Response to comments by anonymous referee #1:

This manuscript presents hygroscopic properties of levoglucosan and D-glucose nanoparticles, mainly growth factors, through combined laboratory nano-HTDMA measurements and model predictions. Measurement data of hygroscopic properties of nanoparticles, especially for sizes down to 6 nm are scarcely lacking. The results from this study may make important contributions to improve our understanding of the hygroscopic properties of small nanoparticles and thus their important roles in new particle formation and growth, also in aerosol aging, in particular, the important roles of the two important biomass burning product in the above aerosol formation and aging processes. The following issues/concerns need to be fully resolved before the manuscript would be considered.

Response: We are grateful to referee #1 for her/his comments and suggestions to improve our manuscript. We have implemented changes based on these comments in the revised manuscript in red. In the following point-by-point response, the reviewer's comments are in italic font and marked blue. The lines mentioned are with respect to the Atmospheric Chemistry and Physics Discussions (ACPD) version.

General comments:

(1) Abstract: The abstract is not concise and not getting to the main ideas of the paper. L37-39, levoglucosan is mentioned in the sentence, however, the RH examples are for D-glucose, why?

Response: Thank you for the comments. We have revised the abstract to be more concise and clarified the sentence in line 37-39, and now the abstract read as:

"**Abstract:** The interaction between water vapor and aerosol nanoparticles is important in atmospheric processes. Hygroscopicity of sub-10 nm organic nanoparticles and their concentration-dependent thermodynamic properties (e.g., water activity) in the highly supersaturated concentration range are, however, scarcely available. Here we investigate the size dependence of hygroscopicity of organics (i.e., levoglucosan, D-glucose) in dry particle diameter down to 6 nm using a nano-hygroscopicity tandem differential mobility analyzer (nano-HTDMA). Our results show that there is only a weak size dependent hygroscopic growth of both levoglucosan and D-glucose nanoparticles with diameters down to 20 nm. In the diameter range smaller than 20

nm (down to 6 nm), we observed a strong size-dependent hygroscopic growth for D-glucose nanoparticles. The hygroscopic growth factors cannot be determined for levoglucosan below 20 nm due to its evaporation. In addition, we compare hygroscopicity measurements for levoglucosan and D-glucose nanoparticles with the E-AIM (standard UNIFAC), the ideal solution theory, and DKA predictions, respectively. The ideal solution theory describes well the measured hygroscopic growth factors of levoglucosan with diameters down to 20 nm and D-glucose nanoparticles with diameters higher than 60 nm, respectively, while the E-AIM (standard UNIFAC) model can successfully predict the growth factors of D-glucose nanoparticles with diameters from 100 down to 6 nm at RH above 88-40 % (e.g., at RH above 88 % for 100 nm D-glucose, at RH above 40 % for 6 nm D-glucose). The use of the DKA method leads to a good agreement with measured hygroscopic growth factors of D-glucose aerosol nanoparticles with diameters from 100 down to 6 nm. Predicted water activity for these aqueous organic solutions (i.e., levoglucosan, D-glucose) from different parameterization methods agrees well with observations in the low solute concentration range (< 20 mol kg^{-1}), and start to deviate from observations in the high solute concentration (> 20 mol kg^{-1})."

(2) Introduction: What is the purpose for the authors to compare the availability of the thermodynamic data between highly supersaturated inorganic aqueous solutions and organic solutions such as levoglucosan and D-glucose (the paragraph in L88-97)? A clear connection and comparability between the inorganic and organic solutions is needed.

Response: Thank you for the comments. The purpose of the paragraph in L88-97 is mainly to explain that the current thermodynamic models are difficult or impossible to predict the hygroscopic growth factor of sub-10 nm organic nanodroplets due to lack of thermodynamic data such as water activity and surface tension from models available in the high supersaturation concentration range. Thus, a Differential Köhler Analysis (DKA) method (Cheng et al., 2015) is introduced to retrieve these thermodynamic data of organic nanodroplets, especially in the high supersaturation concentration.

We have revised the paragraph in L88-97 and now they read as:

Thermodynamic model is widely used to predict the hygroscopic growth factor of organic aerosol particles as a function of RH (Bhandari and Bareyre. 2003; Chan et al., 2005; Koehler et al., 2006; Peng et al., 2010). The thermodynamic model needs thermodynamic data such as water activity, liquid-vapor interfacial energy (surface tension), and density of organic aqueous solutions (Tang and Munkelwitz, 1994; Tang 1996; Pruppacher and Klett, 1997; Clegg et al., 1998). Because

nanodroplets can become more highly supersaturated where no thermodynamic data are available,, it makes the current thermodynamic model difficult or impossible to predict the hygroscopic behavior of organic aerosol nanoparticles. Cheng et al. (2015) pointed out that size effect might be taken models into account. By measuring the hygroscopic growth factor of organic nanoparticles (e.g., levoglucosan and D-glucose) of different sizes, we may be able to retrieve these thermodynamic data using a Differential Köhler Analysis (DKA) method (Cheng et al., 2015). This will further help us to understand the new particle formation, transportation, and their interactions between water molecules.

