

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 ratios 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 data 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.

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 comparison 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.

At the same time, how is the comparison between the two types of hygroscopic growth results obtained within this study, since the authors have conducted both diameter growth and mass change measurements for the same Ca- and Mg-

containing salts? How will the particle morphology or crystalline state influence the agreement between these two types of water uptake measurements? Further discussion is needed to clarify the abovementioned points.

2. In the Experimental section, the authors have mentioned that the H-TDMA system was routinely checked with 100 nm $(\text{NH}_4)_2\text{SO}_4$ and NaCl particles. How were the H-TDMA calibration results and how did they compare with theoretical values, since the absolute uncertainty in measured RH was stated to be $\pm 2\%$ (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 measurements. 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.

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?

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?

Specific comments:

1. **Abstract**, Page 2, line 38

“All the aerosol particles studied in this work, very likely to be amorphous, started to grow at very low RH ...”

The “amorphous” statement appeared here and elsewhere in the manuscript. How was this amorphous state determined? How was it identified from the possible supersaturated droplet condition?

2. **Introduction**, Page 3, line 56

“Mineral dust aerosol has an average lifetime of a few days in the atmosphere and can thus be transported over thousands of kilometers.”

The “a few days” here is a bit confusing, as it would be inappropriate to use “a few days” if longer than weeks. How was a-few-days average lifetime estimated from the transport distance of over thousands of kilometers, and what was the average wind velocity during long-range transportation?

3. **Experimental section**, Page 6, line 132

How is the stability of RH during the H-TDMA measurements? Are the comparisons with previous hygroscopic studies (e.g., in Sect. 3.1.4) always for the same dry diameter? Is any size dependence of the measured hygroscopic properties observed in this work?

Page 7, line 150: *“...after that, RH was set to 0% to dry the sample again.”*

How was $RH = 0\%$ achieved and defined in this study? Could it be really 0, and is 0% RH appropriate for the real experimental conditions?

Page 7, line 153: *“... until a significant increase in sample mass was observed...”*

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?

4. **Results and discussion**, Page 8, line 164

“An abrupt and significant increase in sample mass was observed when RH was increased from 52 to 53%, suggesting that the deliquescence occurred between 52

and 53% RH.”

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.

5. Page 11, line 225

“... ΔH_s is the enthalpy of solution ($J mol^{-1}$)”

Shouldn't ΔH_s reflect the change of enthalpy?

6. Page 12, line 238

“... the estimated ΔH_s value for $MgCl_2 \cdot 6H_2O$ had a large uncertainty (probably a factor of >2) due to the very small dependence of its DRH on temperature.”

How was the “*probably a factor of >2* ” estimated? Any data results can be shown to verify this statement?

7. Page 12, line 244

“The mass change, relative to that at 0% RH, can be used to calculate water-to-solute ratios (WSR, ...)”

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/m_0 values (Table 1) at $RH < DRH$ conditions due to hygroscopic growth or surface water adsorption during hydration?

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?

9. Page 23, line 419

“To our knowledge, CCN activities of $Mg(NO_3)_2$ and $MgCl_2$ aerosols have not been experimentally explored yet, and κ_{ccn} were predicted to be 0.8 for $Mg(NO_3)_2$, 0.3 for $Mg(NO_3)_2 \cdot 6H_2O$, and ~ 1 for $MgCl_2$...”

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?

10. Page 24, line 449

“... the DRH value of $Ca(CH_3COO)_2 \cdot H_2O$, measured by further experiments, was determined to be 90.5 ± 1.0 % at $25^\circ C$ in our work.”

Where can readers find the corresponding details for the “*further experiments*” used in the estimation of the DRH value here? Necessary information is needed.

11. Page 29, line 542

“... This is largely caused by the difference in water solubilities of $Ca(NO_3)_2$, $CaCl_2$, $Ca(HCOO)_2$ and $Ca(CH_3COO)_2$.”

Also in **Conclusion section**, Page 32, line 601

“ $Ca(NO_3)_2$ and $CaCl_2$ are very soluble in water, and thus their κ values derived from our H-TDMA experiments are consistent with those reported by previous CCN activity measurements (Sullivan et al., 2009; Tang et al., 2015); on the other hand, due to limited water solubilities, for $Ca(HCOO)_2$ and $Ca(CH_3COO)_2$, κ values derived from our H-TDMA experiments are significantly smaller than those derived from CCN activities measured in a previous study (Tang et al., 2015).”

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

12. **Table 1**

What does it actually refer to when stating “*All the errors ($\pm 1 \sigma$) are statistical only*” in all the Tables? Are they standard deviations?

13. **Table 2**

The authors have declared that “*WSR were only calculated for RH exceeding the DRH*”. According to the DRH value of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ at 5 °C presented in Table 1, i.e., $60.5 \pm 1.0 \%$, does it mean that the corresponding WSR results at 50% and 60% RH in Table 2 are inaccurate?

14. **Tables 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.

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.

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?

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 provided in the corresponding data interpretation sections.

Technical corrections:

1. Abstract, Page 2, line 40

“... were found to range from 1.26 ± 0.04 for $\text{Ca}(\text{HCOO}_2)_2$ and 1.79 ± 0.03 for $\text{Ca}(\text{NO}_3)_2$...”

2. Introduction, Page 4, line 72

*“... CaCl_2 from heterogeneous reactions with **nitrogen oxides** (Goodman et al., 2000; Liu et al., 2008a; Li et al., 2010; Tang et al., 2012; Tan et al., 2016) and **HCl** (Santschi and Rossi, 2006)”*

It seems that different expression formats were randomly used for the chemical species mentioned in this manuscript. Similar issues can be found elsewhere.

3. Sect. 3.1.4, Page 20, line 365

*“In the second study (Jing et al., 2018), GF were determined to **be** 1.56 and 1.89 at*

80 and 90% RH.”

Page 23, line 414

“2) For CaCl_2 aerosol, ~~κ_{eff}~~ κ_{ccn} were measured to be 0.46-0.58...”

4. **Sect. 3.2**, Page 24, line 436

“The average ratio of sample mass at 95% RH to that at 0% RH~~;~~ was determined to be ~~for~~ 1.043 ± 0.018 for $\text{Ca}(\text{HCOO})_2$ and 1.028 ± 0.008 for $\text{Mg}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ (not shown in Figure 5), probably indicating that the DRH values were >95% for both compounds at 25 °C.”

5. Page 25, line 462

“The RH over the saturated $\text{Mg}(\text{CH}_3\text{COO})_2$ solution at ~ 23 °C was measured ...”

Please check all the units carefully throughout the manuscript.

6. Page 26, line 480

“Table 5 also reveals that a small increase in sample mass (by $\sim 3\%$, relative to that at 0% RH) was observed for $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ when RH was increased to 70% before *its* deliquescence occurred.”

It is better to clarify “its” here.

7. **Conclusion section**, Page 30, line 560

“In this work, phase transition and hygroscopic growth of *these eight* compounds were systematically examined ...”

The “these eight” here might be unclear to readers if without specific introduction in advance.