Dear Editor,

We would like to thank all the reviewers for their detailed and constructive comments and suggestions. Our responses addressing reviewers' comments point-by-point are given below. The revised manuscript tracking the changes is also attached in the end of this file.

Best Regards

Shuang Han and Juan Hong

Answers to Referee #1

The authors appreciate the detailed and constructive comments that the reviewer has given, which will help us to improve the structure and content of our work. All the requested comments and suggestions are addressed and introduced to the revised version of the manuscript.

Major comments:

The authors fall short of establishing/communicating the work's novelty. Several findings have been explored in past works (functional groups, molar mass, O:C, solubility and deliquescence). The authors have done a good job finding these studies. However, authors should discuss and emphasize their own contributions.

Reply: Thanks for the reviewer's specific comments. We revised our abstract, see the reply to the second comment below and the original introduction part and added new material discussing the novelty of our work. The revised introduction is listed below with modification highlighted in yellow:

"Atmospheric aerosol particles consist of numerous organic species with both anthropogenic and biogenic origins (Zhang et al., 2007; Jimenez et al., 2009; Zhang et al., 2015; Wang et al., 2018). These organic species often contribute a significant fraction to the mass of sub-micrometer aerosols, and have vital effects on air-quality and climate (McFiggans et al., 2006; Randall et al., 2007; Zheng et al., 2015). To obtain a systematic understanding of their effects, it is necessary to acquire correct information on the chemical composition and physico-chemical properties of these organics (Seinfeld and Pandis, 2016). Hygroscopicity is one of the most important physico-chemical properties and it describes the ability of particles to take up water and grow in size under sub- and supersaturated conditions (Petters and Kreidenweis, 2007). Thus, it strongly influences the number size distribution, phase state, optical properties as well as multiphase chemistry of aerosol particles (Cheng et al., 2008; Su et al., 2010; Hong et al., 2018; Tang et al., 2019).

Given the large number of organic species in atmospheric aerosols, the determination of their hygroscopicity is quite experimentally difficult. Current models normally use aggregate quantities, such as the atomic oxygen-to-carbon (O:C) ratio or the average oxidation state of organics to simply parameterize the hygroscopicity of organic species in ambient aerosols. However, recent studies show that the hygroscopicity of organic aerosols cannot be fully explained by their oxidation level and the empirical relationship between hygroscopicity and O:C might not be linear (Lambe et al., 2011; Kuwata et al., 2013; Rickards et al., 2013; Marsh et al., 2017). This suggests that this simplified approach to quantify organic hygroscopicity might be problematic and a more mechanistic understanding of the complex link between hygroscopicity and other physico-chemical properties such as molecular functionality, molecular weight and water solubility of organics should be examined.

Due to these challenges, prediction of the hygroscopicity of organic compounds sometimes relies on thermodynamic models which explicitly includes these properties, for instance molecular functionality, molecular weight, into simulations. These thermodynamic models, including the Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) (Zuend et al., 2008; Zuend et al., 2011), the Extended Aerosol Inorganic Model (E-

AIM), and the University of Manchester System Properties (UManSysProp) (Clegg et al., 1998; Topping et al., 2016) use group contribution methods to calculate water activity for organic species of atmospheric relevance. However, involving these thermodynamic simulations in transport or climate models to predict the hygroscopicity for such a large number of organic compounds in ambient aerosols is computationally expensive. Moreover, these models, based on parameterizations from measurements, are semi-empirical, and thus need more experimental data to constrain their predictions (Suda and Petters, 2013). Particularly, when it comes to very dry conditions, these models may perform even worse and cannot capture the non-ideality of the solutions accurately (Ohm et al., 2015). Therefore, quantifying the hygroscopicity of atmospheric relevant organic species through laboratory measurements by systematically varying the type of studied organics is an intrinsic necessity. Chan et al. (2008) studied the hygroscopic properties and CCN activities of a series of dicarboxylic acids and saccharides using an electrodynamic balance (EDB) and found that the CCN activities of highly water soluble organic compounds can be well predicted by the Köhler theory. Suda et al. (2014) examined the hygroscopicity of a few synthetic organic compounds that are atmospheric relevant but not commercially available using a CCN counter (CCNc). They found that the compounds with hydroxyl or carboxyl groups are the most hygroscopic, while the ones with nitrate or methylene are the least. Jing et al. (2016) investigated the hygroscopic properties of a series of dicarboxylic acids with levoglucosan using a HTDMA, but they mainly focused on the multicomponent interactions between organic compounds. Marsh et al. (2017) collected experimental hygroscopicity data for 23 organic compounds by a comparative kinetics EDB (CK-EDB) to compare with thermodynamic predictions and discussed that the hygroscopicity of organic compounds with increasing branching and chain length are poorly represented by models.

All these cases discussed above shows that there is already some experimental hygroscopicity data for organics with high atmospheric abundance and relevance (Peng et al., 2001; Prenni et al., 2007; Chan et al., 2008; Lambe et al., 2011; Kuwata et al., 2013; Marsh et al., 2017; Lei et al., 2018). However, some of these measurements were conducted using different techniques rather than the HTDMA, all of which have different limitations. Measurements using a CCNc could only probe the hygroscopic properties or CCN activities at supersaturated conditions, where many compounds may already fully dissolve in water droplets. The EDB or CK-EDB approaches normally analyze the droplets in the micrometer size range, far beyond the size range of atmospherically relevant aerosols. In contrast, the HTDMA system allows direct measurement of particle hygroscopicity at subsaturated conditions and for particles at the size from tens to a few hundreds nanometers, which is a good complement closing the gaps beyond the reaches of other techniques. Furthermore, some of the aforementioned studies using similar HTDMA systems focused on quite a small number of organics discussing only one or two properties potentially influencing the hygroscopicity, leading to a limited coverage of the experimental datasets. Thus, a general picture in understanding the observed hygroscopicity among different organic species still remains unclear.

Therefore, in this work, we extend the compositional complexity and diversity of the studied organic compounds with varying functional groups, molecular structures and other relevant physico-chemical properties. We try to form a systematic matrix of experimentally-determined HTDMA data synthesizing a large suite of organics, providing unambiguous measurements of particles at atmospherically relevant size range. Combined with these experimental data, we aim to evaluate the roles of different physico-chemical properties that play in organic hygroscopicity and gain some insight on their limitations and applicability. In addition, predictions from two widely used thermodynamic models, E-AIM and the UManSysProp, are compared against our experimental data, which may benefit the validation and improvement of the fidelity of these models."

Further comments on the abstract: As stated above, findings summarized here should emphasize the novelty of the current work. The abstract should end with implications.

Reply: We revised our abstract as: "Aerosol hygroscopicity strongly influences the number size distribution, phase state, optical properties as well as multiphase chemistry of aerosol particles. Due to the big number of organic species in atmospheric aerosols, the determination of the hygroscopicity of ambient aerosols remains challenging. In this study, we measured the hygroscopic properties of 23 organics including carboxylic acids, amino acids, sugars and alcohols using a Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA). Earlier studies have characterized the hygroscopicity either for a limited number of organic compounds using similar techniques or for particles at sizes beyond the micro-scale range or even bulk samples by other methodologies. Here, we validate these studies and extend the data by measuring the hygroscopicity of a broader suite of organics for particles with size under the submicron range that are more atmospheric relevant. Moreover, we systematically evaluate the roles of related physico-chemical properties that play in organic hygroscopicity. We show that hygroscopicity of organics varies widely with functional groups and organics with the same carbon number but more functional groups show higher hygroscopicity. However, some isomers, which are very similar in molecular structures, show quite different hygroscopicity, demonstrating that other physico-chemical properties, such as water solubility may contribute to their hygroscopicity as well. If the organics are fully dissolved in water (solubility > 7×10^{-1} g/ml), we found that their hygroscopicity is mainly controlled by their molecular weight. For the organics that are not fully dissolved in water (slightly soluble: 5×10^{-4} g/ml < solubility < 7×10^{-1} g/ml), we observed that some of them show no obvious water uptake, which probably due to that they may not deliquesce under our studied conditions up to 90 % RH. The other type of slightly soluble organics is moderately hygroscopic and the larger their solubility the higher their hygroscopicity. Moreover, the hygroscopicity of organics generally increased with O:C ratios, although this relationship is not linear. Hygroscopicity of organic compounds were also predicted by two thermodynamic models, including the Extended Aerosol Inorganics Model (E-AIM), and the University of Manchester System Properties (UManSysProp). We show that hygroscopicity results of almost all organic compounds except those tricarboxylic acids were poorly represented by the UManSysProp and the E-AIM over-estimated the hygroscopicity of all amino acids. These discrepancies were likely due to that both models do not consider phase transition and intermolecular interactions of these selected compounds in the simulations. These results may further improve our understandings of the interactions between organics and water molecular and will benefit the estimate of the hygroscopicity and CCN (cloud condensation nuclei) activities of any mixtures, for instance, ambient mixtures based on known composition data.

17 – with additional functional groups – addition to what? This is more complicated than just the addition of functional groups. Carbon number matters as well.

Reply: We agree that carbon number also matters and the comparison of hygroscopicity among different organics would be quite difficult that many other properties rather than functional groups may also be important. Here, in our statement, we actually meant to compare the hygroscopicity of the organic compounds with the same carbon number. We rephrased our statement in the abstract as: “We show that hygroscopicity of organics varies widely with functional groups and organics with the same carbon number but more functional groups show higher hygroscopicity.”

18 – It sounds like you mean isomers. This statement is ambiguous

Reply: We rephrased the sentence in the abstract as: “However, some isomers, which are very similar in molecular structures show quite different hygroscopicity, demonstrating that other physico-chemical properties, such as water solubility may contribute to their hygroscopicity as well.”

23 – “moderately”

Reply： We rephrased the word “moderate” as “moderately” accordingly.

Uncertainty estimates are needed. As it stands, scatter in the data is used to discuss morphology. Although this is a nice discussion, some error bars and acknowledgement of the limitations of the measurement would lend more credibility to these claims.

Reply: Yes, we agree. We added a part introducing how we estimated the measurement uncertainties for the measured GF in the Measurement section (Sect. 2). The estimated uncertainties were added for each measured dot in Figure 1, 2 and 3 in the revised manuscript with according discussions. The measurement uncertainty was introduced before the third paragraph in Sect. 2 as:

“Swietlicki et al. (2008) summarized the potential sources of error in HTDMA measurements and concluded that the reliability of the measured data is strongly associated with the stability and accuracy of DMA2 RH as well as the accurate measurement of particle diameter by DMAs. According to Mochida and Kawamura (2004), the uncertainty in the measured GF can be calculated by Eq. (2):

$$\sqrt{\left(GF\,\frac{\sqrt{2}\varepsilon_{Dp}}{Dp}\right)^2+\left(\varepsilon_{RH}\,\frac{dGF}{dRH}\right)^2}, \qquad (2)$$

where GF is the measured growth factor with respect to any measured RH, ε_{Dp} and ε_{RH} are the errors in the measured Dp and RH. In our system, the accuracy of DMA2 RH was maintained to be ±1% and the uncertainty for the mobility diameter was ±1% according to PSL (Polystyrene Latex particles) calibration. Hence, for our system, ε_{RH} and ε_{Dp}/Dp are 1% and 0.01, respectively. The calculated uncertainty according to the above-mentioned method is added in the measured GF in the following section.”

An example of the revised figure for the measured GF as a function of water activity (response for the third minor comment) for carboxylic acids including measurement uncertainties is shown below. Revision of the other part of our manuscript was made accordingly. Here, the revised discussion (the last two paragraphs of Sect. 4.1.1) for current figure was also shown as an example:

“The humidograms of the three dicarboxylic acids with substitutions (i.e., double bond or hydroxy group) are illustrated in Fig. 1b. The continuous water uptake indicates that these particles may be at liquid state under dry conditions. We observed a small leap of the GFs from 80 % to 85 % RH, implying that these particles were only partially deliquesced and further dissolution occurred at elevated RH. However, considering the measurement uncertainties, the statement of the partial deliquescence could not be fully confirmed and thus further evidence from other measurements is needed. On the other hand, the E-AIM could well represent their hygroscopic properties at RH between 10 -90%, while there are still some deviations between the measurements and the UManSysProp predictions, especially for malic and tartaric acids, even taking into account of their measurement uncertainties. This could be due to that the UManSysProp is a more simplified model taking into account less input data or parameterization. For instance, the phase state or the dissociation process of the studied compound at different conditions could not be assumed or considered in the simulation. Therefore, additional processes or properties should be included into this model for the further improvements of its predictions.

A similar gradual phase transition was observed for aconitic acid and citric acid (Fig. 1c), while the other tricarboxylic acid showed continuous hygroscopic growth over the studied RH range, indicating no obvious phase change for these particles upon hydration. However, it is quite interesting to note that predictions from the UManSysProp become more approaching to the experimental data, especially above 80 % RH, considering the measurement uncertainties."

