Reply to Ref #3

General comments:

The authors presented detailed hygroscopic properties of Ca- and Mg-containing salts by performing both diameter and mass growth measurements using advanced instruments such as HTDMA and vapor sorption analyzer (VSA). The temperature dependences of DRH and water-to-solute rations for three specific Ca- and Mg- containing salts were also discussed based on the corresponding VSA measurements. The techniques used in this study are valid, and the obtained date sets can be served as a database for hygroscopic properties of Ca- and Mg-containing mineral dust and sea salt particles. However, more in-depth discussion and major revisions are needed. I would recommend this manuscript to be accepted after the following comments are well addressed.

Reply: We would like to thank ref #3 for his/her very positive evaluation on our manuscript and detailed comments which have significantly helped us improve the manuscript. We have addressed all the comments adequately, as detailed blow.

Major comments:

1. It is good to see some comparison results between this work and previous studies, such as CCN measurements for the same types of Ca- / Mg-containing salts. It should be noted that hygroscopic measurements in this study were mainly performed under sub-saturated conditions, while previous CCN measurements were conducted under supersaturated conditions. In this sense, how should readers understand all the compassion results of the hygroscopicity parameter, κ, between calculated in this study and derived from previous CCN measurements? How do they differ from each other, and are they really comparable? These concerns should be addressed more clearly.

Reply: Ideally aerosol-water interaction under both subsaturation and supersaturation can be described by a constant single hygroscopicity parameter; nevertheless, discrepancies have been widely reported, due to 1) solution ideality; 2) solubility limit; 3) surface tension. In the revised manuscript we have added a few sentences (line 458-468) to briefly discuss the comparability between κ_{gf} and κ_{ccn}. By doing so and referring readers to a few key references, we have provided necessary theoretical background to understand these comparisons.

Reply: This is a very good comment, and in the revised manuscript (line 635-665) we have added one section, entitled "Comparison between H-TDMA and VSA measurements", to compare the two types of results. While details can be found in our revised manuscript, here we outline our major points in brief:

1) When RH are higher than the DRH, both bulk samples used in VSA measurements and aerosol particles used in H-TDMA experiments would deliquesce to form aqueous solutions, and measured mass change and diameter change can be linked by solution densities which also depend on water activity (i.e. RH).

2) When RH are lower than DRH, the two types of results cannot be reconciled, since VSA measured the hygroscopic properties of crystalline samples while H-TDMA measured the hygroscopic growth of amorphous aerosol particles.

2. In the Experiment section, the authors have mentioned that the H-TDMA system was routinely checked with 100 nm $(NH_4)_2SO_4$ and NaCl particles. How were the H-TDMA calibration results and how did them compare with theoretical values, since the absolute uncertainty in measured RH was state to be ±2% (e.g., in Table 4)? It will be good to show some calibration results to verify the reliability of data obtained from the H-TDMA measurement. In addition, are the GF results reported in this work after data inversion, as no further detailed information has been mentioned when displaying Eq. (3) in Sect.3.1.4? What kinds of inversion algorithms were applied to the H-TDMA data? These need to be explicitly provided and well referenced.

Reply: The following changes have been made in the revised manuscript:

1) The agreement between our measurements and theoretical predictions is very good. Since technical descriptions of our H-TDMA, including its experimental validation, have been detailed in our previous studies, we choose to refer interested readers to our previous studies for further information, and we have rephrased the relevant sentence in the revised manuscript (line 454-158) to provide necessary information: "The performance of the H-TDMA setup was routinely checked by measuring the hygroscopic growth of 100 nm $(NH_4)_2SO_4$ and NaCl aerosol particles, and good

agreement between measured hygroscopic growth curves with those predicted using the E-AIM model (Clegg et al., 1998) was always found for these two types of aerosol particles, as detailed in our previous studies (Jing et al., 2016; Peng et al., 2016)."

2) The TDMAinv algorithm (Gysel et al., 2009) was applied to the H-TDMA data. In the revised manuscript (line 149-150) we have included one sentence to clarify it: "The TDMAinv algorithm (Gysel et al., 2009) was applied to the H-TDMA data."

Another issue is about the κ_{gf} results calculated from the H-TDMA measurements at 12 different RH conditions. How is the variability in derived κ_{gf} results for a specific salt, as the authors have suggested that only the corresponding κ_{gf} results at 90% RH were used for comparison with previous CCN studies?

