b], 1.512[b]		0.073[c] (0.01–10 mg mL^{-1})	Aldrich, 99 %
4-Hydroxybenzoic acid	$C_7H_6O_3$	138.100	1.460, 1.372[d]	0.675 (at 25 °C)	0.070[e]	Alfa Aesar, 99.99 %
Humic acids		NA	0.800[f]	NA	NA	Aldrich, 99 %

[a] Clegg and Wexler (2011a);
[b] Lienhard et al. (2012);
[c] Tuckermann and Cammenga (2004);
[d] Jedelský et al. (2000);
[e] Kiss et al. (2005);
[f] Yates III and Wandruszka (1999).

Table 2. Coefficients of the fitted growth curve parameterization to measured growth factor data using Eq. (1).

Chemical compounds	*a*	*b*	*c*
Levoglucosan	0.38672	−0.50083	0.27942
4-Hydroxybenzoic acid	−0.13457	0.20959	−0.08098
Humic acid	0.36201	−0.61395	0.36949

Table 3. The chemical composition of biomass-burning model mixtures studied, given as mass percentages (wt%).

Mixture name	Ammonium sulfate	Levoglucosan	4-Hydroxybenzoic acid	Humic acid
Mix-bio-dry	68.0 %	26.0 %	3.0 %	3.0 %
Mix-bio-wet	87.2 %	9.2 %	1.5 %	2.1 %

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Hygroscopicity of organic compounds from biomass burning

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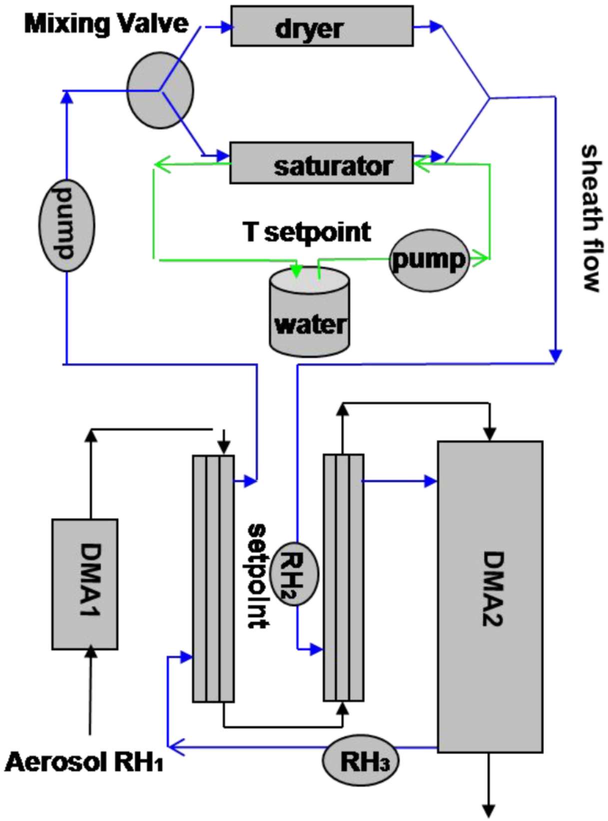

Fig. 1. Schematic of the hygroscopicity tandem different mobility analyzer (HTDMA) system.