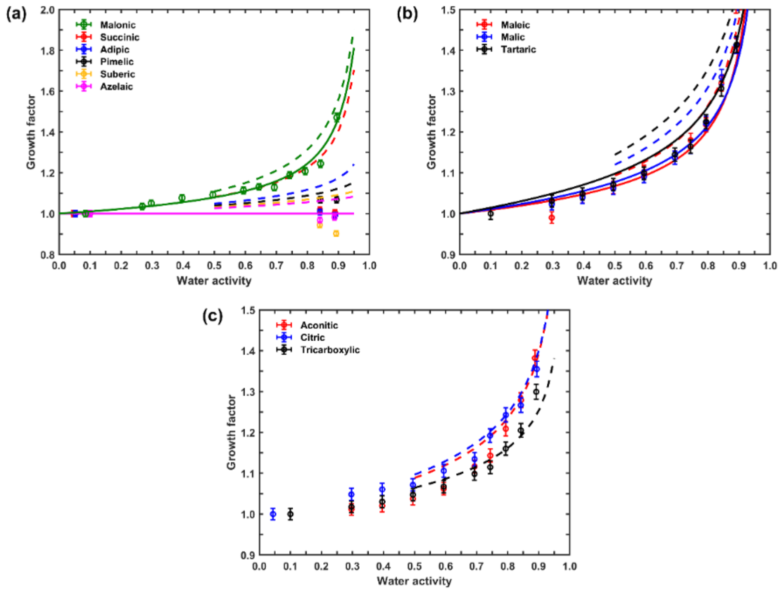

Figure 1: Hygroscopic growth curves of straight-chain dicarboxylic acids (a), dicarboxylic acids with substitutions (b) and tricarboxylic acids (c) particles (200 nm). Points represent the measurement data; the solid lines indicate the E-AIM predictions (solid, non-hygroscopic organic GF=1) and the dashed lines show the UManSysProp calculated predictions.

And the original line 140: "Considering the measurement uncertainties, no water uptake is observed for alanine particles, which has also been reported in previous works (Chan et al., 2005; Darr et al., 2018)."

Some of the conclusions are not supported by the data. On line 184, the authors discuss the order in which the functional groups contribute to hygroscopicity. Is this statement quantitative? If so, what is the observed partial derivative of kappa with respect to each functional group? The statement seems to have little connection to the data presented in Figure 4.

Reply：Unfortunately, this statement is only a qualitative description based on currents results in our study instead of a quantitative comparison. We agree such conclusion in our manuscript might be too strong and we revised the text in the original line 184-185 as: "By summarizing the results in current study, κ increased with the functionality in the following order: ($-CH_3$ or $-NH_2$) < (-OH) < (-COOH or C=C or C=O). However, it has to be noted that this comparison is quite qualitative, might be ambiguous and further evidence from other organic compounds is needed in order to drive a more general conclusion."

On the other hand, our Fig. 4a in the manuscript is an overview of the measured hygroscopicity of the 23 organics with different functional groups. Fig. 4b is described by line 189-192 in the original manuscript. Fig. 4c is explained in line 192-194, while Fig. 4d is actually a schematic illustration for the content in line 178-185, which tells how the hygroscopicity of organics with the same carbon backbone number but different functional groups varies.

Restructuring of particles was observed, and this resulted in a negative growth factor. This was shown and discussed in the main text and in Figure S3, which shows severe discontinuities in water uptake for amino acids. Some of the restructuring-sizing error could be avoided by sizing the particles wet, following Nakao et al. (2014). This should be discussed. Nakao et al. (2014), Droplet activation of wet particles: development of the Wet CCN approach, Atmos. Meas. Tech., 7, 2227–2241.

Reply： We carefully read the paper by Nakao et al. (2014). It is a quite interesting paper. Here, in current work, proper discussion citing Nakao et al. (2014) was added in the original line 145: "The sizing of these structurally-rearranged particles, especially at lower RH range, will be erroneous as the volume change of the particles upon wetting may not only due to the water absorption but also the compaction of the original particles. This phenomena complicates the accurate estimation of the actual water amount absorbed by the particles due to their intrinsic hygroscopicity. In a recent study by Nakao et al. (2014), in order to avoid the influence from particle restructuring upon wetting, they sized wet particles without drying after generation and studied their droplet activation using a wet CCN. This approach they introduced might be an easier attempt, offering an unique solution for current problem from particle restructuring during the hydration processes."

Regarding restructuring, the residence time of the HTDMA is mentioned (2.7 seconds) but the authors do not bring this into the discussion. The authors should mention how this 2.7 s residence time affects particle restructuring, and how this instrument compares to other works.

Reply: Yes, we did a thorough literature review for the hygroscopicity measurements using other techniques, carefully compared their results with ours and brought this content into the discussion.

We extended the discussion in Section 5: Atmospheric implication including the effect from residence time as: "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 also observed 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 not be conclusive. 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."

There is a severe disagreement between the model and the measurements for some compounds, but the authors do not attempt to improve the prediction of water uptake by any calculation or modification to the models.

Reply: In this work, we aim to provide unambiguous HTDMA data of a large suite of organics and understand the roles of different physico-chemical properties that play in organic hygroscopicity, which may benefit the improvement of predictions of different thermodynamic models. These data may help the model developer to further understand the limitations and applicability of current models. However, to make obvious improvement of these models, we may need more information, such as a sufficient acquaintance of the simulation procedure and involving parameterization, which may not be able to be resolved in current study.

We appreciate this comment suggested by the reviewer and made some limited attempts that we can only access to improve the model predictions. Specifically, we changed some of the input properties of the studied organics in both models. For instance, we changed the phase state of the studied organic compound occurring in the liquid droplet. However, no significant change was observed in the obtained GF. Moreover, for the amino acids we studied, we used a reduced surface tension in both models instead of that of water due to their surface partitioning. However, the discrepancies between the measurements and the predictions became even larger. These are so far the attempts we made to improve the predictions, though it didn’t work out. Future work with substantial efforts, requiring detailed discussions with the model developer are needed as these models we used are online versions that only limited modification can be made.

The authors do not discuss the disagreement between UManSysProp and E-AIM. Why do these models behave differently? There is valuable information here and it should be discussed.

Reply: Both models are online predictors for the water uptake of some specific compounds or their mixtures. There are some differences between these two models. For instance, E-AIM mainly calculates the properties of bulk samples, while size-resolved information can be obtained from UManSysProp. Moreover, the phase state of the studied compound exist in the particles or droplets could be assumed in E-AIM, while no such input data can be included in UManSysProp, which is more simplified model that only molecular structure, surface tension and size can be modified. From the assumptions and input parameterization used for both models, we can deduce that the calculation mechanism or the involving physico-chemical processes might be different in these two models. This could also be the major reason for the disagreement between E-AIM and UManSysProp. We brought this information into our discussion (the third paragraph in Sect. 4.1.1) as: "This could be due to that the UManSysProp is a more simplified model taking into account less input data or parameterization. For instance, the phase state or the dissociation process of the studied compound at different conditions could not be assumed or considered in the simulation. Therefore, additional processes or properties should be included into this model for the further improvements of its predictions."

Minor Comments

Solubility: Line 219, 241, and elsewhere – there are too many "types" here, consider clarifying these paragraphs by using more specific and consistent terminology for solubility regimes. See, for example, Petters and Kreidenweis (2008). Petters and Kreidenweis (2008), A single parameter representation of hygroscopic growth and cloud condensation nucleus activity – Part 2: Including solubility, Atmos. Chem. Phys. 8, 6273–6279.

Reply: Yes, we clarified these paragraphs accordingly.

Line 206-207 was revised the second sentence in the first paragraph in Sect. 4.2.2 as: "(B) compounds that are not fully dissolved (slightly or sparingly soluble compounds with solubility in the range between 1e^{-3} to 3e^{-1} g/ml or saturated regime) in the aqueous droplets under 90 % RH condition."

Line 219-220 was revised the fifth sentence of the second paragraph in Sect. 4.2.2 as: "Compared to these non-hygroscopic slightly/sparingly soluble organic compounds, there are some other slightly/sparingly soluble organics, showing moderately water uptake with κ values larger than 0.1."

Line 241 was revised the fourth sentence of the second paragraph in Sect. 4.2.3 as "The other slightly/sparingly soluble organics shaded in red area in Fig. 6 is a moderate-hygroscopic group with a slightly stronger O:C-dependence."

Implementation of Kohler theory: On line 87, in the equation, ((1 – Ke/RH)Ke)/RH could be simplified to (Ke/RH-1).

Reply: Thank for your suggestion. Considering your suggestion, we simplified the equation as following:

$$\kappa = (GF^3 - 1)(\frac{Ke}{RH} - 1)$$

Because growth factor as a function of RH is diameter dependent, the results would be more general if the RH is divided by the Kelvin term, here expressed Ke (on line 87). This means that instead of RH you have growth factor as a function of water activity. aw = RH/Ke.

Reply: Thank you for your specific comments. We agree with your suggestion and revised the equation in Sect. 2 as following:

$$Ke = exp\ (\frac{4\sigma_{sol}M_w}{RT\rho_w D(RH)}),$$

$$RH/100\ \% = a_w Ke,$$

$$\kappa = \frac{(GF^3-1)(1-a_w)}{a_w},$$

where a_w is the water activity, M_w and ρ_w are the molar mass and the density of pure water at temperature *T*, respectively; σ_{sol} is the solution droplet surface tension, which was assumed to be the surface tension of water (0.072 J m^{-2}) and *R* is the ideal gas constant.

Also, the figures (Figure 1, Figure 2 and Figure 3) were plotted against water activity instead of RH in the revised manuscript.

33 – the citation does not match the statement in any way

Reply: We replaced “Wang et al., 2015” with “Seinfeld and Pandis, 2016”.

147,147 – how do you know that the water mass fraction always increased when the growth factor “shrank or grew” ? This calculation should be described here or in the supplement.

Reply: We originally meant that according to EDB measurements, the water mass fraction increased although our measured GF shrank. We deleted current sentence in our revised manuscript.

Figures: In general, the thick grey lines behind the data are distracting (all figures)

Reply: Yes, all figures without grids were used instead in the revised manuscript.

Figure 4 – Size and style of panel D should be consistent with the rest of the figure

Reply: Yes, the figures were modified accordingly in the revised manuscript.

Figure 6 – fonts are difficult to read and should be enlarged. There should be spaces between the words.

Reply: Yes, the figures were modified accordingly.

The table of contents in the supplement is very confusing. Why are figures each described twice, except for Figure S4? Also: there is no Figure S4. Please clarify this text.

Reply: We agree that the table of content is quite confusing and we deleted the table of content in the supplement.

Technical corrections

The references arranged either alphabetically or chronologically (forward or reverse).

Reply: Yes, we rearranged the references accordingly.

Do not capitalize the names of organic acids (line 114 and elsewhere).

Reply: Thank you for your comments, we revised the names of organic acids in the manuscript.

Caption of Figure 1 – (a) and (b) are listed together but the text differentiates these. Please be more descriptive in the caption as well

Reply: We revised the figure caption in Fig. 1 as: "Figure 1: Hygroscopic growth curves of straight-chain dicarboxylic acids (a), dicarboxylic acids with substitutions (b) and tricarboxylic acids (c) particles (200 nm). Points represent the measurement data; the solid lines indicate the E-AIM predictions (solid, non-hygroscopic organic GF=1) and the dashed lines show the UManSysProp calculated predictions."

Caption of Figure 1 – space between 200 and nm

Reply: We added a space between 200 and nm.

31 – McFiggans capitalize F

Reply: We capitalized F in "McFiggans".

37 – "large" not big

Reply: We switched the word from "big" to "large".

44 – "relies"

Reply: Thank you for your comment, we changed "rely" to "relies".

47 – "(E-AIM)," add comma, define UManSysProp

Reply: Yes, we agree with your comments. We defined UManSysProp in line 47 as well as in the abstract, and we added comma after (E-AIM).

55 – "molecular interactions" … "and water."

Reply: In the revised manuscript, current sentence was deleted.

62 – "experimental hygroscopicity data for organics"

Reply: We added "experimental" into the revised sentence.

66 – "experimentally-determined"

Reply: Due to a revision of the introduction part of our manuscript, current statement was deleted.

68,76 –Strike “self-assembled” or replace with, e.g., “home-built”, “custom-made”, “custom engineered”, or “HTMDA built in-house.” “Self-assembled” implies that the instrument assembled itself spontaneously.

Reply: Yes, we agree with your comments, we changed “self-assembled” to “custom-made”.

74 – “using ultrapure”

Reply: We added “using”before “ultrapure”.

Table 1 title: “Substances”

Reply: We revised “Substance” to “Substances”.

Table 1 header row: “Supplier, purity”

Reply: We changed “Supplier / purity” to “Supplier, purity”.

