Answers to Referee #2

The authors appreciate the critical and constructive comments that the reviewer has given, which will help us to improve the communication with other researchers for the understanding of HTDMA work. All the requested comments are replied and corresponding suggestions are addressed in the revised version of the manuscript.

Major comments:

The authors present hygroscopicity data for 23 organic compounds measured with an HTDMA instrument. They compare these data with two thermodynamic models (AIOMFAC and E-AIM) and conclude that the models do not represent the hygroscopicity well.

Unfortunately, the study is conceptually flawed. The experimental design allows studying the hygroscopic growth starting from dry conditions to elevated relative humidities. This way, as the authors illustrate in Fig. S2 for an inorganic salt (ammonium sulfate), they can only probe the properties of the aqueous system at relative humidities, beyond those corresponding to the solubility limit of each binary system. However, what is relevant for the atmospheric application, where an aerosol particle consist of a multitude of organic compounds, is the water activity (or hygroscopicity) of the liquid state, because the organics will not crystallize under realistic atmospheric conditions (e.g. Marcolli et al., 2004).

Reply: The reviewer thinks the organics will not crystallize under realistic atmospheric conditions and considers the experimental design, which we dried our aerosols and made them crystallize, is not atmospherically relevant and conceptually flawed.

However, some of the organics may crystallize under realistic atmospheric conditions. For instance, Chan et al. (2008) reported the efflorescence RH (ERH) is 55-59% for succinic acid, >85% for adipic acid, 51-53% for pimelic acid. Chan et al. (2005) reported the ERH for a series of amino acids is 67-70%, 53-55% and 72-74% for alanine, glycine and glutamine, respectively. These results suggested that these organic compounds will crystallize under relative high RHs, which is likely occur in the real atmosphere. Moreover, when organic aerosols mixed with inorganic components, crystallization was still observed in previous studies (Lei et al., 2014; Luo et al., 2020), though this process is composition-dependent. Furthermore, Pajunoja et al. (2015) used an aerosol bounce instrument (ABI) to directly characterize the phase state of different SOA generated in a flow tube reactor and found that most of the generated particles are solid or semisolid at intermediate RH, for example (<70% RH), which are under realistic atmospheric conditions (see a copy of their result in Fig. 1 below). These results further confirmed that organic compounds, even present in mixtures, could still crystallize under ambient conditions. In our study, we dried the aerosols to relatively quite low RH, ensuring the crystallization of the organic compounds that likely crystallize under real conditions. Thus, the measured hygroscopic growth at elevated RHs could represent their hygroscopic behavior under ambient conditions, forming a realistic dataset.

We agree that there remains some other organics that will not crystallize under realistic atmospheric conditions. Hygroscopicity of these organics could also be measured by current experimental design, as organic compounds that exist in liquid state will show continuous water uptake without prompt change in measured growth factor during hydration using HTMDA system. This was confirmed by our results of malonic acid and serine, which show continuous increase in growth factor upon wetting, indicating they are in liquid state. We assume these results are exactly what the reviewer expected.

Based on these aforementioned evidences, we conclude that to study the water uptake of particles from dry condition to elevated RH according to current experimental design is reasonable with highly atmospheric relevance. Moreover, it could also provide us some information that which compound at which RH conditions would crystallize. This will further benefit the deduction of the effect from mixing on the water uptake of mixtures, which might not be straight-forward and provide benchmark information for more complicated mixtures, for instance, ambient particles under various conditions.

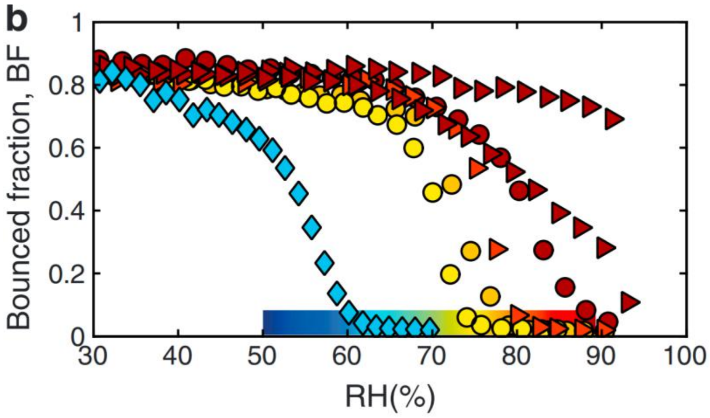

Figure 1: A copy of Figure 1b of Pajunoja et al. (2015). Bounced fraction (BF) of aerosols as a function of relative humidity for flow tube generated aerosols using different precursors. When BF >0, aerosols are considered as solid or semisolid and aerosols at BF = 0 behave mechanically as liquids.