(3) Methodology: There are too many subsections in this part. Some of them are very short. It is not necessary to divide this part into so many subsections. Better rearrangement for this section is needed.

Response: Many thanks. According to reviewer's suggestions, we have rearranged for this section "2.2 Theory and Modeling Methods". The 2.2.1-2.2.3 sections have been revised in the 2.2 section. The 2.2.4 section has been shown in SI section.

Line 208-222, we have moved 2.2.4 section in SI section.

Line 154-207, we have revised 2.2.1-2.2.3 sections.

Related additions and changes included in the revised manuscript:

2.2 Theory and modeling methods

2.2.1 Köhler theory

The fractional ambient relative humidity ($\frac{RH}{100}$) over a spherical droplet in equilibrium with the environment is described by Köhler equation (Köhler 1936):

$$\frac{RH}{100} = a_w exp\left(\frac{4\sigma_{sol}v_w}{RTG_fD_s}\right) \tag{1}$$

where a_w is the water activity of the solution droplet, σ_{sol} is the liquid-vapor interfacial energy of solution droplet (also called surface tension), v_w is the partial molar volume of water, R is the universal gas constant, T is the temperature, G_f is the diameter growth factor of aerosol particles, and D_s is the dry diameter of spherical aerosol particles. The hygroscopic growth curve (G_f vs RH) is estimated based on the assumptions in models or theories described in the following sections (2.2.2-2.2.3).

2.2.2 Water activity

The expression for water activity used in the Simplified Kohler Theory (SKT) assumes the droplet contains n_w moles of water and n_s moles of nonvolatile solute.

$$a_w = \frac{n_w}{n_w + v n_s} \tag{2}$$

v is the number of ions of solute present in solution (v=1 for organic composition). This expression has been applied to the diluted solution (Kreidenweis et al., 2005; Koehler et al., 2006).

The following KD expression proposed by Kreidenweis et al. (2005) (KD= Kreidenweis) is to present the relationship between a_w and Gf determined in hygroscopic growth measurements:

$$Gf = \left[1 + (a + b * a_w + c * a_w^2) \frac{a_w}{1 - a_w} \right]^{\frac{1}{3}} \tag{3}$$

The coefficients a, b, and c for organic solution droplet in this study from Lei et al. (2014, 2018) and Estillore et al. (2017) as shown in Table S2.

Differential Köhler analysis (DKA) proposed by Cheng et al. (2015) is theoretically based on Köhler equation (Köhler, 1936) to determine water activity by measuring hygroscopic growth factors of aerosol nanoparticles in different sizes.

$$a_w = \frac{s_{w1}^{\left(\frac{D_{S1}}{D_{S1} - D_{S2}}\right)}}{s_{w2}^{\left(\frac{D_{S2}}{D_{S1} - D_{S2}}\right)}} \tag{4}$$

where s_{w1} and s_{w2} are water saturation ratio measured at the same g_f but at the different initial dry diameters (D_{s1}, D_{s2}), respectively. Using the DKA method can calculate the water activity in the highly supersaturated concentration range.

2.2.3 Growth factor

For idea solution, the hygroscopic curve can be estimated assuming that the water activity a_w of the solution containing non-volatile and non-electrolyte solute component is equal to the molar ratio of water in the solution. Here, the partial molar volume of pure water in the solution is equal to the molar volume of pure water. Since the hygroscopic diameter growth factor measurements are on volume basis using nano-HTDMA system, the expression of G_f as a function of molar ratio (x_j), molar mass (M_j), and mass density (ρ_j) of components j as follows:

$$G_f = \left[\frac{\Sigma_j\left(x_j M_j \frac{1}{\rho_j}\right)}{\Sigma_{j,j\neq w}\left(x_j M_j \frac{1}{\rho_j}\right)} \right]^{\frac{1}{3}} \tag{5}$$

