

Comments by Referees are in blue.

Our replies are in black.

Changes to the manuscript are highlighted in red both here and in the revised manuscript.

General comments:

Based on the HTDMA and VSA measurements, this work has reported a large dataset of hygroscopicity of Ca- and Mg-containing samples, and discussed the temperature-dependence of DRH values. The calculated κ results were comparable to those of previous hygroscopic studies. This can enrich the knowledge of water uptake by Ca- and Mg-containing mineral dust and sea salts in the troposphere. The quality of this manuscript could be largely improved, providing a better organization of the main contents with clearer and more concise descriptions. A native or professional speaker is recommended for the language revision including a thorough grammar check. The presented work has its scientific importance, while major revision is suggested before the final publication.

Reply: We would like to thank ref #3 for reviewing our manuscript. His/her comments have been carefully addressed in our revised manuscript, as detailed below. In addition, we have asked a professional editor to edit our manuscript thoroughly.

Specific comments:

1. Page 8, line 175: The authors have suggested a “baseline drift” for the determination of the mass growth factor, or rather the DRH value. However, it is confusing to readers that how “a significant increase in sample mass” was defined. What is the corresponding reference value for the investigated salts? Does the baseline drift in sample mass always correspond to a same value for different types of Ca- and Mg- containing samples?

Reply: Here we state that the DRH was RH at which a significant increase in sample mass occurred. The mass measurement was affected by signal noise and baseline drift; only when the mass increase was significant when compared to signal noise and baseline drift, the mass increase was due to the occurrence in deliquescence. As shown in Figure 1a for example, when RH was increased from 52 to 53%, the mass was increased by 15% and was still increasing; for comparison, the baseline drift was <2%. Therefore, we concluded that deliquescence occurred at 52-53% RH.

2. Page 8, line 176: Experiments are repeatable, but how “each measurement” could be repeated?

Reply: As suggested, in the revised manuscript (page 8, line 176) we have changed “measurement” to “experiment”.

3. Page 8, line 180: It is unclear that when did “an equilibrium” or “a new equilibrium” state actually reach during the experiments, at least it is difficult to tell from the corresponding figures, e.g., it is still able to expect some increase in the sample mass as displayed in Fig. 5. In addition, the determination of an equilibrium condition will directly influence the accuracy of water-to-solute ratio, mass growth factor, and DRH results reported in this work. In this sense, how to quantify the influence of this “equilibrium” state on measured change in m/m_0 or in normalized sample mass with varying RH, and further on DRH and comparison of different hygroscopic results?

Reply: As we stated in the original manuscript (page 8, line 177-179), an equilibrium was reached when the mass change was <0.1% in 30 min; nevertheless, the time required to reach an equilibrium varied in different experiments, depending on RH, sample mass, and compounds under investigation. Indeed the mass was still increasing in Figure 5a. However, the total mass change was very small (by ~3%) because the hygroscopicity of $\text{Ca}(\text{HCOO})_2$ was very low, and further increase in mass, given enough time, is expected to be very small.

Since an equilibrium was only reached when the mass change was $<0.1\%$ in 30 min, we expect that m/m_0 has an uncertainty of $\sim 0.1\%$ or even smaller, and such uncertainty was negligible for deliquesced samples. WSR values measured in this and our previous work (Gu et al., 2017a; Gu et al., 2017b; Jia et al., 2018) agree well with those reported by others for a number of compounds, further suggesting that our criterion used to judge whether an equilibrium was reached (as well as our experimental method) is robust.

4. Page 9, line 188: Following the comment #3, there is no definition of “normalized sample mass”, which is also important for the determination of DRH. I feel lost in the authors’ response to Specific comment #15 of Ref #3, which explained that “When plotting these three figures (i.e., Figs. 1, 3, and 5), 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 .” How to quantify the change in sample mass accurately, if the “normalized sample mass” was not always normalized by the initial dry mass? Accordingly, which kinds of mass were used for the normalization if “not always” to normalize, and how should the readers evaluate the comparability among these normalized sample mass results with increasing RH if without a constant comparison standard/baseline in the same experiment?

Reply: When we plot the figures, we do not always normalize the sample mass to the dry particle mass; in fact, when we show the change of RH and sample mass with time, we can even present the actual sample mass without any normalization.

We agree with the referee that it is vital to normalize the sample mass to its dry mass if we want to quantify the change in sample mass due to water uptake. It is why we always normalized the sample mass to its dry mass (i.e. m/m_0), as we explained in the original manuscript (Tables 2, 3 and 6), when we calculate the change in sample mass.

5. Page 9, line 193: The authors have stated that “such a large mass increase cannot be solely caused by water adsorption”. Why? Can you provide some clues or evidence to clarify this point, instead of making an assertion without any proof?

Reply: In the revised manuscript (page 9, line 193-194) we have added one sentence to clarify our claim: “such a large mass increase cannot be solely caused by water adsorption, since the mass of several monolayers of adsorbed water is estimated to be $<1\%$ of the dry particle mass (Gu et al., 2017b).”

