# 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 & 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 et al., 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. 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. Moreover, comparison of the hygroscopic data using different techniques is also quite challenging due to a low understanding of the effect of different technical characteristics on particle hygroscopicity. 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 >  $7 \times 10^{-1}$  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:  $5 \times 10^{-4}$  g/ml < solubility <  $7 \times 10^{-1}$  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 moderate 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 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," in the revised manuscript.

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

Reply: We rephrased the sentence 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." in the revised manuscript.

## 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 in the revised manuscript (Sect. 2) as:

"Swietlicki et al. (2008) summarized the potential sources of error in HTMDA 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 & Kawamura (2004), the uncertainty in the measured GF

can be calculated by  $\sqrt{\left(GF\frac{\sqrt{2}\varepsilon_{Dp}}{Dp}\right)^2 + \left(\varepsilon_{RH}\frac{dGF}{dRH}\right)^2}$ , where GF is the measured growth factor

with respect to any measured RH,  $\varepsilon_{Dp}$  and  $\varepsilon_{RH}$  are the errors in the measured Dp and RH. In our system, the accuracy of DMA2 RH was maintained to be  $\pm$  1% and the uncertainty for the mobility diameter was  $\pm$  1% according to PSL (Polystyrene Latex particles) calibration. Hence, for our system,  $\varepsilon_{RH}$  and  $\varepsilon_{Dp}/Dp$  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 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 RHs. 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. Therefore, additional processes or properties, for instance, acid dissociation or phase state should be included into this model for the further improvements of its simulations.

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 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, the  $\kappa$  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."

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 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 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 as: "(B) compounds that are not fully dissolved (slightly or sparingly soluble compounds with solubility in the range between 1e<sup>-3</sup> to 3e<sup>-1</sup> g/ml or saturated regime) in the aqueous droplets under 90 % RH condition."

Line 219-220 was revised as: "Compared to these non-hygroscopic sparingly soluble organic compounds, there are some other sparingly soluble organics, showing moderate water uptake with  $\kappa$  values larger than 0.1."

Line 241 was revised as "The other 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:

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

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 as following:

$$Ke = exp\left(\frac{4\sigma_{sol}M_w}{RT\rho_w D(RH)}\right);$$
$$RH = a_w Ke;$$
$$\kappa = \frac{(GF^3 - 1)(1 - a_w)}{a_w}.$$

Also, the figures 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 & 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, the 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 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 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 schematic" 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:  $Ke = exp \left(\frac{4\sigma_{sol}M_w}{RT\rho_w D(RH)}\right)$ .

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 sentence 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 added "period" after "RH".

### 130 – "relatively higher"

Reply: We revised "relative higher" to "relatively higher".

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

Reply: The sentence was revised as: "This could be due to that the UManSysProp is a more simplified model taking into account less input data or parameterization. Therefore, additional processes or properties, for instance, acid dissociation or phase state should be included into this model for the further improvements of its simulations."

### 134 - visible how? Detectable?

Reply: The whole paragraph 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 corrected "lower RHs" to "lower RH".

#### 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 removed comma after "though".

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 made 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 whole paragraph 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 (a) sugars, (b) alcohols. 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 these sentences 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 sentence was revised as: "In this study, we plotted our measured  $\kappa$  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 this sentence 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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