The HTDMA instrument as used by the authors probe only the thermodynamics of the 23 binary systems in the water activity range, which is accessible to bulk methods, the technique used here is simply not appropriate to determine thermodynamic data with high accuracy.

This is best illustrated by comparing the data presented in this work for the amino acid alanine with previous data by Chan et al. (2005): The authors observe no growth up to a relative humidity of 90 % which seems to be the highest they can reach in their setup. That is consistent with the data of Chan et al. upon humidification. But the data of interest are the ones when starting at high humidity and drying whith the metastable, subcooled binary liquid being probed. These can be compared to the thermodynamic data as done by Chan et al. (2005) for different UNIFAC parameterizations.

Reply: We understand the reviewer's worries, but we think the measurement for size-resolved aerosols, which is particularly relevant for atmospheric aerosols, is still a must. Thermodynamic data of bulk samples cannot always represent the ones at nano size ranges, particularly in the size range of the atmospheric aerosol accumulation mode (particle diameters around ~ 10^2 nm). For instance, Lei et al. (2014) measured the growth factor of levoglucosan at 90% RH as 1.38 using a HTDMA system, while Chan et al. (2005) reported a value of 1.30 using an EDB. This clearly suggests that bulk data may not always be consistent with size-resolved ones. Cheng et al. (2015) also suggested that particle size can be an important factor influencing the solid-liquid equilibrium upon phase transition. Pöschl et al. (2015) and Reid et al. (2018) reported that thermodynamic properties of aerosols are strongly related to particle size, for instance, viscosity or diffusion coefficient. Therefore, different approaches with capabilities accessing different particle size ranges, requiring different sample volumes are essentially needed.

On the other hand, HTDMA has been a widely used technique in aerosol hygroscopicity studies since decades, including both field measurements and laboratory experiments. In our study, we calibrated our instrument using ammonium sulfate, a commonly-used reference in hygroscopicity community. Our obtained DRH and corresponding GF agree quite well with previous studies as well as the E-AIM prediction, confirming the accuracy of our measured data. Moreover, during our measurements, we observed a moderate water uptake for glutamine and serine particles, while no deliquescence was observed for both compounds by Chan et al. (2005) using an EDB, where bulk samples were collected. We believe that such a large discrepancy between our results and others cannot simply prove our method is not appropriate to determine thermodynamic data, but on the contrary, a strong evidence to confirm the difference between bulk samples and size-resolved particles. Hence, size-resolved data similar to ours is important, not only for filling the data gap due to the different capacities of techniques, but also helping the understand of the kinetic limitations for the mass transfer and transport of water molecules in the particle phase with the considering of particle size.

As the reviewer stated again that the data of interest are the ones when starting at high humidity and drying with the metastable, subcooled binary liquid being probed, we agree that these data are of interest. However, starting at dry conditions and measuring their hygroscopic behavior at elevated RH is also of interest, as some organic compounds may crystallize under relative high RHs, which is likely occur in the real atmosphere and how these crystallized organics behave towards changing ambient relative humidity is also very important for atmospheric science community. Moreover, the other reasons for its importance were also described in the answer to the first comment above clearly. We believe that a more thorough comparison of the results during a complete water cycle, including both hydration and dehydration is necessary for future studies.

In addition to this conceptual flaw, the experimental data raise questions as well. In Fig. 1(a) the authors observe considerable deviations between their data for malonic acid and the AIOMFAC model in the range of 60% to 80 % RH. However, if I compare AIOMFAC with existing experimental bulk data the agreement is very satisfactory in the same range of humidities:

As the bulk data are clearly the reference, the authors need to explain the difference to those, before concluding that the thermodynamic models are failing for the binary aqueous components. One possible reason could be that the authors are using ideal mixing to convert from size growth to mass concentration?