75 – physicochemical –either “physico-chemical” or “physicochemical” – make consistent throughout paper

Reply: Yes, we used “physico-chemical” throughout the whole paper.

79 – under dry conditions

Reply: Thank you for your advice, and we revised “dry condition” to “under dry condition”

80 – “the detailed schematic”

Reply: We changed “the detailed principle” to “the detailed schematic”.

81 – period after (2013)

Reply: We added “period” after “(2013)”.

88 – Mw is erroneously included inside the subscript of sigma

Reply: We corrected this equation: $Ke = exp\ (\frac{4\sigma_{sol}M_w}{RT\rho_w D(RH)})$.

89, 90 – italicize T and R

Reply: Yes, we used the italicized version.

94 – UManSysProp is defined here – should be defined above, or in both places

Reply: We agree, and we defined UManSysProp in the abstract.

109 – please clarify sentence

Reply: We revised the third sentence of the first paragraph in Sect. 4.1.1 as: “To achieve a comprehensive overview of the hygroscopicity of carboxylic acids, we measured the water uptake of several common straight-chain dicarboxylic acids in the atmosphere and further extended the hygroscopic measurements for dicarboxylic acids with substitutions and tri-carboxylic acids.”

115 – “dicarboxylic acids”

Reply: We modified “dicarboxylic acid” to “dicarboxylic acids”.

128 – period after “RH.”

Reply: We revised this sentence.

130 – “relatively higher”

Reply: Due to a revision of the results part of our manuscript, current statement was deleted.

131,132 – “current models have insufficient data” – break sentence into more than once sentence

Reply: The sixth sentence of the third paragraph in Sect. 4.1.1 was revised as: “This could be due to that the UManSysProp is a more simplified model taking into account less input data or parameterization. For instance, the phase state or the dissociation process of the studied compound at different conditions could not be assumed or considered in the simulation. Therefore, additional processes or properties should be included into this model for the further improvements of its predictions.”

134 – visible how? Detectable?

Reply: The last paragraph of Sect. 4.1.1 was revised as: “A similar gradual phase transition was observed for aconitic acid and citric acid (Fig. 1c), while the other tricarboxylic acid showed continuous hygroscopic growth over the studied RH range, indicating no obvious phase change for these particles upon hydration. However, it is quite interesting to note that predictions from the UManSysProp become more approaching to the experimental data, especially above 80 % RH, considering the measurement uncertainties.”

136 – “lower RH.”

Reply: We revised our manuscript, current statement was deleted.

138,139 – “Continuous water uptake”

Reply: Thank you for your comments, we deleted “The”, corrected to “Continuous water uptake”.

142,143 – “Previous studies”

Reply: We revised “Previous literatures” to “Previous studies”.

144 – remove period after “2018)”

Reply: Yes, we removed “period” after “2018)”.

147 – remove comma after “though”

Reply: We deleted current phrases in the revised manuscript.

147 – “shrank or grew slightly”

Reply: We deleted current phrases in the revised manuscript.

148 – agrees with which previous results? Both of the prior citations? Please elaborate.

Reply: The whole section was revised and detailed literature comparison was given in the second paragraph in Section 5.

148,149 – “Actually, it cannot be defined” – this sentence is unclear, please rephrase. Remove or replace the word “actually.”

Reply: We removed the sentence.

150 – “are generally in better agreement with”

Reply: We revised to “are generally in better agreement with”.

155 – “growth was”
Reply: We corrected “growths were” to “growth was”.

160 – “literature”

Reply: We changed “literatures” to “literature”.

163 – please rephrase

Reply: We rephrased the second paragraph in Sect. 4.1.3 as: “Similarly, phase transition or microstructural rearrangements of particles was not included in the models. Thus, these sugars and sugar alcohols were generally less hygroscopic than the values predicted by the E-AIM (except L-arabitol) under low RH conditions. However, at elevated RHs, whereas particles are fully dissolved, the E-AIM predictions agree well with most of the measured hygroscopic GFs within the measurement uncertainties.”

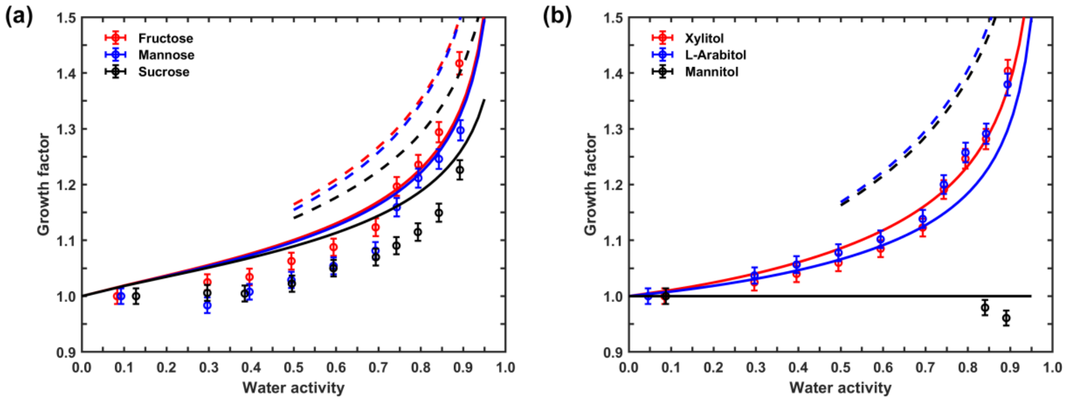

Figure 2 (Figure 3 in the manuscript): Hygroscopic growth curves of sugars (a) and alcohols (b). Points represent the measurement values; the solid lines indicate the E-AIM predictions (solid, non-hygroscopic organic GF=1) and the dashed lines represent the UManSysProp calculated predictions.

168 – “Note that”

Reply: Yes, we corrected to “Note that”.

177 – “adding an”

Reply: Thank you for your comments, we revised this sentence to “adding an carboxylic acid group…”.

209,210, … – here and elsewhere, capitalize Hoff

Reply: We capitalized “Hoff” throughout the whole paper.

220 – “moderately”

Reply: We corrected “moderate” to “moderately”.

221 – “hygroscopicity”

Reply: We corrected “hygroscopic” to “hygroscopicity”.

223-225 – please clarify these sentences

Reply: We clarified the last three sentences of the second paragraph in Sect. 4.2.2 as: “This is physically reasonable that the aqueous droplet of these organics with limited solubility can be considered as being composed of an effectively insoluble core with a saturated solution. The organic with higher water solubility would dissolve more and have a higher molar concentration in the saturated solution. The higher molar concentration corresponds to a stronger reduction in water activity, which would lead the particles to become more hygroscopic.”

229-231 – this is a run-on sentence – split the sentence and clarify

Reply: The second sentence of the first paragraph in Sect. 4.2.3 was revised as: “In this study, we plotted our measured κ of the 23 organic compounds with their O:C ratios in Fig. 6, and for a wider atmospheric implication we compared them against previous results from different atmospheric environments.”

234 – “arises”

Reply: We corrected “arise” to “arises”.

242 – “good” not “well”

Reply: We changed “well” to “good”.

246 – “to our’

Reply: We replaced “as our” to “to our”.

251 – “This, on the other hand, indicates”

Reply: Yes, we replaced “on the other side” to “on the other hand”.

253 – “whose constitute may be diverged” – this is unclear, rephrase

Reply: We rephrased the eleventh sentence of the second paragraph in Sect. 4.2.3 to “The use of a simplified average property (i.e., O:C ratio) to describe the hygroscopicity of ambient organics, whose constitute may be complex, is quite risky as compounds with similar O:C ratio may vary considerably in hygroscopicity.”

263 – “groups”

Reply: We corrected “group” to “groups”.

264 – “processes”

Reply: We corrected “process” to “processes”.

285 – “A detailed description of the HTDMA implementation, “

Reply: Yes, we replaced this sentence to “A detailed description of the HTDMA implementation”.

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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.

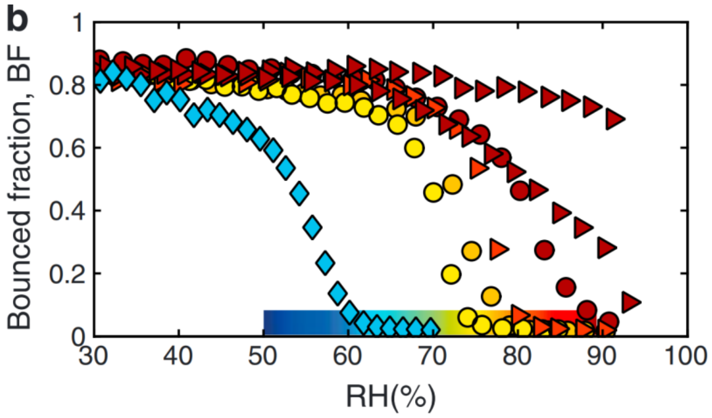
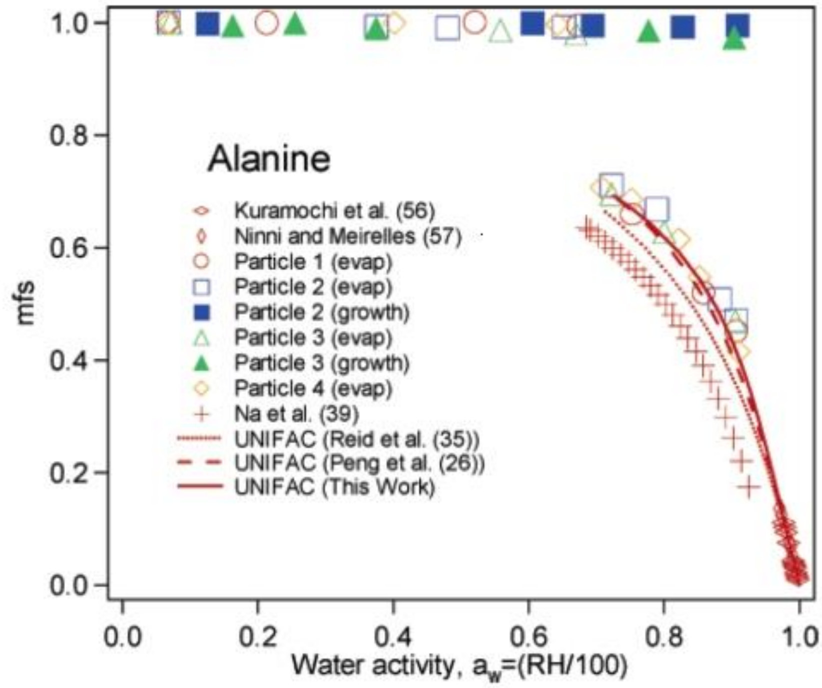


Figure R1: A copy of Figure 1b of Pajunoja et al. (2015). Bounced fraction (BF) of aerosols as a function of relative humidity for flow tube generated aerosols using different precursors. When BF >0, aerosols are considered as solid or semisolid and aerosols at BF = 0 behave mechanically as liquids.

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):



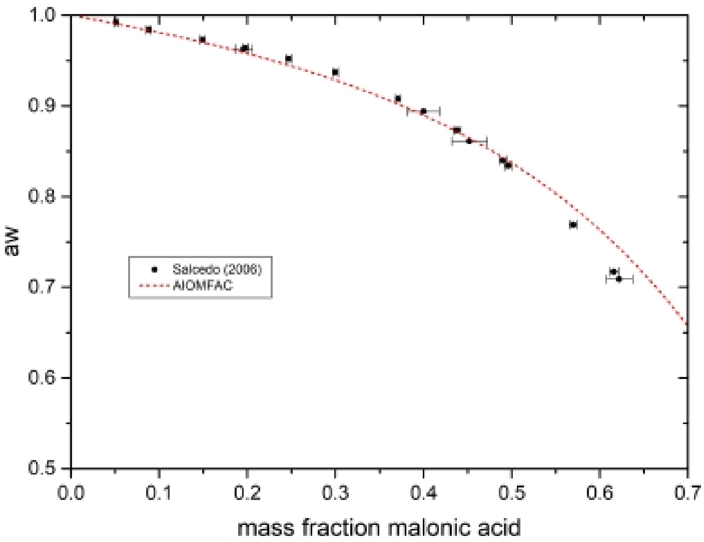
The authors observe no growth up to a relative humidity of 90 % which seems to be the highest they can reach in their setup. That is consistent with the data of Chan et al. upon humidification. But the data of interest are the ones when starting at high humidity and drying whith the metastable, subcooled 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 higher 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 R2 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.