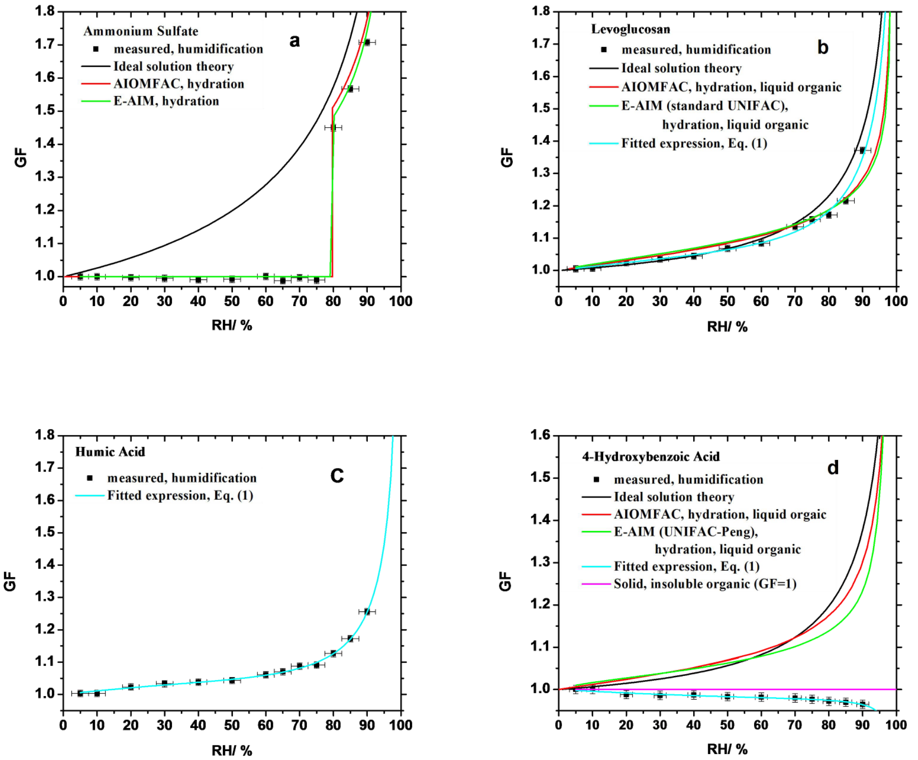

Fig. 2. Hygroscopic diameter growth factor (GF) for 100 nm (dry diameter RH < 5 %) aerosol particles. The measurements, model calculations, and fitted expression Eq. (1) represent conditions of particle growth during a hydration experiment from 5 % RH to 90 % RH at 298.15 K systems: **(a)** ammonium sulfate, **(b)** levoglucosan, **(c)** humic acid, and **(d)** 4-hydroxybenzoic acid.