The hygroscopic growth curve of aerosol particles is commonly evaluated from Extend-Aerosol Inorganic Model (E-AIM). It is a thermodynamic equilibrium model used for calculating phase partitioning (gas/liquid/solid). Most importantly, the E-AIM mode can model thermodynamic properties (e.g., water activity, liquid-vapor interfacial energy, and solution density) in the highly supersaturated concentration solution (Dutcher et al., 2013). Also, the standard universal quasi-chemical functional group activity coefficients (UNIFAC) within E-AIM can be used to predict a_w, σ_{sol}, and ρ_{sol} of organic aqueous solution (Fredenslund et al., 1975; Hansen et al., 1991). Note that, The E-AIM calculations based on the standard UNIFAC group contribution method are to predict hygroscopic growth factors of organic aerosol particles. (i.e.., E-AIM model (standard UNIFAC)) growth curve as a function of RH is based on Eq. (1) and Eq. (6).).

$$G_f = \left(\frac{\rho_s}{x_s \rho_{sol}}\right)^{\frac{1}{3}} \tag{6}$$

ρ_s and ρ_{sol} are the density of solute and solution, respectively, and x_s is the solute mass fraction.

(4) In Fig.2, it is not clear where the observations are from, is it from this study or from Chan et al.? The authors ought to clarify the data source. If it is from this study, why to mention Chan et al.'s measurements. If it is from the latter, why a comparison between the two is not seen in the figure.

Response: Thank you for your comments. Yes, observations are from Chan et al. (2005). We have revised this Fig. 2. Also, following the review's suggestions, we have revised the Fig. 6, and now they have been shown as follows:
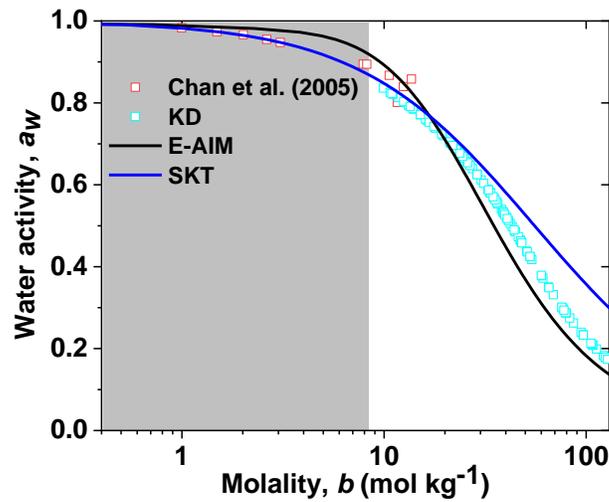
Figure 2. Concentration-dependent water activity (a_w) of levoglucosan solution. The KD-derived a_w (KD=Kreidenweis, cyan open square) is compared with observations (red open square), E-AIM (Extend-Aerosol Inorganic Model, black line), and a_w model (SKT, blue line). The light grey shaded areas mark the sub-saturated concentration with respect to bulk solution.
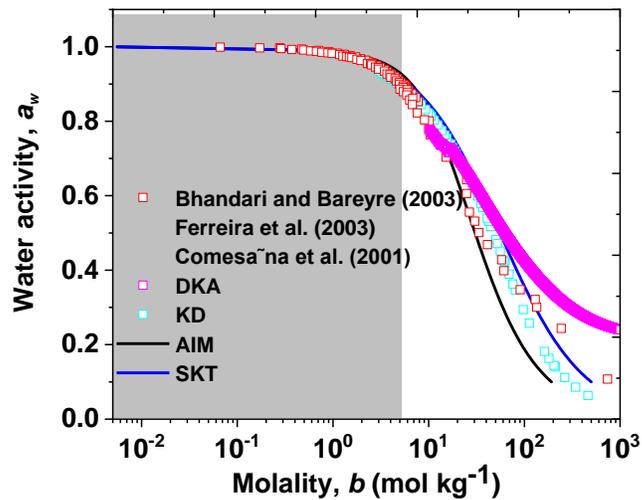
Figure 6. Concentration-dependent water activity (a_w) of D-glucose solution. The DKA-derived a_w (Differential Köhler Analysis, magenta open square) is compared with observations (red open square), E-AIM (Extend-Aerosol Inorganic Model, black line), a_w model (SKT, blue line), and parameterization model for a_w (KD=Kreidenweis, cyan open square). The light grey shaded areas mark the sub-saturated concentration with respect to bulk solution.

(5) L287-309, it is quite interesting to note that the levoglucosan nanoparticles become significantly evaporated below 20 nm. The authors attribute this trend to the Kelvin effect. However, if it is because of Kelvin effect, why it does not occur for other organic nanoparticles such as D-glucose?