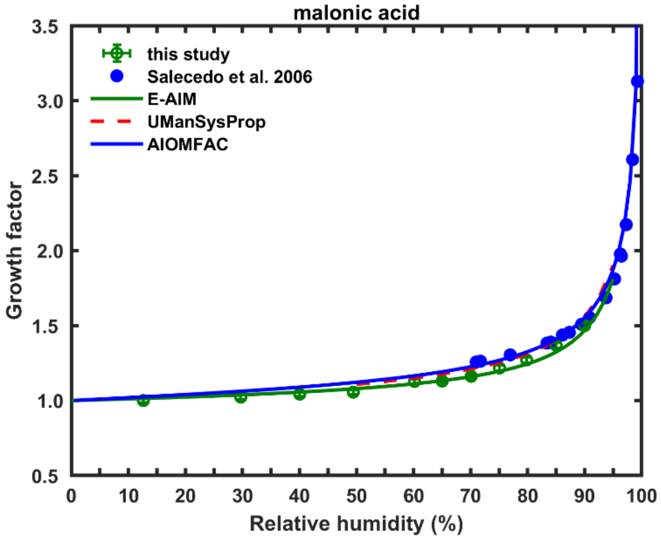


Figure R2: Measured and predicted growth factor as a function of relative humidity (RH) for malonic acid as.

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. (R1):

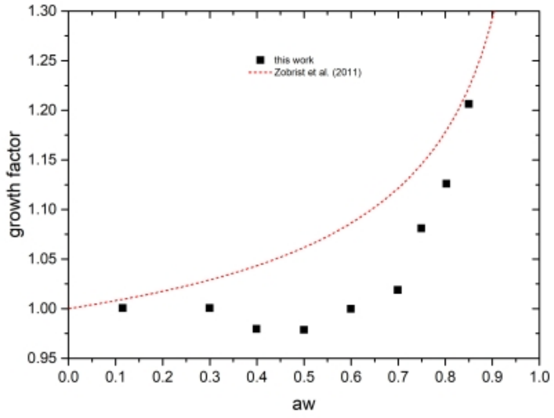
$$GF = \left[1 + \frac{n_w M_w/\rho_w}{\sum_i (m_i/\rho_i)}\right]^{\frac{1}{3}}, \tag{R1}$$

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. (R2):

$$GF = \left[\frac{(\sum_i m_i + n_w M_w)/\rho_{solution}}{\sum_i (m_i/\rho_i)}\right]^{\frac{1}{3}}, \qquad \text{(R2)}$$

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 a proxy for viscous or even glassy aerosol particles during the last years in a large number of studies. Its hygroscopicity is very well established. However, the authors do not at all compare their data with data available 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 hygroscopicity of sucrose (e.g. Zobrist et al, 2011):



The gap between measurement and parameterization at RH smaller about 0.8 is probably due to kinetic water uptake limitations.

Overall, I feel this work does not contribute much new science, needs more thorough comparison to existing literature. It also uses a method not really suited for determining water activity of binary systems if the interest is in comparing to thermodynamic models.

Reply: We agree with the reviewer that comparison with the other data for sucrose should be conducted. We therefore compared our results (repeated ones) 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.

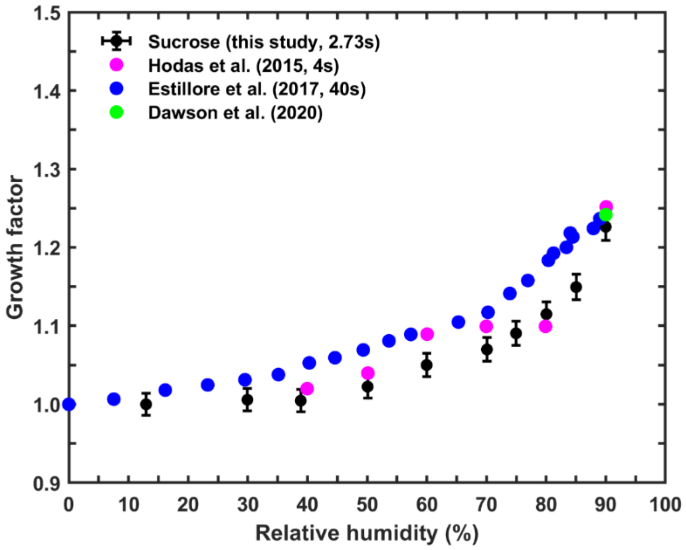


Figure R3: Comparison of the measured growth factor for sucrose as different RH with other studies using different HTDMA.

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 content in Sect. 5 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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Hygroscopicity of organic compounds as a function of organic functionality, water solubility, molecular weight and oxidation level

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Abstract. Aerosol hygroscopicity strongly influences the number size distribution, phase state, optical properties as well as multiphase chemistry of aerosol particles. Due to the big number of organic species in atmospheric aerosols, the determination of the hygroscopicity of ambient aerosols remains challenging. In this study, we measured the hygroscopic properties of 23 organics including carboxylic acids, amino acids, sugars and alcohols using a Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA). Earlier studies have characterized the hygroscopicity either for a limited number of organic compounds using similar techniques or for particles at sizes beyond the micro-scale range or even bulk samples by other methodologies. Here, we validate these studies and extend the data by measuring the hygroscopicity of a broader suite of organics for particles with size under the submicron range that are more atmospheric relevant. Moreover, we systematically evaluate the roles of related physico-chemical properties that play in organic hygroscopicity. We show that hygroscopicity of organics varies widely with functional groups and organics with the same carbon number but more functional groups show higher hygroscopicity. However, some isomers, which are very similar in molecular structures, show quite different hygroscopicity, demonstrating that other physico-chemical properties, such as water solubility may contribute to their hygroscopicity as well. If the organics are fully dissolved in water (solubility > 7×10^{-1} g/ml), we found that their hygroscopicity is mainly controlled by their molecular weight. For the organics that are not fully dissolved in water (slightly soluble: 5×10^{-4} g/ml < solubility < 7×10^{-1} g/ml), we observed that some of them show no obvious water uptake, which probably due to that they may not deliquesce under our studied conditions up to 90 % RH. The other type of slightly soluble organics is moderately hygroscopic and the larger their solubility the higher their hygroscopicity. Moreover, the hygroscopicity of organics generally increased with O:C ratios, although this relationship is not linear. Hygroscopicity of organic compounds were also predicted by two thermodynamic models, including the Extended Aerosol Inorganics Model (E-AIM), and the University of Manchester System Properties (UManSysProp). We show that hygroscopicity results of almost all organic compounds except those tricarboxylic acids were poorly represented by the UManSysProp and the E-AIM over-estimated the hygroscopicity of all amino acids. These discrepancies were likely due to that both models do not consider phase transition and intermolecular interactions of these selected compounds in the simulations. These

results may further improve our understandings of the interactions between organics and water molecular and will benefit the estimate of the hygroscopicity and CCN (cloud condensation nuclei) activities of any mixtures, for instance, ambient mixtures based on known composition data.

1 Introduction

Atmospheric aerosol particles consist of numerous organic species with both anthropogenic and biogenic origins (Zhang et al., 2007; Jimenez et al., 2009; Zhang et al., 2015; Wang et al., 2018). These organic species often contribute a significant fraction to the mass of sub-micrometer aerosols, and have vital effects on air-quality and climate (McFiggans et al., 2006; Randall et al., 2007; Zheng et al., 2015). To obtain a systematic understanding of their effects, it is necessary to acquire correct information on the chemical composition and physico-chemical properties of these organics (Seinfeld and Pandis, 2016). Hygroscopicity is one of the most important physico-chemical properties and it describes the ability of particles to take up water and grow in size under sub- and supersaturated conditions (Petters and Kreidenweis, 2007). Thus, it strongly influences the number size distribution, phase state, optical properties as well as multiphase chemistry of aerosol particles (Cheng et al., 2008; Su et al., 2010; Hong et al., 2018; Tang et al., 2019).

Given the large number of organic species in atmospheric aerosols, the determination of their hygroscopicity is quite experimentally difficult. Current models normally use aggregate quantities, such as the atomic oxygen-to-carbon (O:C) ratio or the average oxidation state of organics to simply parameterize the hygroscopicity of organic species in ambient aerosols. However, recent studies show that the hygroscopicity of organic aerosols cannot be fully explained by their oxidation level and the empirical relationship between hygroscopicity and O:C might not be linear (Lambe et al., 2011; Kuwata et al., 2013; Rickards et al., 2013; Marsh et al., 2017). This suggests that this simplified approach to quantify organic hygroscopicity might be problematic and a more mechanistic understanding of the complex link between hygroscopicity and other physico-chemical properties such as molecular functionality, molecular weight and water solubility of organics should be examined.

Due to these challenges, prediction of the hygroscopicity of organic compounds sometimes relies on thermodynamic models which explicitly includes these properties, for instance molecular functionality, molecular weight, into simulations. These thermodynamic models, including the Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) (Zuend et al., 2008; Zuend et al., 2011), the Extended Aerosol Inorganic Model (E-AIM), and the University of Manchester System Properties (UManSysProp) (Clegg et al., 1998; Topping et al., 2016) use group contribution methods to calculate water activity for organic species of atmospheric relevance. However, involving these thermodynamic simulations in transport or climate models to predict the hygroscopicity for such a large number of organic compounds in ambient aerosols is computationally expensive. Moreover, these models, based on parameterizations from measurements, are semi-empirical, and thus need more experimental data to constrain their predictions (Suda and Petters, 2013). Particularly, when it comes to very dry conditions, these models may perform even worse and cannot capture the non-ideality of the solutions accurately (Ohm et al., 2015). Therefore, quantifying the hygroscopicity of atmospheric relevant organic species through laboratory measurements by systematically varying the type of studied organics is an intrinsic necessity. Chan et al. (2008) studied the hygroscopic properties and CCN activities of a series of dicarboxylic acids and saccharides using an electrodynamic balance (EDB) and found that the CCN activities of highly water soluble organic compounds can be well predicted by the Köhler theory. Suda et al. (2014)

examined the hygroscopicity of a few synthetic organic compounds that are atmospheric relevant but not commercially available using a CCN counter (CCNc). They found that the compounds with hydroxyl or carboxyl groups are the most hygroscopic, while the ones with nitrate or methylene are the least. Jing et al. (2016) investigated the hygroscopic properties of a series of dicarboxylic acids with levoglucosan using a HTDMA, but they mainly focused on the multicomponent interactions between organic compounds. Marsh et al. (2017) collected experimental hygroscopicity data for 23 organic compounds by a comparative kinetics EDB (CK-EDB) to compare with thermodynamic predictions and discussed that the hygroscopicity of organic compounds with increasing branching and chain length are poorly represented by models.

All these cases discussed above shows that there is already some_experimental hygroscopicity data for organics with high atmospheric abundance and relevance (Peng et al., 2001; Prenni et al., 2007; Chan et al., 2008; Lambe et al., 2011; Kuwata et al., 2013; Marsh et al., 2017; Lei et al., 2018). However, some of these measurements were conducted using different techniques rather than the HTDMA, all of which have different limitations. Measurements using a CCNc could only probe the hygroscopic properties or CCN activities at supersaturated conditions, where many compounds may already fully dissolve in water droplets. The EDB or CK-EDB approaches normally analyze the droplets in the micrometer size range, far beyond the size range of atmospherically relevant aerosols. In contrast, the HTDMA system allows direct measurement of particle hygroscopicity at subsaturated conditions and for particles at the size from tens to a few hundreds nanometers, which is a good complement closing the gaps beyond the reaches of other techniques. Furthermore, some of the aforementioned studies using similar HTDMA systems focused on quite a small number of organics discussing only one or two properties potentially influencing the hygroscopicity, leading to a limited coverage of the experimental datasets. Thus, a general picture in understanding the observed hygroscopicity among different organic species still remains unclear.

Therefore, in this work, we extend the compositional complexity and diversity of the studied organic compounds with varying functional groups, molecular structures and other relevant physico-chemical properties. We try to form a systematic matrix of experimentally- determined HTDMA data synthesizing a large suite of organics, providing unambiguous measurements of particles at atmospherically relevant size range. Combined with these experimental data, we aim to evaluate the roles of different physico-chemical properties that play in organic hygroscopicity and gain some insight on their limitations and applicability. In addition, predictions from two widely used thermodynamic models, E-AIM and the UManSysProp, are compared against our experimental data, which may benefit the validation and improvement of the fidelity of these models.

2 Measurements

Submicron aerosol particles were generated by nebulizing the aqueous solutions (0.1 g L^{-1}) of each compound using a constant output atomizer (TSI, 3076). The solutions were prepared by using ultrapure water (Millipore, resistivity ≥ 18.2 MΩ). The physico-chemical properties of the studied 23 compounds are summarized in Table 1.

After particle generation, the particles were introduced into a custom-made HTDMA system where their hygroscopic growth factor (GF(RH)) can be measured. GF(RH) is defined as Eq. (1):

$$GF(RH, D_0) = \frac{D(RH)}{D_0} \ , \tag{1}$$

where D(RH) and D_0 are the equilibrium mobility diameter of the particles at a given RH and under dry conditions (< 10 % RH), respectively. Figure S1 shows the schematic of the HTDMA system. The detailed schematic of the HTDMA system can be found in Tan et al. (2013). Residence time for humidication of the generated aerosols is around 2.7 seconds. Calibration of the system was performed using ammonium sulfate (AS) and the results shown in Fig. S2 display that the measured hygroscopic behaviour of AS agreed well with previous studies with the deliquescence RH around 78 %.