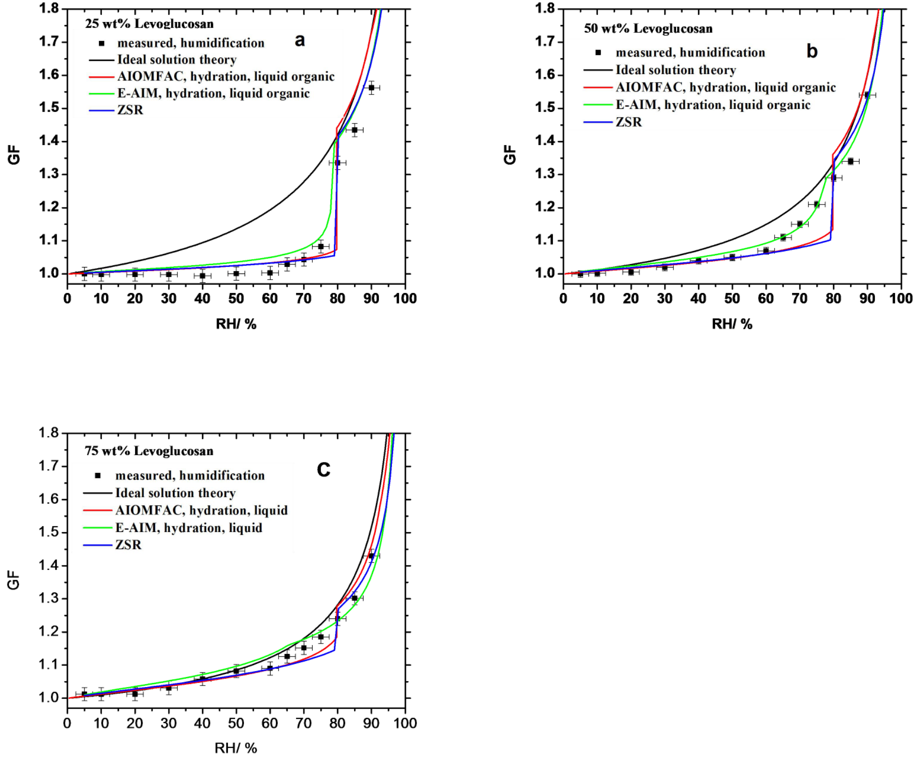

Fig. 3. Hygroscopic growth factors of aerosol particles containing mixtures of levoglucosan with ammonium sulfate at three different dry state mass fractions. The measurements and model calculations represent the particle growth during a hydration experiment from 5 to 90 % RH at 298.15 K. Mass ratio of AS : Levoglucosan: **(a)** 3 : 1, **(b)** 1 : 1, **(c)** 1 : 3.

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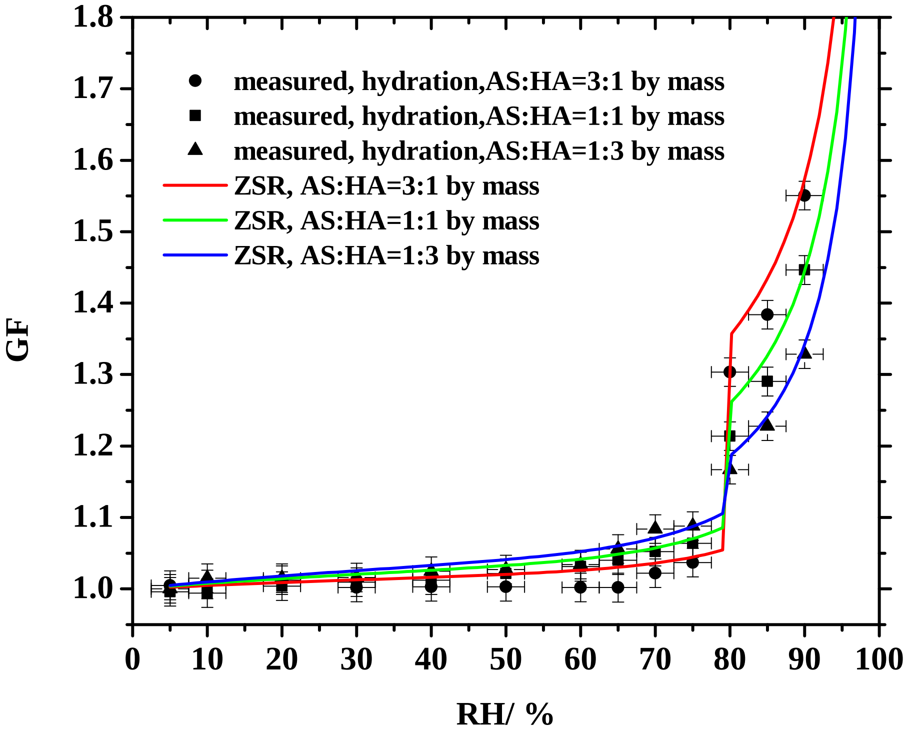

Fig. 4. Hygroscopic growth factors of aerosol particles containing mixtures of humic acid (HA) and ammonium sulfate at three different dry state mass ratios. The measurements and ZSR model calculations represent the particle growth during hydration experiments from 5 to 90 % RH at 298.15 K.