Reply: CCN measurements are carried out at supersaturation when aerosol particles (or cloud droplets) are highly diluted droplets. H-TDMA measurements are carried out at subsaturation when aerosol particles are much more concentrated droplets, and these droplets become more diluted at higher RH. Therefore, when one wants to reconcile H-TDMA measurements with CCN measurements, growth factors measured at high RH are always used. This is why GF measured at 90% RH, instead of those at lower RH, have been used in our and many previous studies to calculate κ_{gf}, as we stated in our original manuscript.

3. How will the obtained hygroscopic data be compiled into the thermodynamic models? How to consider the crystalline reference state for those Ca- / Mg-containing sea salt or dust particles if no detailed information was available?

Reply: In the revised manuscript, we have added a few sentences (line 666-700) to discuss how our data can be used by aerosol thermodynamic models. In brief, key outputs of common aerosol thermodynamic models include RH-dependent water-to-solute ratios and volumes of solutions for RH above DRH; since both parameters were measured as a function of RH in our work, experimental data obtained in our work can be used to assess the performance of aerosol thermodynamic models. More details can be found in our revised manuscript.

For RH below DRH, indeed no detailed information is available yet regarding the crystalline state of aerosol particles investigated in our work. Since H-TDMA measurements are of direct atmospheric relevance, we suggest that for RH below DRH, H-TDMA results should be used for atmospheric applications; in addition, we have discussed which types of experiments can be used to reveal the crystalline states of aerosol particles examined in our work.

Specific comments:

Reply: Based on our observation that aerosol particles showed continuous water uptake, we concluded that these particles were likely to be amorphous. Our conclusion is also supported by a number of previous studies using vibrational spectroscopy, EDB and H-TDMA. This has been also discussed in our original manuscript (line 343-350).

Reply: To make the statement more specific, in the revised manuscript (line 57) the sentence has been changed to "Mineral dust aerosol has an average lifetime of 2-7 day in the atmosphere and can thus be transported over thousands of kilometers (Textor et al., 2006; Uno et al., 2009)."

Reply: We have included one sentence in the revised manuscript (line 153-154) to make the uncertainties in RH clear: "The absolute uncertainties in RH were estimated to be within ±2%." The stated uncertainties here took into account the RH stability in each individual experiments as well as RH reproducibility in replicate experiments.

Reply: Except for Park et al. (2009), all the other previous studies used a dry particles diameter of 100 nm. In the revised manuscript we have provided the size information.

Park et al. (2009) explored the hygroscopic growth of $CaCl_2$ and $MgCl_2$ aerosol particles at three different diameters (20, 30 and 50 nm), and no size effect was observed. In the revised manuscript we have added one sentence (line 426-428) to provide more information: "Three dry diameters (20, 30 and 50 nm) were used for $CaCl_2$ and $MgCl_2$ aerosol particles (Park et al., 2009), and no significant size dependence of their hygroscopic properties was observed."

Reply: The actual RH was measured to be <1%. In the revised manuscript (line 171) we have stated it more clearly: "after that, RH was set to 0% (the actual RH was measured to be <1%) to dry the sample again."

Page 7, line 153: How did the authors define the "significant increase" in this study? Accordingly, can you provide any specific details for the threshold value of mass change?

Reply: In our work, a significant increase in mass was considered to have occurred if the observed increase was larger than the magnitude of baseline drift. To make it clearer, in the revised manuscript (line 175) we have changed the sentence to "RH was then increased stepwise with an increment of 1% until a significant increase in sample mass (when compared to the baseline drift) was observed, and the RH at which the sample mass showed a significant increase was equal to its DRH."

4. Results and discussion, Page 8, line 164: Did the mass change here really suggest "deliquescence" or likely due to the mass increase by surface water adsorption during hydration process? This needs to be explained in the manuscript.

Reply: In the revised manuscript, at the end of this paragraph (line 191-193) we have added one sentence to further justify our claim: "Therefore, its DRH was measured to be 52.5±0.5 %. It should be noted that the mass change was >15% when RH was changed from 52 to 53%, as shown in Figure 1a; such a large mass increase cannot be caused by water adsorption."

5. Page 11, line 225: Shouldn't ΔHs reflect the change of enthalpy?

Reply: I checked the textbook by Seinfeld and Pandis (2006), and ΔHs is termed as "enthalpy of dissolution" instead of "enthalpy of solution". We have corrected it in the revised manuscript (line 258).

6. Page 12, line 238: How was the "probably a factor of >2" estimated? Any data results can be shown to verify this statement?