Swietlicki et al. (2008) summarized the potential sources of error in HTDMA measurements and concluded that the reliability of the measured data is strongly associated with the stability and accuracy of DMA2 RH as well as the accurate measurement of particle diameter by DMAs. According to Mochida and Kawamura (2004), the uncertainty in the measured GF can be calculated by Eq. (2):

$$\sqrt{\left(GF\frac{\sqrt{2}\varepsilon_{Dp}}{Dp}\right)^2+\left(\varepsilon_{RH}\frac{dGF}{dRH}\right)^2}, \qquad (2)$$

where GF is the measured growth factor with respect to any measured RH, ε_{Dp} and ε_{RH} are the errors in the measured Dp and RH. In our system, the accuracy of DMA2 RH was maintained to be ±1% and the uncertainty for the mobility diameter was ±1% according to PSL (Polystyrene Latex particles) calibration. Hence, for our system, ε_{RH} and ε_{Dp}/Dp are 1% and 0.01, respectively. The calculated uncertainty according to the above-mentioned method is added in the measured GF in the following section.

According to κ-Köhler theory, we converted the measured hygroscopic growth factor to the single hygroscopicity parameter κ (Eq. 3-6) to facilitate the comparison of the hygroscopic properties among different compounds (Petters and Kreidenweis, 2007):

$$\kappa = (GF^3 - 1)(\frac{Ke}{RH} - 1), \qquad (3)$$

$$Ke = exp\,(\frac{4\sigma_{sol}M_w}{RT\rho_w D(RH)}), \qquad (4)$$

$$RH/100\ \% = a_w Ke, \qquad (5)$$

$$\kappa = \frac{(GF^3-1)(1-a_w)}{a_w}, \qquad (6)$$

where a_w is the water activity, M_w and ρ_w are the molar mass and the density of pure water at temperature T, respectively; σ_{sol} is the solution droplet surface tension, which was assumed to be the surface tension of water (0.072 J m^{-2}) and R is the ideal gas constant.

3 Modeling

The E-AIM and UManSysProp are applied in this study to simulate the hygroscopic behaviour of the 23 organic species. E-AIM is a thermodynamic model for calculating gas, liquid and solid partitioning in aerosol systems (Clegg et al., 1998; Wexler, 2002), while UManSysProp (University of Manchester System Properties) is an online model to predict the hygroscopic growth factors of organic and inorganic species. Both models use the group contribution method of Universal quasi-chemical Functional group Activity Coefficients (UNIFAC) to characterize the subgroups of organic molecules and calculate activity coefficients based on the contributions from these subgroups (Fredenslund et al., 1975; Hansen et al., 1991). The detailed input setting and calculations for E-AIM and UManSysProp are given in Supplement.

4 Results and discussion

4.1 Hygroscopicity of individual organics

In this section, we summarized the measured and predicted hygroscopic properties of the 23 organic species, which are classified into three groups based on their functionality. Particles at the dry size of 200 nm were selected for analysis.

4.1.1 Carboxylic acids

Carboxylic acids are the most abundant water-soluble components identified in atmospheric aerosols (Chebbi and Carlier, 1996; Mochida et al., 2003; Kundu et al., 2010). Hygroscopic properties of straight-chain dicarboxylic acids have been extensively investigated in previous studies (Chan et al., 2008; Kuwata et al., 2013; Rickards et al., 2013), however, experimental data for dicarboxylic acids with additional substitutions and tricarboxylic acids are limited. To achieve a comprehensive overview of the hygroscopicity of carboxylic acids, we measured the water uptake of several common straight-chain dicarboxylic acids in the atmosphere and further extended the hygroscopic measurements for dicarboxylic acids with substitutions and tri-carboxylic acids. Figure 1 shows the measured and predicted humidograms of straight-chain dicarboxylic acids (Fig. 1a), dicarboxylic acids with substitutions (Fig. 1b) and tricarboxylic acids (Fig. 1c), respectively. Need to note that the E-AIM model cannot simulate the dissociation of tricarboxylic acids in aqueous phase. Hence, the hygroscopic growth of tricarboxylic acids was only modeled with the UManSysProp.

Among the studied straight-chain dicarboxylic acids, only malonic acid showed continuous hygroscopic growth with increasing RH and the measured GF at 90 % RH was 1.47, which agrees well with previous studies (Peng et al., 2001; Prenni et al., 2001; Wise et al., 2003). Figure 1a also shows that the hygroscopic behaviour of malonic acid was well represented by the E-AIM but overestimated by the UManSysProp. The other straight-chain dicarboxylic acids (i.e., succinic, adipic, pimelic, suberic and azelaic acids) did not show any water uptake at RH <= 90 %, which was not captured by the UManSysProp. Assuming a solid state of these dicarboxylic acids, the E-AIM was capable to predict their non-hygroscopicity. Similar results were also found in previous studies (Prenni et al., 2001; Kuwata et al., 2013; Rickards et al., 2013; Jing et al., 2016) and Chan et al. (2008) explained that these dicarboxylic acids have quite low-solubility in water and once they crystallized, they would not deliquesce even under high RH conditions (e.g., RH < 90 %). Moreover, we found that the measured GFs of these dicarboxylic acids were less than 1, which could be attributed to the adsorption of a small amount of water at the particle surface, leading to the rearrangements of the microstructure and compaction of the particle (Mikhailov et al., 2004; Mikhailov et al., 2009).

The humidograms of the three dicarboxylic acids with substitutions (i.e., double bond or hydroxy group) are illustrated in Fig. 1b. The continuous water uptake indicates that these particles may be at liquid state under dry conditions. We observed a small leap of the GFs from 80 % to 85 % RH, implying that these particles were only partially deliquesced and further dissolution occurred at elevated RH. However, considering the measurement uncertainties, the statement of the partial deliquescence could not be fully confirmed and thus further evidence from other measurements is needed. On the other hand, the E-AIM could well represent their hygroscopic properties at RH between 10 -90 %, while there are still some deviations between the measurements and the UManSysProp predictions, especially for malic and tartaric acids, even taking into account of their measurement uncertainties. This could be due to that the UManSysProp is a more simplified model taking into account less input data or parameterization. For instance, the phase state or the dissociation process of the studied compound at different conditions could not be assumed or considered in the simulation. Therefore, additional processes or properties should be included into this model for the further improvements of its predictions.

A similar gradual phase transition was observed for aconitic acid and citric acid (Fig. 1c), while the other tricarboxylic acid showed continuous hygroscopic growth over the studied RH range, indicating no obvious phase change for these particles upon hydration. However, it is quite interesting to note that predictions from the UManSysProp become more approaching to the experimental data, especially above 80 % RH, considering the measurement uncertainties.

4.1.2 Amino acids

Figure 2 shows the measured humidograms of the 5 amino acids and their corresponding thermodynamic predictions. Continuous water uptake was observed for particles of serine, glutamine and aspartic acid, indicating that there was no phase transition occurred during the hydration cycle. Considering the measurement uncertainties, no water uptake is observed for alanine particles, which has also been reported in previous works (Chan et al., 2005; Darr et al., 2018). For glycine, we observed a continuous shrink in wet particle size from 30 % RH to 80 % RH, and above 80 % RH the GFs increased slightly. Previous studies have reported that glycine particles started to absorb water above 60 % RH (Chan et al., 2005; Marsh et al., 2017; Darr et al., 2018) prior to deliquescence due to capillary effect, which could also be the potential reason for the shrinkage in particle size of glycine during hydration as a result of the microstructural rearrangement of particles upon humidification. The sizing of these structurally-rearranged particles, especially at lower RH range, will be erroneous as the volume change of the particles upon wetting may not only due to the water absorption but also the compaction of the original particles. This phenomena complicates the accurate estimation of the actual water amount absorbed by the particles due to their intrinsic hygroscopicity. In a recent study by Nakao et al. (2014), in order to avoid the influence from particle restructuring upon wetting, they sized wet particles without drying after generation and studied their droplet activation using a wet CCN. This approach they introduced might be an easier attempt, offering an unique solution for current problem from particle restructuring during the hydration processes.

Predictions of serine, glutamine, alanine and aspartic acid are generally in better agreement with measurements than that of glycine, although overestimation was observed for all the 5 amino acids. Luo et al. (2020) discussed that the UNIFAC ignored the intramolecular interactions between amine and carboxylic groups in both models, resulting in the observed difference in the measured and predicted GFs.

4.1.3 Sugars and Sugar alcohols

Two-stage-like gradual hygroscopic growth was also observed for particles of fructose, mannose, sucrose, xylitol and L-arabitol, shown in Fig. 3. The experimental results of those sugars and sugar alcohols are consistent with previous literature data (Chan et al., 2008; Estillore et al., 2017). Compared to other sugars and sugar alcohols, sucrose is slightly less hygroscopic with a mild downward trend in GFs at low RHs and the GF at 85 % RH was around 1.21, which is similar with the results of Estillore et al. (2017). Moreover, mannitol is the least hygroscopic or even hydrophobic with GF less than unity at 90 % RH, which also agrees with previous literature (Ohrem et al., 2014; Martău et al., 2020).

Similarly, phase transition or microstructural rearrangements of particles was not included in the models. Thus, these sugars and sugar alcohols were generally less hygroscopic than the values predicted by the E-AIM (except L-arabitol) under low RH conditions. However, at elevated RHs, whereas particles are fully dissolved, the E-AIM predictions agree well with most of the measured hygroscopic GFs within the measurement uncertainties.

4.2 Relating the hygroscopicity of organic compounds to their physico-chemical properties

In this section, we explore the effects from different physico-chemical properties such as molecular functionality, water solubility and organic oxidation level that potentially contribute to the observed hygroscopicity κ. Note that the hygroscopicity parameter κ discussed in this section was converted by using growth factor data measured at 90 % RH.

4.2.1 κ vs. organic functionality

Figure 4a shows the measured hygroscopicity of the 23 organics as a function of carbon number. The functional groups with their corresponding numbers are indicated with colors and symbols. In order to facilitate the comparison of the compounds with the same carbons, the carbons with only one compound are not illustrated. For the studied organic compounds with the same carbon number, the hygroscopicity was increased by the addition of extra functional groups to the carbon backbone. For instance, maleic, malic, tartaric and aspartic acid with extra functional groups (e.g., C=C, -OH and -NH2) with respect to succinic acid with only two -COOHs are more hygroscopic. For C7 compounds, adding an carboxylic acid group to the carbon backbone leads to an elevated hygroscopicity from pimelic to tricarboxylic acid. Moreover, organic compounds with the same carbon numbers but different molecular functionality presented quite distinct hygroscopicity. For example, for C3 compounds, if replacing the -CH3 with an -OH or replacing the -OH group by an -COOH in their parental molecules, the hygroscopicity was significantly increased. Taking another example from C4 compounds, the organics with a hydroxyl group (-OH) instead of an -NH2 or with a double bond (C=C) instead of the hydroxyl group in their carbon backbones were more hygroscopic. Similar difference in hygroscopicity was also observed between aconitic acid (C6) with a C=C and citric acid (C6) with a (-OH). By summarizing the results in current study, κ increased with the functionality in the following order: (-CH3 or -NH2) < (-OH) < (-COOH or C=C or C=O). However, it has to be noted that this comparison is quite qualitative, might be ambiguous and further evidence from other organic compounds is needed in order to drive a more general conclusion. Suda et al. (2012) and Chen et al. (2019) concluded that the hygroscopicity of organic compounds is closely related to their individual polarity and highly polar compounds are usually more hygroscopic. Kier (1981) ranked the polarity of different functional groups in the sequence of -CH3< -NH2< -OH< -CHO< -NH2OH< -COOH, which could explain the difference in the hygroscopicity of organics with various functionalities in our study.

Figure 4b shows that the measured hygroscopicity of the straight-chain dicarboxylic acids alternate with the parity of the carbon numbers. It has to be noted that data of glutaric acid (C5) is quoted from Chan et al. (2008). Bilde et al. (2003) observed an alternation in the volatility of dicarboxylic acids with the number of carbon atoms similar to the ones we observed for their hygroscopicity. They attributed this to the alternation in the molar enthalpies of fusion of those compounds. Moreover, we observed that some compounds (xylitol vs. L-arabitol and fructose vs. mannose) share the same molecular formular or functionality but vary differently in hygroscopicity as shown in Fig. 4c. Both findings suggest that other physico-chemical properties of organics besides molecular functionality may also contribute to the observed variation in their hygroscopicity. Previous studies (Marcolli and Peter, 2005; Petters et al., 2017) reported that the position of the functional groups could influence the hygroscopicity properties of organic compounds. For instance, Petters et al. (2017) suggested that organic molecules with the hydroperoxyl group close the end of carbon chain were more hygroscopic. Similarly, fructose observed in our study, with the hydroxyl group in the tail of the carbon chain and being far away from the C=O group, is more hygroscopic than mannose of which these two groups are much closer to each other.