Response: Many thanks. The impact of enhanced evaporation on the particle size depends on the volatility of organic compounds. For low volatile compounds, a much less fraction exists in the gas phase, which is still negligible given enhanced evaporation due to the Kelvin effect. However, for semi-volatile compound such as Levoglucosan (Hennigan et al., 2010), the effect is strong below 20 nm. Different from levoglucosan, the volatility of D-glucose is much smaller than that of levoglucosan, e. g., the vapor pressure of D-glucose and levoglucosan is 0.0026 Pa and 1.47 Pa at 122 °C (Oja and Suubery 1999). Therefore, there is an obvious partial levoglucosan evaporation from DMA1 to DMA2 within several seconds, but no clear evaporation for D-glucose aerosol nanoparticles.

Related additions and changes included in the revised manuscript:

Line 300-301, we added and revised: "Levoglucosan is semi-volatile at ambient condition (Hennigan et al., 2010). Due to Kelvin effect, sub-20 nm levoglucosan aerosol particles become more volatile."

Line 309, we added: "Therefore, there is an obvious partial levoglucosan evaporation from DMA1 to DMA2 within several seconds"

(6) Conclusions: L408-415, it is abrupt to introduce the biomass burning and the mixing state in the conclusion. What is the point to present them as illustrated at the end of the paper?

Response: Thank you for your comments. An introduction of biomass burning and the mixing state is main to extend our study in future.

We have removed this part from the conclusion.

Minor comments:

(1) L23, indicting? You mean "indicating"? L29, predicating? Predictedï¼›L57ï¼Œquantification of the biomass; L64-65, have focused on.

Response: Many thanks. It is "indicating" and we have corrected this. We have also carefully checked the whole manuscript, and included additional corrections of grammar, wording, and sentence structure.

Line 21-24, we revised: "The hygroscopic growth factors cannot be determined for levoglucosan below 20 nm due to its evaporation."

Line 29-32, we revised: "Predicted water activity for these aqueous organic solutions (i.e., levoglucosan, D-glucose) from different parameterization methods agrees well with observations in the low solute concentration range (< 20 mol kg^{-1}), and start to deviate from observations in the high solute concentration (> 20 mol kg^{-1})."

Line 54-58, we revised: "Levoglucosan aerosol nanoparticles have attracted increasing interest in recent years (Simoneit et al., 1999; Mochida and Kawamura, 2004; Mikhailov et al., 2009; Elias et al., 2010; Lei et al., 2014, 2018; Bhattarai et al., 2019) due to relative stability and high emission factors, which are considered as an ideal tracer for characterization and quantification the biomass burning (Fraser and Lakshmanan, 2000)."

Line 64-68, we revised: "Most of the previous lab studies have focused on investigation of the hygroscopic behavior of 100-nm levoglucosan and D-glucose aerosol nanoparticles, which mainly utilized the humidified tandem differential mobility analyzers (DMAs) (Mikhailov et al., 2004; Mochida and Kawamura. 2004; Koehler et al., 2006; Lei et al., 2014; 2018)."

(2) L83-83, this sentence seems quite awkward and it is suggested to change to "It is not clear how the size effect influences the hygroscopic growth of organics, especially those without DRH and ERH".

Response: Many thanks. We have revised in the following sentence and now they read as:

Line 83-84: "It is not clear how the size effect influences the hygroscopic growth of organics, especially those without DRH and ERH."

(3) L85, organic, not organics; L90, "are limiting" changed to "limit" ï¼›L173-174, please revise the ill sentence; L183, there is no A in eq. 4, please double check; L188, ideal, not idea; L195, Growth factor predicted by ...; L202-203, no coma is needed after note that and "are to predict" here "are to" is redundant and should be deleted; L214, the equation (equation (8)) shows the relationship between...; L216, no capital for V of vapor.

Response: Thank you for your comments. We have revised in the following sentence and now they read as:

Line 84-87: "Besides technique limitation (Lei et al., 2020; Wang et al., 2017), another reason is the high diffusion of sub-100 nm organic nanoparticles, especially in the sub-10 nm size range, which results in nanoparticle losses in the HTDMA system (Seinfeld and Pandis, 2006)."

Line 173-174: "The following KD expression proposed by Kreidenweis et al. (2005) (KD= Kreidenweis) is to present the relationship between a_w and G_f determined in hygroscopic growth measurements:"

Line 183-184, we deleted and revised: "where s_{w1} and s_{w2} are water saturation ratio measured at the same g_f but at the different initial dry diameters (D_{s1}, D_{s2}), respectively."

Line 188-190: "For ideal solution, the hygroscopic curve can be estimated assuming that the water activity a_w of the solution containing non-volatile and non-electrolyte solute component is equal to the molar ratio of water in the solution."