Reply: We have carefully considered this comment. Because the change in DRH with temperature may be insignificant, in the revised manuscript we have chosen not to report ΔH_s for $MgCl_2 \cdot 6H_2O$ because such estimation may have very large errors. In the revised manuscript, we have revised this sentence (line 266-268): "The variation of DRH values with temperature (5-30 ºC) was very small and even insignificant for $MgCl_2 \cdot 6H_2O$; as a result, we did not attempt to

estimate the ΔH_s values for $MgCl_2 \cdot 6H_2O$ using Eq. (2) since such estimation would have large errors." In addition, we have updated Table 1 accordingly.

7. Page 12, line 244: It is important to demonstrate that the measurements were conducted when particles have reached an equilibrium state under completely dry conditions before calculating the "water-to-solute ratios". Accordingly, are the m/m0 values (Table 1) at RH < DRH conditions due to hygroscopic growth or surface water adsorption during hydration?

Reply: Yes, in our work we used the mass of the sample in equilibrium to calculate water-to-solute ratios. This can be confirmed in the following two aspects: 1) in order to ensure that the equilibrium was reached, in our measurement we only changed RH to the next value when the sample mass change was <0.1% within 30 min, as explained in Section 2.2; 2) our measured water-to-solute ratios agree very well with those reported by previous work (for example, as shown in Table 2), further suggesting that equilibria were reached.

Changes in m/m_0 for RH below DRH were due to water adsorption/desorption and baseline drift, and in the revised manuscript we have added one sentence (line 275-278) to further explain it: "Small changes in m/m_0 (typically <2%) were observed for some compounds (as shown in Tables 2 and 6) when RH was below corresponding DRH values, mainly due to water adsorption/desorption and baseline drift."

8. Page 22, Eq. 4: What kinds of assumptions or simplification have been made to obtain this equation? How to understand the influences of Solute effect and Kelvin effect, since no explicitly relevant parameters were displayed in the current format?

Reply: The Kelvin effect is negligible for hygroscopic growth of aerosol particles with a dry diameter of 100 nm. In the revised manuscript (line 443-454) we have provided the original equation which takes into account the Kelvin effect and explained how Eq. (4) is derived. Please refer to the revised manuscript for details.

9. Page 23, line 419: How were the κ_{ccn} values for $Mg(NO_3)_2$ and $MgCl_2$ estimated here? What kinds of assumptions were applied into the corresponding κ calculation?

Reply: The main assumption is solution ideality. In the revised manuscript we have added one sentence (line 493-495) to clarify it: "These calculations were performed using the Köhler theory, assuming solution ideality (Kelly et al., 2007)."

10. Page 24, line 449: Where can readers find the corresponding details for the "further experiments" used in the estimation of the DRH value here? Necessary information is needed.

Reply: As suggested, in the revised manuscript we have rephrased this sentence (line 519-521) to provide necessary details: "In further experiments significant increase in sample mass was observed when RH was increased from 90 to 91% for $Ca(CH_3COO)_2 \cdot H_2O$ at 25 $^{\circ}C$, suggesting that its DRH was measured to be 90.5 ± 1.0 %."

11. Page 29, line 542; also in Conclusion section, Page 32, line 601: The authors have attributed the discrepancy between κ_{gf} and κ_{ccn} mainly to the difference in water solubility of these Ca-containing salts, however, without discussing any possible differences in the particle water uptake measurements under both sub- and supersaturated conditions.

Reply: Since this concern was also raised in Major comments #1, it has been addressed in our reply to Major comments #1. To summarize, in the revised manuscript we have added a few sentences (line 458-468) to provide necessary theoretical background to understand the comparison between κ_{gf} and κ_{ccn}.

In addition to this main concern raised in Major comments #1, how did the authors evaluate the uncertainties in calculated kgf results from H-TDMA measurements in this study, e.g., uncertainties related to GF observation, RH fluctuation, and κ_{gf} derivation?

Reply: We have taken into account the uncertainties in measured GF in calculating κ_{gf}, and in the revised manuscript (line 472-474) we have added one sentence to clarify it:"The uncertainties in our derived κ_{gf} have taken into account the uncertainties in measured GF at 90% RH."

12. Table 1: What does it actually refer to when stating "All the errors ($\pm$ 1 σ) are statistical only" in all the Tables? Are they standard deviations?

Reply: Yes, they are standard deviations. In the revised manuscript, we have change the table captions to make this clearer.