Reply: We are quite confused with current comment raised by the reviewer. In our study, we did not use AIOMFAC, but E-AIM. Moreover, in our original manuscript, we stated that "Figure 1a also shows that the hygroscopic behaviour of Malonic acid was well represented by the E-AIM but overestimated by the UManSysProp", which agrees with the results the reviewer presented as well. We agree that there are some slight deviations between the measurement and the model predictions in the RH rang of 60% to 80%. But this is also similar to the figure the reviewer presented to us at a_w of 60%-80% RH, see figure below. Based on current comments, we repeated the measurements again for malonic acid, presented below, and confirmed that the hygroscopic behaviour of malonic acid was well represented by the E-AIM, considering the measurement uncertainties.

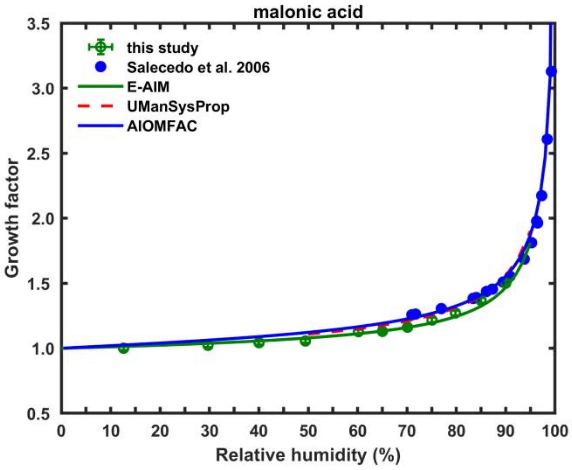

Figure 1: Measured and predicted growth factor as a function of relative humidity (RH) for malonic acid as.

Moreover, the bulk data may not always represent the reference. For instance, Chan et al. (2008) measured the hygroscopicity for a series of monosaccharides and disaccharides using an EDB. Though the predictions agree well with the measurements for monosaccharides, there remains significant deviations between model predictions and measurements for disaccharides. Similarly, in our study, though the hygroscopic growth of malonic acid was well represented by the E-AIM, some deviations between model predictions and measurements were still observed for other compounds, for instance, amino acids. The potential sources for the discrepancies between the model predictions and the measurements, including both bulk measurements and size-resolved ones could all be due to that the phase transition, intermolecular interactions as well as other non-ideality were not considered in the simulations. Detailed discussions for phase transition and intermolecular interactions were given in our manuscript.

Considering the last suggestion the reviewer raised, we agree that to calculate size growth from mass concentration assuming ideal mixing may contribute to the deviations between model and measurements. Clearly, in E-AIM, GF values of the pure component was originally calculated according to Eq. (1):

$$GF = \left[1 + \frac{n_w M_w/\rho_w}{\sum_i (m_i/\rho_i)}\right]^{\frac{1}{3}}$$

where M_w is the molar mass of water, ρ_w is the density of water, m_i and ρ_i are the mass and density of the pure component i, n_w is the mole number of water at a certain RH. We agree with the reviewer that the GF value from E-AIM were calculated from mass concentration to size growth assuming ideal mixing. As suggested by the reviewer that the non-ideality of the aqueous solution should be considered, we made a sensitivity analysis for ammonium sulfate due to the limited data for the density of the aqueous solution of our studied compounds at various RH conditions. Specifically, we calculated the GF for ammonium sulfate by using the density of their aqueous solution ($\rho_{solution}$) as Eq. (2):

$$GF = \left[\frac{(\sum_i m_i + n_w M_w)/\rho_{solution}}{\sum_i (m_i/\rho_i)}\right]^{\frac{1}{3}}$$

After the deliquescence of ammonium sulfate, the difference in GF value using different density data is less than 0.01, well within the measurement uncertainties. For other organic compounds, the difference between the density of their aqueous solution with water is relatively smaller than that of ammonium sulfate. Hence, we estimate the difference in GF value might be even smaller for other organic compounds by using different density values. Therefore, we think to calculate size growth from mass concentration assuming ideal mixing might not be the major reason for the discrepancies between the model predictions and the measurements.