4.2.2 κ vs. water solubility and molar volume

Previous studies suggested that for highly soluble compounds which are fully dissolved in the aqueous droplet, their hygroscopicity are mainly controlled by their molar volume (M_{org}/ρ_{org}); while for slightly soluble compounds, their hygroscopicity is limited by their low water solubility (Petters et al., 2009; Kuwata et al., 2013; Nakao, 2017; Wang et al., 2019). Hence, we considered two regimes in our study: (A) compounds that fully dissolved (highly soluble with solubility > 7×10^{-1} g/ml in this work or not saturated regime) and (B) compounds that are not fully dissolved (slightly or sparingly soluble compounds with solubility in the range between $1e^{-3}$ to $3e^{-1}$ g/ml or saturated regime) in the aqueous droplets under 90 % RH condition. In regime A, as shown in Fig. 5, the hygroscopicity decrease with increasing molar volume. Besides molar volume, the van't Hoff factor (i), which accounts for the degree of dissociation of a compound in water, could also contribute to the overall hygroscopicity for fully dissolved compounds. Sugars, as non-electrolytes with van't Hoff factor of 1, do not dissociate in aqueous solutions (Giebl et al., 2002; Koehler et al., 2006; Rosenørn et al., 2006) and thus are less hygroscopic than the dicarboxylic acids which can dissociate in water and contribute to the reduction in water activity. Frosch et al. (2010) related the van't Hoff factor with the pKa values for a series of carboxylic acids and found that the stronger the acid with smaller values of pKa, the larger the van't Hoff factor. This could explain why maleic acid, even with a larger molar volume but a smaller pKa value (1.8) is more hygroscopic than malonic acid (pKa = 2.4).

Organic compounds with low water solubility (regime B) could be obviously divided into two categories according to their hygroscopicity. One is non- or almost non-hygroscopic organics with κ close or equal to 0. These organics might present at solid or crystalline state and did not deliquesce at our measurement conditions during the whole RH range. Thus, their hygroscopicity is not only limited by their low water solubility but also their phase state and the energy that needed for the phase transition. Compared to these non-hygroscopic slightly/sparingly soluble organic compounds, there are some other slightly/sparingly soluble organics, showing moderately water uptake with κ values larger than 0.1. These organics with limited solubility may already partially deliquesce under our studied RH conditions (Hartz et al., 2006; Chan et al., 2008), and we found that their hygroscopicity increase with water solubility. This is physically reasonable that the aqueous droplet of these organics with limited solubility can be considered as being composed of an effectively insoluble core with a saturated solution. The organic with higher water solubility would dissolve more and have a higher molar concentration in the saturated solution. The higher molar concentration corresponds to a stronger reduction in water activity, which would lead the particles to become more hygroscopic.

4.2.3 κ vs. O:C ratio

Previous studies have suggested that the hygroscopicity parameter of organic species (κ_{org}) is closely related with their O:C ratios (Jimenez et al., 2009; Chang et al., 2010; Massoli et al., 2010; Cappa et al., 2011; Lambe et al., 2011; Kuwata et al., 2013; Rickards et al., 2013). In this study, we plotted our measured κ of the 23 organic compounds with their O:C ratios in Fig. 6, and for a wider atmospheric implication we compared them against previous results obtained from different atmospheric environments (Mei et al., 2013; Wu et al., 2013; Hong et al., 2015; Wu et al., 2016; Deng et al., 2018; Hong et al., 2018; Kuang et al., 2020). Clearly, ambient organics show much lower O:C value as seen in Fig. 6. Ng et al. (2010) compiled the measured O:C data from different environments and concluded that at most sites, ambient organic aerosols mainly consist of oxygenated organic material (OOA) and hydrocarbon-like organic material (HOA). HOA, which arises from vehicle emissions, is the least oxidized with the average O:C value less than 0.2 (Ng et al., 2010; Xu et al., 2015; Xu et al., 2016; Cao et al., 2019; Li et al., 2020). Hence, with the inclusion of HOA in ambient aerosols, the average O:C value of the bulk organic is less than 1, being generally lower than our laboratory-generated aerosols.

A general trend of the increase of κ_{org} with increasing O:C has also been observed for laboratory results but the correlation between κ and O:C falls into two categories. One is a non-hygroscopic organic group with a weak O:C-dependence as the blue shaded area in Fig. 6. We suggested these compounds with limited water solubility might not deliquesce yet under 90 % RH as discussed previously. The other slightly/sparingly soluble organics shaded in red area in Fig. 6 is a moderate-hygroscopic group with a slightly stronger O:C-dependence. However, the correlation of both categories is not good, which may be effected from the other properties which discussed above. Compared to those laboratory-generated pure organic compounds, ambient organics are more complex, with divergent O:C-dependent hygroscopicity among different environments. For instance, the hygroscopicity of urban aerosols in Beijing was almost constant, being less sensitive to the variations of the organic oxidation level, which is similar to our non-hygroscopic organics (Wu et al., 2016). On the contrast, the suburban aerosols in central Germany (Wu et al., 2013) and in Guangzhou (Hong et al., 2018) exhibit a slightly stronger influence from their O:C ratio, being close to the behaviour (slope ≈ 0.12) of the moderate hygroscopic organics with relative higher water solubilities in our study. As discussed in previous works (Rickards et al., 2013) some of the laboratory-generated pure organics share identical O:C ratio but differ widely in hygroscopicity. However, no molecular-specific information could be concluded further for those ambient organics. This, on the other hand, indicates that great uncertainties may arise from the approximation of organic hygroscopicity based on their atomic O:C ratio for ambient aerosols. The use of a simplified average property (i.e., O:C ratio) to describe the hygroscopicity of ambient organics, whose constitute may be complex, is quite risky as compounds with similar O:C ratio may vary considerably in hygroscopicity. Additional measurements of other properties (e.g., functionality or water solubility) may be difficult due to both the highly complex mixture of ambient aerosols and technique limitations. However, laboratory-generated surrogate mixtures representing the complexity of ambient aerosols at least should be examined to test the variety in the relationship between the O:C ratio and κ.

5 Atmospheric implication

Our laboratory observations reveal that current thermodynamic models may not always accurately simulate the hygroscopic behavior of organic compounds, despite their previous success. Phase transition may occur during the hydration cycle, which are not reasonably considered in the thermodynamic models. This will lead to significantly biased predictions of organic hygroscopic behaviour, as can be seen in the case of the slightly soluble organics in our study. Moreover, the interactions between functional group and water molecules were previously believed to dominate particle hygroscopicity rather than the interactions between functional groups. However, we found that the groups-groups interaction may be also important in water uptake processes. This effect is clearly revealed in our study by the discrepancy in the hygroscopicity of amino acids between measurements and model prediction. These limitations suggest that an improved mechanism with the inclusion of these processes (e.g., phase transition and intramolecular interactions) into these thermodynamic models is needed and require comprehensive data from empirical measurements to complement these models for validating predictions. Furthermore, extra care must be taken to deal with even more complex systems, such as multi-component mixtures with the presence of inorganic compounds in atmospheric particles.

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 also observed 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 not be conclusive. 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."

In the previous section discussing the role of different physico-chemical properties of organics plays in aerosol hygroscopicity, the parameter κ was converted by the measured GF under 90 % RH. For those low or sparingly soluble organic compounds, the GF_derived κ (also known as apparent κ) is RH-dependent (see Fig. S3 as an example) and cannot express their intrinsic κ (expressed by fully dissolved compounds), when compounds are sufficiently soluble in water. As the RH increases, further dissolution of these organic compounds with promoted hygroscopicity is expected. In the real atmosphere, different RH conditions including both sub- and supersaturation can be reached. The measured GF or the apparent κ of ambient aerosols at a certain RH may not be able to reveal their real hygroscopicity under various atmospheric conditions. Further calculations of other variables, for instance the liquid water content (LWC), surface area of wet particles and number concentration of CCN associated with the apparent κ will be significantly biased. If possible, hygroscopicity measurements over large saturation range up to supersaturation, especially with the combination of CCN measurements provide an option to reduce the uncertainties, but requiring fast and stable scanning of RHs during the experiments. Technical improvement, for example in HTDMA system is essentially needed.

Data availability.

The details data can be obtained from the corresponding author upon request.

Supplement.

A detailed description of the HTDMA implementation, calibration of instrument by using ammonium sulfate, calculations for E-AIM and UManSysProp models, hygroscopicity parameter κ as a function of RH for sparingly soluble organics.

Author contributions.

SH contributed to investigation, data curation, visualization and writing original draft. JH and NM contributed to resources, writing review and editing. HBX contributed software, HBT, JCT, YQZ, LP, YH contributed to resources. QQW contributed to fund acquisition. JNS contributed to investigation. YFC, HS contributed to resources and fund acquisition.

Competing interests.

The authors declare no competing financial interest.

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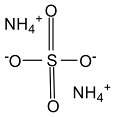
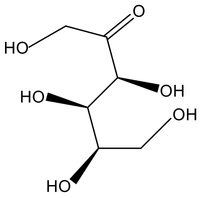
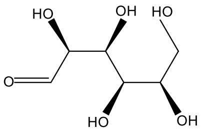
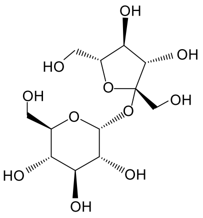
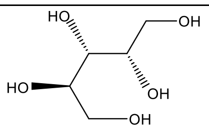
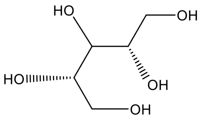
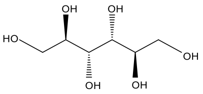
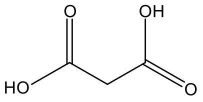
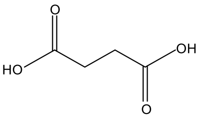
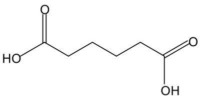
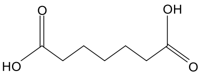
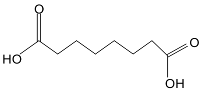
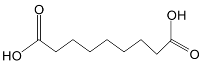
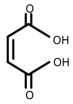
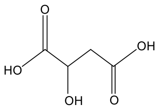
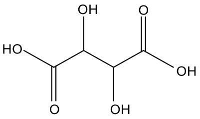
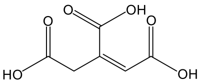
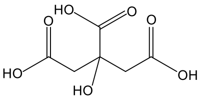
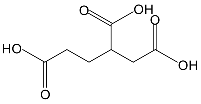
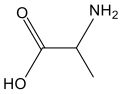
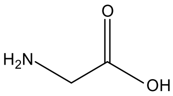
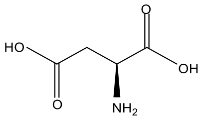
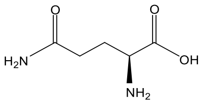
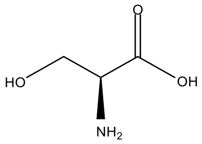
Table 1. Substances and their relevant properties investigated in this study.