13. Table 2: The authors have declared that "WSR were only calculated for RH exceeding the DRH". According to the DRH value of $Ca(NO_3)_2 \cdot 4H_2O$ at 5 °C presented in Table 1, i.e., 60.5 ± 1.0%, does it mean that the corresponding WSR results at 50% and 60% RH in Table 2 are inaccurate?

Reply: The referee is corrected, and WSR could only be calculated for $Ca(NO_3)_2 \cdot 4H_2O$ at 5 °C when RH was >60%. We made an error when we prepared this table for the original manuscript, and in the revised manuscript we have corrected this error.

14. Table 4 and 6: GF results measured with the H-TDMA setup at different RH conditions were presented in these tables. However, the corresponding κ_{gf} results, if also shown in the tables or displayed in separate plots, would be more straightforward for readers when in comparison with previous hygroscopic results.

Reply: This is a very good point. As suggested, we have included a new table (Table 5) in our revised manuscript to compare our measured κ_{gf} with κ_{ccn} measured in previous work. We have also changed relevant discussion accordingly (please refer to Sections 3.1.4 and 3.2.2 for further details).

15. Figures 1, 3, and 5: Are the RH values shown in the y-axis corresponding to the specific RH set points or real RH conditions achieved during the experiments?

How to explain the decrease in normalized mass during 700 ~ 1,000 min in Figure 1?

How did the authors define when the particles were completely dry and the particle mass reached the lowest value, as which was applied in the normalization of particle mass with changing RH conditions? For example in Figure 3, particles didn't seem to be completely dried at ~ 4,200 min when the normalized mass was taken as 1.0.

Reply: 1) Specific RH set points were plotted in these three figures, and the difference between actual and set RH was <1%, as stated in Section 2.2. It may take several minutes (estimated using the flow rate and the chamber volume) to reach the set RH when RH was changed, and this was short because at each RH the sample was in contact with its environment for at least 30 min.

2) This small decrease in sample mass was likely due to desorption of residual water. In the revised manuscript we have added one sentence (line 193-196) to explain it: "The continuous but small decrease in sample mass (about 1% in total) with time (around 500-1000 min) before deliquescence took place, as displayed in Figure 1a, was likely caused by desorption of residual water contained by the sample under investigation."

3) When plotting these three figures, we did not always to normalize the sample mass to the dry particle mass. This is why the right y-axis in these three figures is labelled as normalized sample mass instead of m/m_0. As stated in Section 2.2, the equilibrium was considered to be reached only when the sample mass change was <0.1% within 30 min, and the data shown in Figure 3 fulfilled this criterion. For further discussion on the criterion to determine if the sample was completely dry, please refer to **our reply to Specific comment #7**.

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According to the x-axis in these figures, the time scales corresponding to a specific experiment are significantly different. Is the time taken for each experiment of the eight salts always so different? Have the authors tried to repeat these VSA experiments, and how were the replicability and corresponding uncertainties in these measurements?

Reply: The time to reach the equilibrium was largely determined by the dry sample mass (for the same compound, it took longer to reach the equilibrium if the dry sample mass was larger) and also varied with compounds. We have added one sentence (line 179-181) in the last paragraph of Section 2.2 to clarify it: "The time to reach a new equilibrium varied with compounds and was largely affected by the dry sample mass, i.e. samples with larger dry mass would took longer to reach the equilibrium."

Each VSA measurement was repeated at least three times, and the reproducibility was very good (as shown in Tables 1-2). In the last paragraph of Section 2.2, we have added one sentence (line 176-177) to clarify it: "Each measurement was repeated for at least three times, and the average value and standard deviation were reported."

16. Figures 6: How to explain the decrease trend in observed GF (i. e., GF < 1.0 at around 60~80% RH conditions) in Figure 6b? More detailed discussion should be provide in the corresponding data interpretation sections.

Reply: We believe that such a decrease may not be significant if the uncertainties in GF measurements were considered. At the end of this paragraph we have added two sentences (line 583-587) to discuss this issue: "Careful inspection of Figure 6b and Table 6 reveals that a small decrease in GF from 1.03 ± 0.01 to 1.00 ± 0.01 for $Ca(CH_3COO)_2$ aerosol when RH was increased from 50 to 70%. Since GF is typically expected to increase with RH, the small decrease in GF (~0.03) for RH between 50 and 70% may reflect the uncertainties in GF measurements (i.e. our H-TDMA measurements cannot resolve a GF difference as small as 0.03)."

Technical corrections:

Reply: We appreciate ref #3 very much for reading our manuscript very carefully and pointing out typos in our original manuscript. All the corrections have been implemented in our revised manuscript.