And a last comment. Sucrose has been used as aproxy for viscous or even galssy aerosol particles during the last years in a large number of studies. Its hygroscopicity is very well etsablished. However, the authors do not at all comapre their data with data availbel in the literature. Besides this problem, it is obvious that they are not aware of the kinetic limitations to water uptake by viscous aerosol. Most likely, the short residence time in the HTDMA limits the water uptake for aqueous sucrose at intermediate and low humidities. This can be seen by comparing the data of this work with standard paramterizations for hygrscopicity of sucrose (e.g. Zobrist etal, 2011):

Reply: We agree with the reviewer that comparison with the other data for sucrose should be conducted. We therefore compared our results with the others using similar HTDMA system but with different residence time. We noticed that at intermediate and low humidities, our measured values for sucrose were lower than the other two. This could be due to the short residence time of our HTMDA system, limiting the water uptake for aqueous sucrose, as suggested by the reviewer.

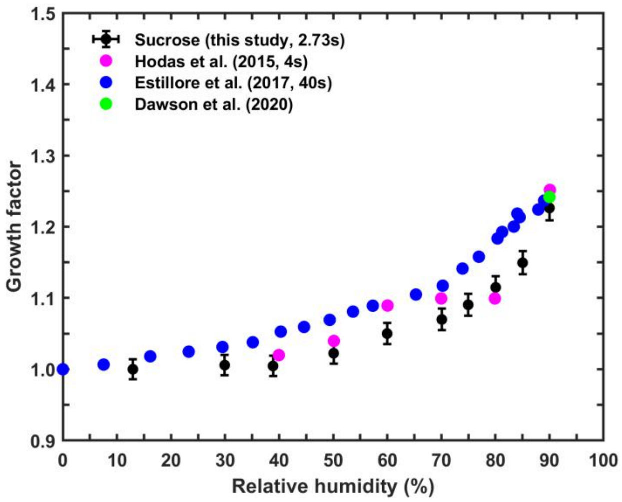

Figure 2: Comparison of the measured growth factor for sucrose as different RH with other studies using different HTDMA.

For this reason, we added a new section in atmospheric implication to discuss the effect of residence time of humification on the water uptake of particles. Besides sucrose, we also made a thorough comparison of the hygroscopicity for other compounds using different techniques. Based on the comparison results, the influence of the residence time on the organic hygroscopicity is difficult to conclude, implying a more complicated mechanism for the discrepancies between different studies using different techniques. On the other hand, we also found that our measured GF value at high RH, e.g., 90% RH was quite close to other results, suggesting equilibrium might already been reached. In our manuscript, there is an important section discussing the role of different physico-chemical properties on the organic hygroscopicity. The analysis in this section was all based on the measured GF at the highest RH we reached in our system. We hope at this point (i.e., 90% RH), the influence from residence time, which may affect the equilibrium state of particles upon hydration, can be largely reduced and we suggest a comprehensive study to thoroughly investigate at which condition the liquid-solid equilibrium of organics could be reached upon wetting is needed. Particularly, the new section was listed below:

"Previous studies (Swietlicki et al; 2008; Duplissy et al., 2009; Wu et al., 2011; Suda et al., 2013) suggested that the residence time for humidification may also potentially influence the observed water uptake of particles as the measured particles, especially for some organic compounds, may not reach their equilibrium humidified sizes during a quite short time of wetting. However, extending the humidification time for hours using the EDB, no water uptake was observed neither for most of our studied dicarboxylic acids (Chan et al., 2008) as well as for glycine and alanine particles (Chan et al., 2005), which was also confirmed by Darr et al., (2018), using another different measurement technique, i.e., ATR-FTIR (Attenuated Total Reflection Fourier Transform Infrared) with a residence time of 2 minutes. Estillore et al. (2017) reported a quite similar value of GF at 90% RH (1.24) for sucrose as ours using a different HTDMA with a much longer residence time (40s), similar as the one by Hodas et al., (2015) based on DASH-SP (Differential Aerosol Sizing and Hygroscopicity Spectrometer Probe) with a residence time of 4s. However, at intermediate RHs, our measured GF were much lower than theirs. Moreover, for glutamine and serine particles, no deliquescence was observed by Chan et al. (2005) even with a much longer residence time, while in our study a moderate water uptake for both compounds were observed. Using an STXM (Scanning Transmission X-ray Microscopy) with a residence time of 5-10 minutes, Piens et al. (2016) obtained a lower GF of fructose compared to ours, which should not be caused by the evaporation losses due to its low volatility. These aforementioned comparisons pointed out the influence of residence time on the observed water uptake of particles might be inconclusive. Therefore, other technical reasons should be raised for the measurement discrepancies between different instruments and studies using similar technique but different residence times should be suggested for understanding the effect from residence time on hygroscopicity."

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