6. Page 12, line 227: Is the corresponding RH determined to be $57\pm 5\%$? Accordingly, can you really tell that they are “in broad consistence with” the results reported in this work?

Reply: Yes, the DRH was determined to be $57\pm 5\%$, and it is more accurate to state that this value is slightly larger than that reported in our work. The following change was made in our revised manuscript (page 12, line 228-230): “In another study (Al-Abadleh et al., 2003), RH over the saturated $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution was measured to be $57\pm 5\%$ at room temperature; in other words, Al-Abadleh et al. (2003) reported a DRH of $57\pm 5\%$ for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, slightly larger than that ($49.5\pm 1.0\%$ at $25\text{ }^\circ\text{C}$) determined in our work.”

7. Page 12, line 242: In the expression of “could have unknown systematical errors”, I was confused by the “unknown” here, as this sentence was supposed to provide the specific reasons. Besides, why can you assume that it is due to systematical errors if it’s even unknown?

Reply: Since the values reported by Apelblat (1992) are always larger than those reported by other studies, we suspect that the measurements by Apelblat (1992) may have some systematical errors; nevertheless, the exact reason is not clear. Therefore, we stated in the original manuscript “This may imply that water vapor pressure measurements by Apelblat (1992) could have unknown systematical errors.”

8. Page 14, line 275: “Small changes in m/m₀ (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.” This sentence sounds somewhat ambiguous. What does the “small changes” refer to, the increase or decrease in mass change? How to relate the small mass change with the corresponding causes, i.e., water adsorption, water desorption, and baseline drift?

Reply: To response to this comments, in the revised manuscript (page 14, line 277) we have changed “small changes” to “small increases” to make it more precise. The small mass increase (typically <2%) occurred before deliquescence, very likely due to water adsorption and baseline drifts.

9. Page 16, line 296: “Water activities of Ca(NO₃)₂ solutions at 25 °C were measured to be 0.904, 0.812 and 0.712 when the concentrations were 2.0, 3.5 and 5.0 mol kg⁻¹, respectively.” The results might be wrongly sequenced in either RH values or molality concentrations, as which are opposite to the corresponding details included in the following sentence. To avoid such mistakes, please also check for the Mg(NO₃)₂ sample and data results elsewhere carefully.

Reply: The RH values were incorrectly sequenced in the original manuscript, and it has been corrected in our revised manuscript (page 16, line 301). We have also carefully checked data elsewhere.

10. Page 16, line 297: Please confirm the physical meaning of “water activity” and “RH of air”.

Reply: Water activity and RH are both basic parameters in aerosol hygroscopicity, and we feel these two terms do not need further explanation for readers interested in our manuscript.

11. Page 18, line 330: How was the mass increase (i.e., 48±7%) determined here, which seemed not reflected in Fig.3? What is the baseline drift or reference mass value used for the normalization of sample mass?

Reply: As shown in Figure 3, when RH was increased from 0% to 20%, the normalized sample mass was increased from 1 to ~1.5; therefore, the mass was increased by ~50% (48±7%, more exactly).

12. Page 24, line 430: Try to rephrase the whole sentence starting with “For comparison” into a more concise one, so does the beginning sentence in the following paragraph. This will help the readers to catch the point more easily.

Reply: We believe that it is necessary to provide exact values reported by the two studies in the comparison so that the readers would know the details. Nevertheless, as suggested by the referee, in the revised manuscript (page 24, line 432) we have rephrased these two sentences to further increase the readability.

13. Page 24, line 443: In the section of “Comparison between hygroscopic growth with CCN activities”, equations used for the κ_{gf} calculation and relevant details belong to theoretical methodologies other than observed results. It would make more sense to reorganize the corresponding contents, e.g., into the Experimental section.

Reply: We agree that some of this section can be moved into the experimental section. Nevertheless, this section is the first place where we introduce κ values and in this section we also discuss the assumptions/caveats used in κ_{gf} calculation; therefore, we believe that it is also suitable to leave details related to κ_{gf} calculation in this section.

14. Table 5: Corresponding references are needed for “previous studies”.

Reply: In this table when we use κ values reported by previous studies, we cite the corresponding references. Therefore, it is not necessary to cite these references in the table caption.

15. Page 28, line 519: How much does the “significant increase” refer to?

Reply: To make it more clearer, in the revised manuscript (page 28, line 523) we have expanded the sentence to “In further experiments significant increase in sample mass (by >10%, and the sample was still increasing sharply when the experiment was terminated) was observed when RH was increased from 90 to 91% for $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ at 25 °C,”

Line 521: Why is the DRH determined to be $90.5 \pm 1.0\%$ instead of $\pm 0.5\%$? A similar issue existed in Line 533: “giving a measured DRH of $71.5 \pm 1.0\%$ ”. Please also have a check on the corresponding values such as in the Conclusion section.

Reply: Our RH measurements have an uncertainty of $\pm 1.0\%$, as stated in Section 2.2; therefore, we believe that the uncertainty of our measured DRH values should be $\pm 1.0\%$ or larger.