Compounds	Molecular structure	Chemical formula	Molar weight (g mol^{-1})	Density (g cm^{-3})	O/C	Solubility (g ml^{-1})	Supplier, purity
Ammonium sulfate		$(NH_4)_2SO_4$	132.14[a]	1.77[a]	-	0.77[a]	Macklin, 99.99%
Sugars							
D(-)-fructose		$C_6H_{12}O_6$	180.16[a]	1.59[a]	1	3.75[a]	Sigma Aldrich, ≥99%
D(+)-mannose		$C_6H_{12}O_6$	180.16[a]	1.54[a]	1	2.48[a]	Sigma Aldrich, ≥99%
Sucrose		$C_{12}H_{22}O_{11}$	342.30[a]	1.58[a]	0.9	2.1[b]	Sigma Aldrich, 99%
Sugar alcohols							
Xylitol		$C_5H_{12}O_5$	152.15[a]	1.52[a]	1	0.642[b]	Sigma Aldrich, ≥99%
L-(-)-arabitol		$C_5H_{12}O_5$	152.15[a]	1.15[a]	1	0.664[d]	Sigma Aldrich, ≥98%
D-mannitol		$C_6H_{14}O_6$	182.17[a]	1.52[a]	1	0.216[b]	Sigma Aldrich, ≥99.0%
Carboxylic acids							
Malonic acid		$C_3H_4O_4$	104.06[a]	1.62[a]	1.33	0.763[b]	Sigma Aldrich, 98%

Succinic acid		$C_4H_6O_4$	118.09[a]	1.19[a]	1	0.0832[b]	Sigma Aldrich, ≥99.0%
Adipic acid		$C_6H_{10}O_4$	146.14[a]	1.36[a]	0.67	0.03[b]	Sigma Aldrich, 99%
Pimelic acid		$C_7H_{12}O_4$	160.17[a]	1.33[a]	0.57	0.05[b]	Yuanye Bio-Technology, 98%
Suberic acid		$C_8H_{14}O_4$	174.19[a]	1.30[a]	0.5	0.0006[a]	Yuanye Bio-Technology, 99%
Azelaic acid		$C_9H_{16}O_4$	188.22[a]	1.03[a]	0.44	0.0024[a]	Yuanye Bio-Technology, 98%
Maleic acid		$C_4H_4O_4$	116.07[a]	1.59[a]	1	0.79[a]	Aladding, ≥99.0%
DL-malic acid		$C_4H_6O_5$	134.09[a]	1.61[a]	1.25	0.592[b]	Sigma Aldrich, ≥99%
Tartaric acid		$C_4H_6O_6$	150.09[a]	1.79[b]	1.5	1.43[e]	CATO, 99.7%
cis-Aconitic acid		$C_6H_6O_6$	174.11[a]	1.66[a]	1	0.4[d]	Sigma Aldrich, ≥98%
Citric acid		$C_6H_8O_7$	192.12[a]	1.54[a]	1.17	0.383[b]	Sigma Aldrich, ≥99.5%
Butane-1,2,4-tricarboxylic acid		$C_7H_{10}O_6$	190.15[a]	1.48[a]	0.86	0.3897[c]	Bidepharm, 97%
Amino acids							
DL-alanine		$C_3H_7NO_2$	89.09[a]	1.42[a]	0.67	0.164[b]	Macklin, 99%
Glycine		$C_2H_5NO_2$	75.07[a]	1.59[a]	1	0.25[a]	Sigma Aldrich, ≥99.0%

L-aspartic		$C_4H_7NO_4$	133.10[a]	1.66[a]	1	0.005[a]	Sigma Aldrich, ≥99%
L-glutamine		$C_5H_{10}N_2O_3$	146.14[a]	1.47[a]	0.6	0.0413[b]	Sigma Aldrich, ≥99.5%
L-serine		$C_3H_7NO_3$	105.09[a]	1.60[a]	1	0.425[b]	Sigma Aldrich, ≥99%

[a] https://www.chemicalbook.com/ [b] https://pubchem.ncbi.nlm.nih.gov/ [c] https://www.chemspider.com/

[d] https://hmdb.ca/ [e] Peng et al. (2001)

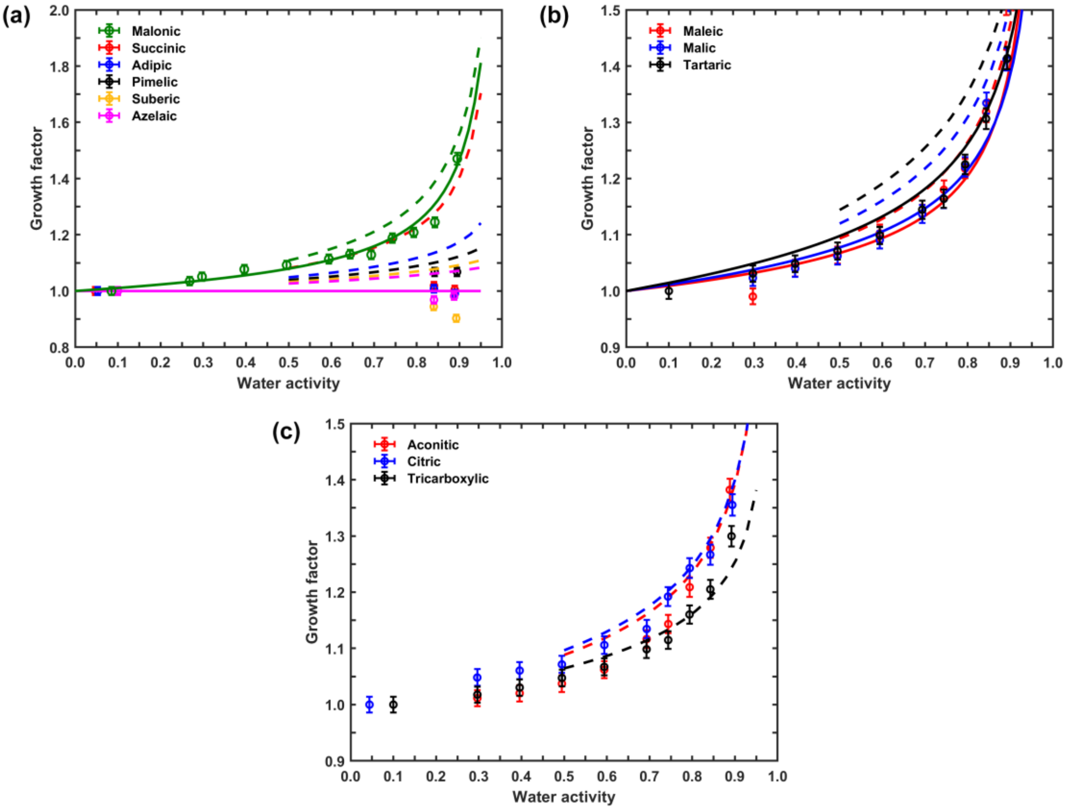


Figure 1: Hygroscopic growth curves of straight-chain dicarboxylic acids (a), dicarboxylic acids with substitutions (b) and tricarboxylic acids (c) particles (200 nm). Points represent the measurement data; the solid lines indicate the E-AIM predictions (solid, non-hygroscopic organic GF=1) and the dashed lines show the UManSysProp calculated predictions.

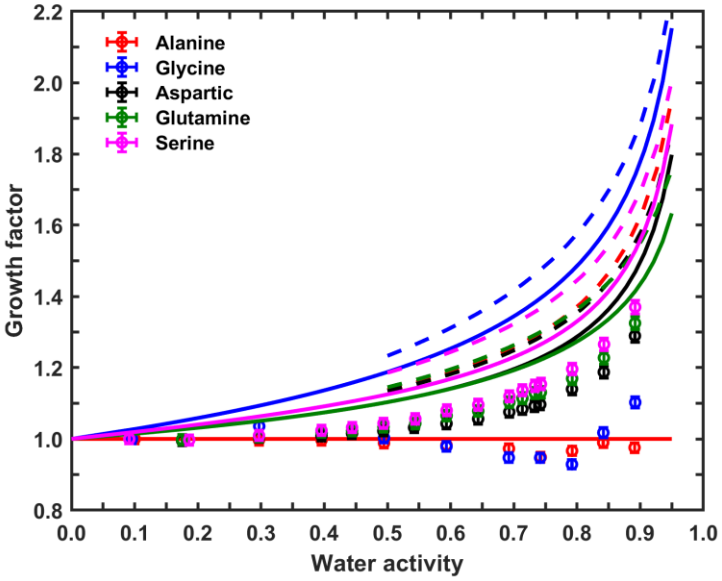


Figure 2. Hygroscopic growth factors of amino acids. Points represent the measurement values; the solid lines indicate the E-AIM predictions (solid, non-hygroscopic organic GF=1) and the dashed lines represent the UManSysProp predictions.

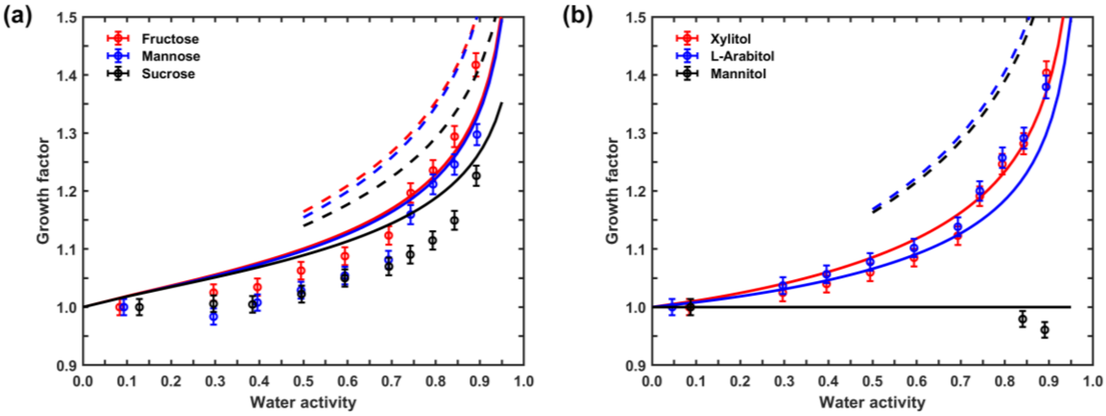


Figure 3. Hygroscopic growth curves of sugars (a) and alcohols (b). Points represent the measurement values; the solid lines indicate the E-AIM predictions (solid, non-hygroscopic organic GF=1) and the dashed lines represent the UManSysProp calculated predictions.

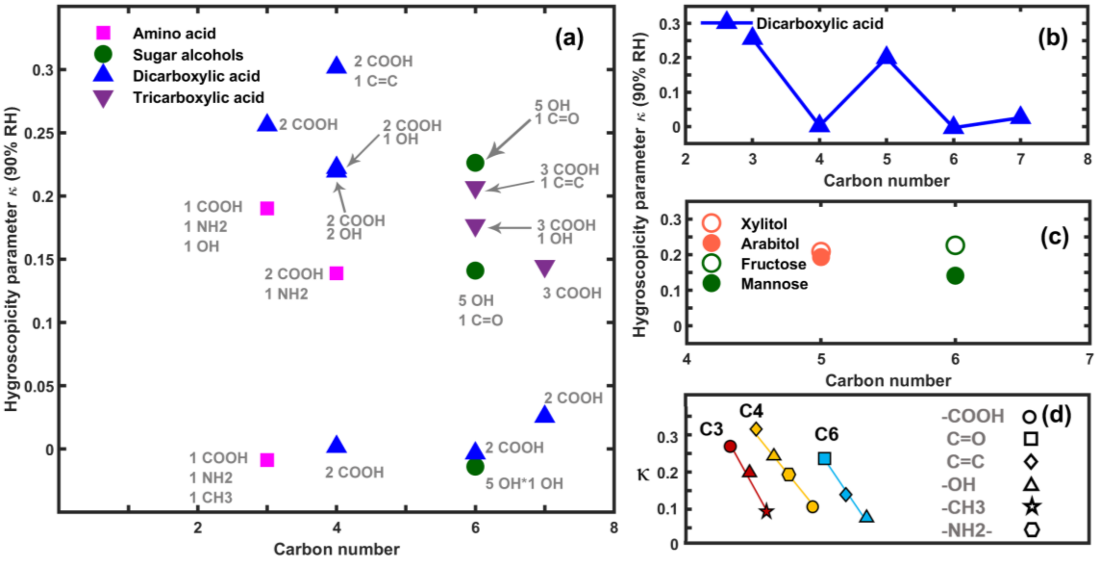


Figure 4. Hygroscopicity of organics as a function of carbon number (a); hygroscopicity of dicarboxylic acids vs carbon number (b); hygroscopicity of isomers (c); organic hygroscopicity as a function of their functionality with the same carbon number (d).

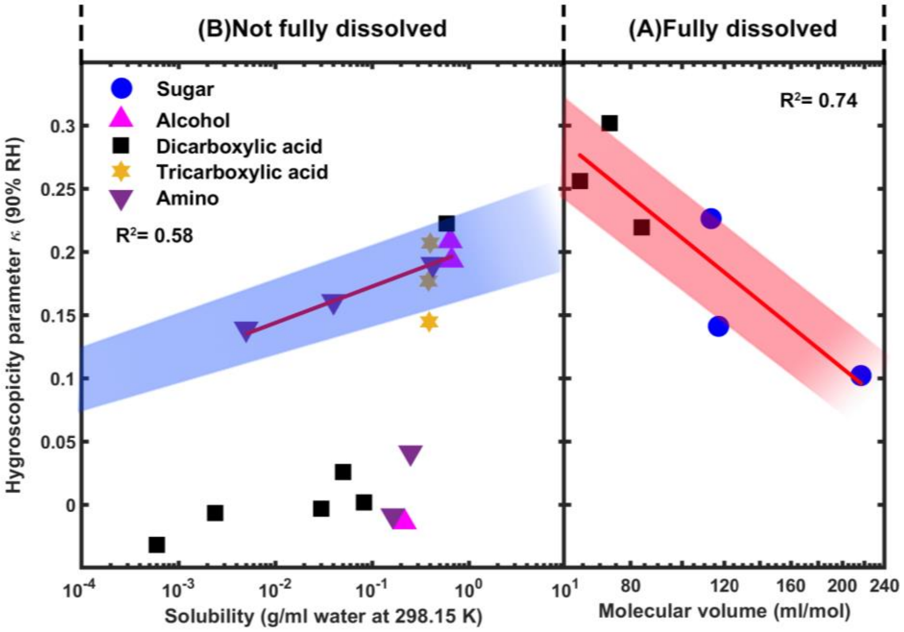


Figure 5. Hygroscopicity of organic compounds as a function of molecular volume (A) and solubility (B).