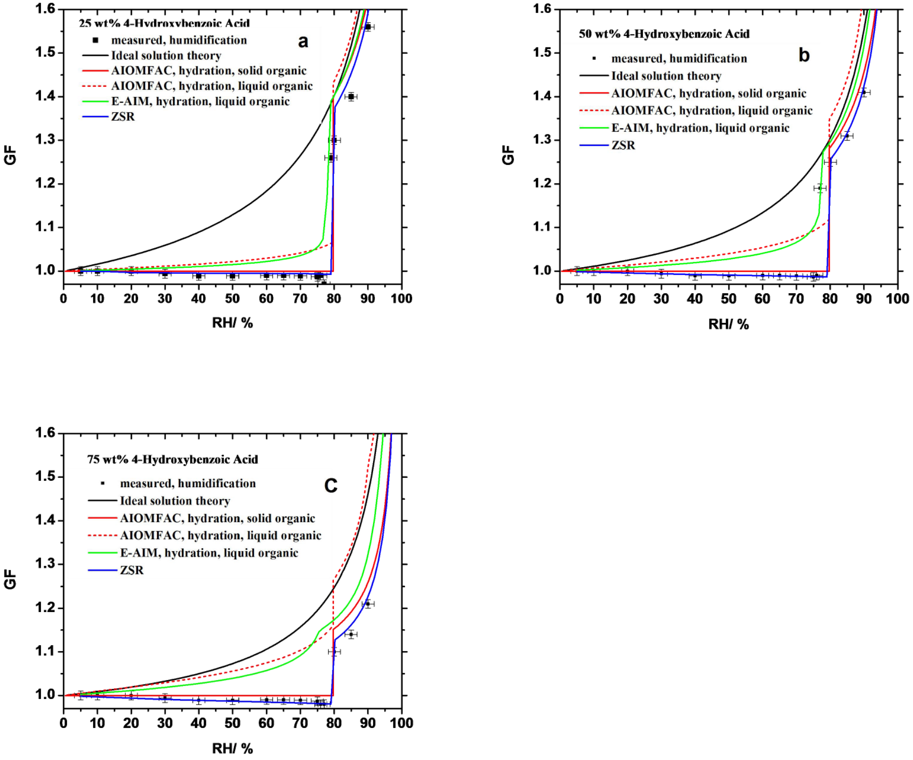

Fig. 5. Hygroscopic growth factors of aerosol particles containing mixtures of 4-hydroxybenzoic acid with ammonium sulfate at three different dry mass ratios. The measurements and model calculations represent particle growth during hydration experiment from 5 to 90 % RH at 298.15 K. Mass ratio of AS : 4-Hydroxybenzoic Acid: **(a)** 3 : 1, **(b)** 1 : 1, **(c)** 1 : 3.

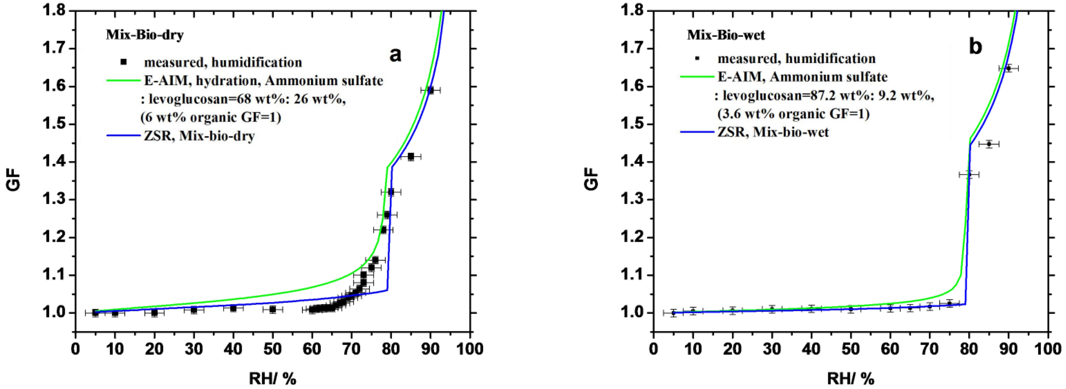

Fig. 6. Hygroscopic growth factors of 100 nm (dry diameter) particles consisting of mixtures of organic surrogate compounds with ammonium sulfate representing particles of **(a)** dry and **(b)** wet seasonal periods in the Amazon. The measurements and model calculations describe the particle growth during hydration experiments from 5 % to 90 % RH at 298.15 K systems.