16. Page 32, line 585: The last sentence is really confusing. What is the connection between “GF is typically expected to increase with RH” and “small decrease in GF (~ 0.03) for RH between 50 and 70% may reflect uncertainties in GF measurements”? What kinds of uncertainties in GF measurements are you trying to suggest? What is the possible influence of particle phase state on measured growth factors? Besides, what does it mean that “HTDMA measurements cannot resolve a GF difference as small as 0.03”, since the presented GF results (i.e., 1.03 ± 0.01 and 1.00 ± 0.01) were actually measured with HTDMA and the uncertainties in the corresponding GF values are as small as ± 0.01 ? A more scientific/convincing explanation for this observed decrease in GF will need to be provided.

Reply: We agree with the referee that the decrease in GF may be related to particle phase state, and more specifically, caused by change in particle morphology (i.e. particle restructuring); in addition, the small change in GF (~ 0.03) may not be significant compared to the uncertainties in H-TDMA measurements, and the uncertainty (~ 0.01) in our reported GF is only the statistical error for three repeated experiments. In response to this comment, we have changed this sentence in the revised manuscript (page 32, line 589-592) to “The decrease in GF may be caused by restructuring of particles or change in particle morphology (Vlasenko et al., 2005; Koehler et al., 2009); in addition, the small change in GF (~ 0.03) may not be significant when compared to the uncertainties in our H-TDMA measurements.”

17. Page 34, line 635: This Sect.3.3.1 was designed to compare the hygroscopicity results between HTDMA and VSA measurements. However, the organization of the whole section was a bit misleading. It seems that only one sentence is directly related to the topic (i.e., “To directly link the mass change (measured using VSA) with diameter change (measured using H-TDMA), solution densities, which also vary with RH, are needed.”). I didn’t see more details about how these two types of growth factors were actually reconciled. Although the authors have tried to explore the atmospheric relevance of their experimental results (e.g., applicability to the conditions when RH is below or exceeds DRH), it’s important to distinguish the difference in hygroscopicity for both bulk powder samples and individual particles. For clearer clarification, such information might be necessary before detailing the corresponding water uptake results.

Reply: We feel this section is well-organized, as described below: 1) in the first paragraph, we provide necessary background needed to compare two types of measurements; 2) in the second paragraph, we compare the two types of measurements for RH above the DRH; 3) in the third paragraph, we compare the two types of measurements for RH below the DRH.

As pointed out by the referee, it is important to distinguish the two types of samples, and in fact this aspect has been emphasized in our original manuscript (e.g., Section 3.3.1 and elsewhere). Line 662-663: This sentence is confusing. Whether is it suggesting a possible way for the future investigations of the particle phase state with changing RH, or is it trying to answer the open

question with the results obtained from previous studies? Then what is the conclusion or possible answers to the question according to previous work?

Reply: This sentence is to suggest a possible way for future investigation, and Li et al. (2017) presented a method which can be used to measure particle phase state. In the revised manuscript (page 36, line 668) we have rephrased this sentence to make it more clear: “In this aspect, measurements of particle phase state of $\text{Ca}(\text{NO}_3)_2$ and other aerosols considered in our work, using the apparatus described previously (Li et al., 2017), can shed some light.”

A similar issue also exists in the last two sentences of this section. Haven't you already measured the water-to-solute ratios and mass growth factors in this study? Why not trying to address the question using your own experimental data?

Reply: When RH is above the DRH of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2$ aerosol particles are deliquesced and their WSR were measured in this work; however, when RH is below the DRH of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, we do not know the WSR for $\text{Ca}(\text{NO}_3)_2$ aerosol particles. In the revised manuscript (page 36, line 669-670), we have expanded this sentence to make it more clearer: “Furthermore, how do water-to-solute ratios change with RH for $\text{Ca}(\text{NO}_3)_2$ aerosol particles when RH is below the DRH of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$?”

References:

- Gu, W. J., Li, Y. J., Zhu, J. X., Jia, X. H., Lin, Q. H., Zhang, G. H., Ding, X., Song, W., Bi, X. H., Wang, X. M., and Tang, M. J.: Investigation of water adsorption and hygroscopicity of atmospherically relevant particles using a commercial vapor sorption analyzer, *Atmos. Meas. Tech.*, 10, 3821-3832, 2017.
- Gu, W. J., Li, Y. J., Tang, M. J., Jia, X. H., Ding, X., Bi, X. H., and Wang, X. M.: Water uptake and hygroscopicity of perchlorates and implications for the existence of liquid water in some hyperarid environments, *RSC Adv.*, 7, 46866-46873, 2017.
- Jia, X. H., Gu, W. J., Li, Y. J., Cheng, P., Tang, Y. J., Guo, L. Y., Wang, X. M., and Tang, M. J.: Phase transitions and hygroscopic growth of $\text{Mg}(\text{ClO}_4)_2$, NaClO_4 , and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$: implications for the stability of aqueous water in hyperarid environments on Mars and on Earth, *ACS Earth Space Chem.*, 2, 159-167, 2018.