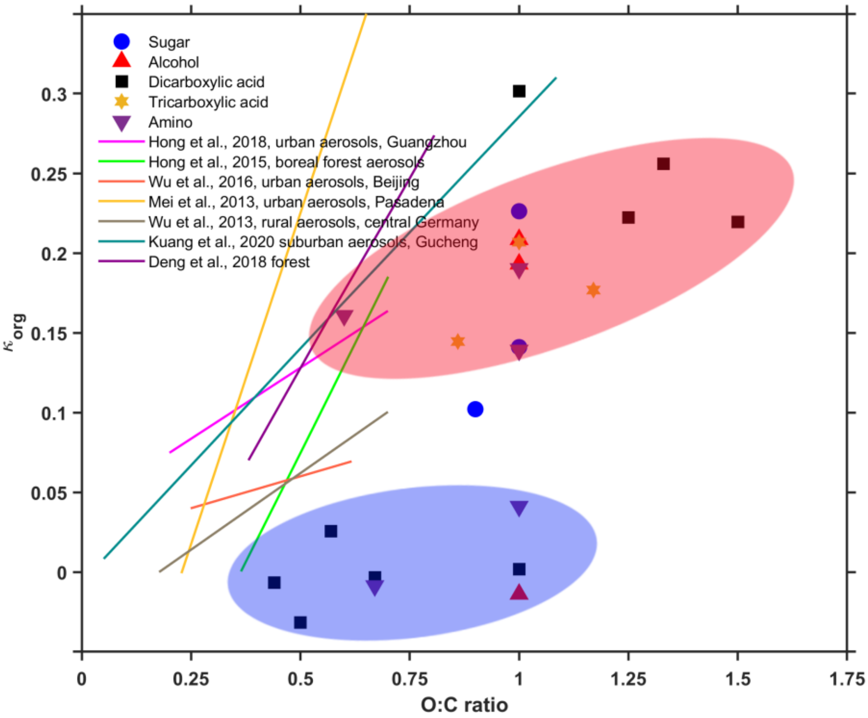


Figure 6. Correlation between O:C ratio and κ_{org}, and comparison with previous literature results. Blue and red shades represent the fitting of results of non-hygroscopic and more hygroscopic organics, respectively.

Supplement of

Hygroscopicity of organic compounds as a function of organic functionality, water solubility, molecular weight and oxidation level

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The principle of HTDMA can be described as follow: the generated aerosol particles passed through a silica diffusion dryer and a Nafion dryer (Perma Pure, MD-700-24S-3), and were dried to RH < 8 %. Subsequently, the dried particles were neutralized and obtained Boltzmann charge distribution by using a Kr85 neutralizer (TSI Inc.). After charging, the monodisperse aerosols with specific diameters were selected by the first differential mobility analyzer (DMA1, Model 3081L, TSI Inc.). Afterwards, the monodisperse aerosol particles entered into a Nafion humidifier (Perma Pure, PD-100T-24MSS) with a residence time about 2.7s, and they were humidified to a given RH (10-90 %). After humidifying, there was a similar system including another DMA (DMA2, Model 3081L, TSI Inc.) and a condensation particle counter (CPC, Model 3772, TSI Inc.) to measure the number size distribution of the humidified particles. The whole experiment system was controlled by air conditioning with the room temperature of around 24 ℃, and the internal temperature was kept at ±0.5K around the standard value. It should be noted that, because of we just measure the mode value of GF distribution of humidified particles, the multiple charge correction was ignored (Tan et al., 2013).

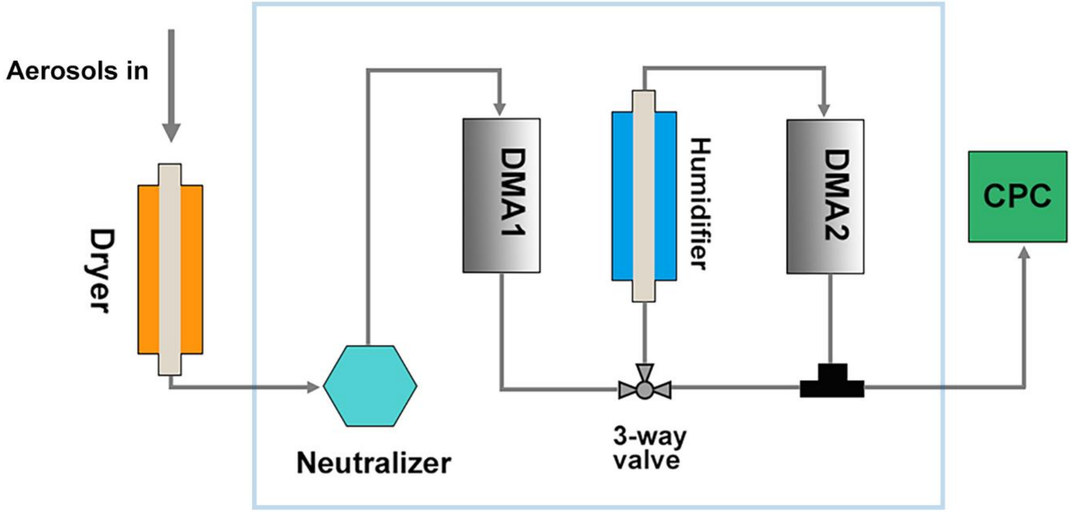

Figure S1. A schematic of the HTDMA instrument system.

To show the measured hygroscopic data is agree well with the E-AIM predictions and as well as previous studies, and the deliquescence RH is around 78 %. Therefore, our HTDMA is accurate according to the calibration result of ammonium sulfate, in addition, the measured GF at given RH are the average values of 5 times measurements, within the corresponding standard deviation less than 0.03. In our system, the accuracy of DMA2 RH was maintained to be ±1% and the uncertainty for the mobility diameter was ±1% according to PSL (Polystyrene Latex particles) calibration. Hence, for our system, ε_{RH} and ε_{Dp}/Dp are 1% and 0.01, respectively, the detailed calculation of GF uncertainty is described in section 2.

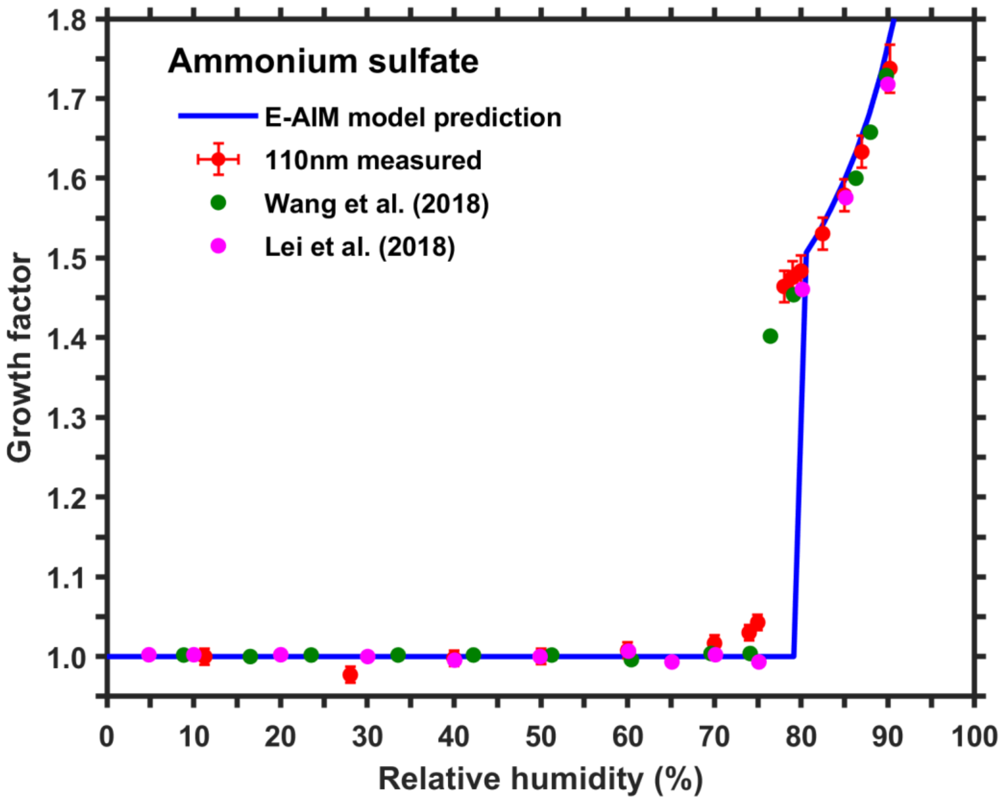

Figure S2. Hygroscopic growth factors of 110nm ammonium sulfate, and the blue line represents the E-AIM predictions. The green and magenta dots indicate the GFs of ammonium sulfate from Wang et al. (2018) and Lei et al. (2018), respectively.

In E-AIM, RH was varied between 5 % to 90 % and GF values of the pure component was calculated as Eq. (S1) (Wang et al., 2018):

$$GF = \left[1 + \frac{n_w M_w/\rho_w}{\sum_i (m_i/\rho_i)}\right]^{\frac{1}{3}} , \qquad \text{(S1)}$$

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. In UManSysProp, molecular subgroups were converted according to their Simplified Molecular Input Line Entry System (SMILES) and the input setting of RH was varied between 50 to 99 % (Topping et al., 2016).

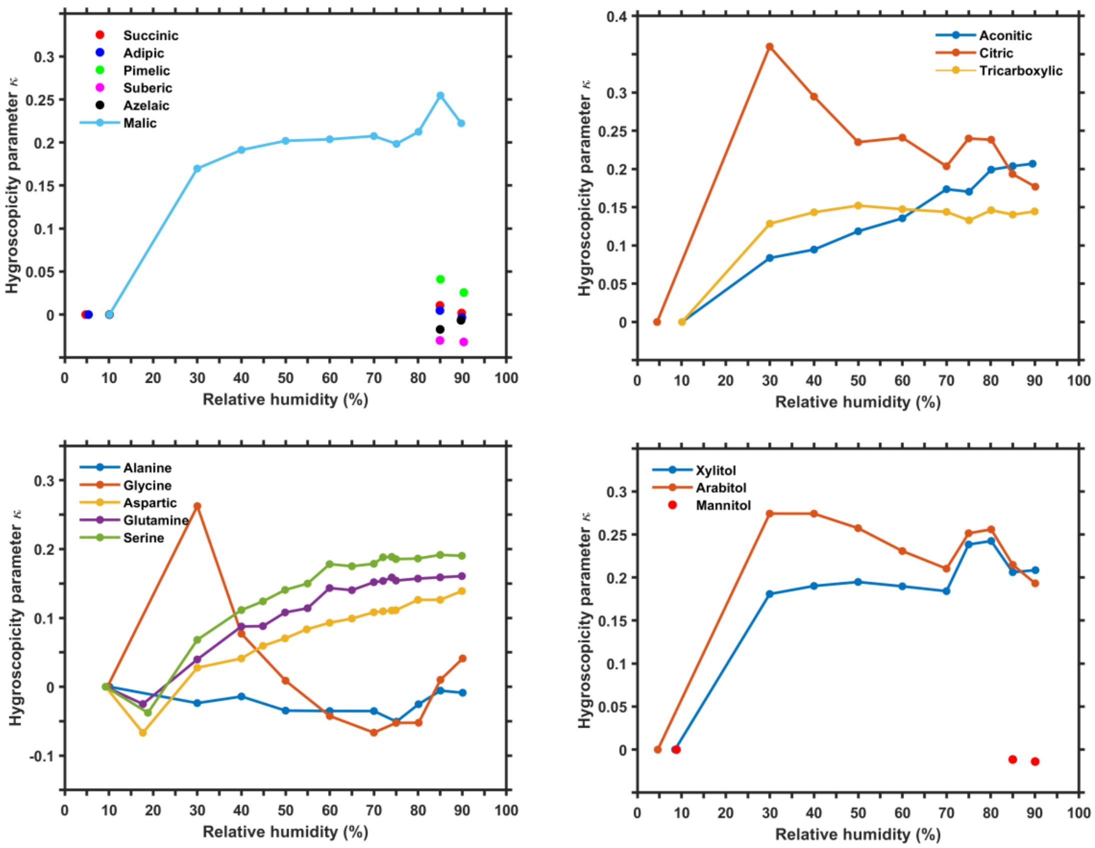

Figure S3 Hygroscopicity parameter, κ of organic components at different RHs (initial dry diameter of 200 nm at RH < 10 %).

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