Line 195, we deleted: "2.2.3.2 Growth factor prediction by E-AIM model"

Line 202-205: "Note that the E-AIM calculations based on the standard UNIFAC group contribution method predict hygroscopic growth factors of organic aerosol particles. (i.e.., E-AIM model (standard UNIFAC)) growth curve as a function of RH is based on Eq. (1) and Eq. (6).)."

Line 214-216: "This equation (Eq. 8) shows a relationship between mass in gas phase (m_{gas}) and pressure (P), volume (V), mole mass (M), the ideal gas constant (R), and temperature."

Line 215: According to the following equation, volume (V) is capital.

$$m_{gas} = \frac{PVM}{RT} \tag{R1}$$

(4) L228-230, no subject is found in this sentence; L237, become highly supersaturated and article "the" should not be added before highly; L261, those of this study.

Response: Thank you for your comments. We have revised in the following sentence and now they read as:

Line 227-230, we revised: "By applying a water activity parameterization model (KD, Eq. 3) to measured growth factors of levoglucosan aerosol nanoparticles with diameters from 20 to 100 nm using a nano-HTDMA, as shown in Fig. 2, we obtain water activity of aqueous levoglucosan nanoparticles with molality up to 140 mol kg^{-1}."

Line 235-237, we revised: "However, a derivation of SKT from the KD-derived water activity is observed as the molality increases from 20 to 120 mol kg^{-1}, indicating levoglucosan nanoparticles become highly supersaturated."

Line 257-261, we revised: "The reason is that Mikhailov et al. (2008) used minimum mobility diameter measured in the hydration and dehydration modes instead of the initial dry mobility diameter measured in the hydration or dehydration modes to calculate the hygroscopic growth

factor of levoglucosan nanoparticles, which could lead to the higher hygroscopic growth factors of levoglucosan nanoparticles than those of this study.

(5) L243-261, are the notations between "deliquescence and efflorescence modes" and "hydration and dehydration modes" the same? Please clarify.

Response: Many thanks. Yes, they are the same. We have changed the notion of hydration and dehydration mode to deliquescence and efflorescence modes to avoid confusion.

(6) L308, indicating, not indicting; L316, among them? L328, delete during

Response: Thank you for your comments. We have revised in the following sentence and now they read as:

Line 306-309, we revised: "However, the ratio of gas-phase concentration to the total concentration is dramatically enhanced for sub-20 nm levoglucosan aerosol nanoparticles, which is consistent with measurement observations, indicating the larger impact of evaporation of sub-20 nm levoglucosan nanoparticles on the measurement results."

Line 315-316, we revised: "a good agreement among them is observed in the solute concentration below 20 mol kg^{-1}."

Line 328-329, we revised: "No prompt phase transitions are observed in both deliquescence and efflorescence measurement modes."

(7) L342-344, this sentence is hard to understand, please revise it "To have a clear observation for size dependence of the hygroscopic growth factor of D-glucose aerosol nanoparticles with diameters down to 6 nm, Fig. 8b shows the change in the hygroscopic growth factor of D-glucose aerosol nanoparticles with diameters from 100 down to 6 nm."

Response: Thank you for the comments. We have revised in the following sentence and now they read as:

Line 342-345, we revised: "Figure 8b further shows the clear change in the hygroscopic growth factor of D-glucose aerosol nanoparticles with diameters from 100 down to 6 nm at 87 % RH."

(8) L382, has been.

Response: Many thanks. We have revised in the following sentence and now they read as:

Line 382-383, we revised: "Thus, nanosize effect on these thermodynamic properties has been taken into account the models and theories (Cheng et al., 2015)."

Reference:

Atkins, P., De Paula, J., and Walters, V.: Physical Chemistry, W. H. Freeman, 2006.

Martin, S. T. Phase transitions of aqueous atmospheric particles.Chem. Rev. 100,3403–3454 (2000).

Hennigan, Christopher J.; Sullivan, Amy P.; Collett, Jeffrey L.; Robinson, Allen L., Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals. Geophysical Research Letters, 37(9), doi:10.1029/2010gl043088, 2010.

Huffman, J. A.; Docherty, K. S.; Mohr, C.; Cubison, M. J.; Ulbrich, I. M.; Ziemann, P. J.; Onasch, T. B.; Jimenez, J. L. (2009). Chemically-Resolved Volatility Measurements of Organic Aerosol from Different Sources. Environmental Science & Technology, 43(14), 5351–5357. doi:10.1021/es803539d, 2009.

Oja, V., and E. M. Suuberg, Vapor pressures and enthalpies of sublimation of D-glucose, D-xylose, cellobiose, and levoglucosan,J. Chem. Eng. Data, 44(1), 26–29, doi:10.1021/je980119b.1999.