

Comments by Referees are in blue.

Our replies are in black.

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

### **Reply to Ref #1**

#### **General comments:**

The authors presented a comprehensive study of the hygroscopic properties of calcium- and magnesium- containing salts using a vapor sorption analyzer and a HTDMA. The change of sample mass with RH and the corresponding DRH value was reported for these eight compounds together with their hygroscopic growth factor values at 90% RH. The dataset is rich, however, the comparison and discussion is not sound that major revisions are needed. The manuscript may be acceptable for publication in ACP after the following concerns are fully addressed.

**Reply:** We would like to thank Ref #1 for his/her insightful and detailed comments, which have largely helped us improve our manuscript. We have addressed all the comments adequately in the revised manuscript, as detailed below.

#### **Major comments:**

1. This work used a vapor sorption analyzer to measure the change of sample mass with relative humidity and the deliquescence relative humidity of eight different compounds. However, as I understand, the materials the author used in this study are not atmospheric particles, but actually bulk samples. Please clarify how these results represent atmospheric conditions. The hygroscopic properties and DRH of aerosol particles would probably deviate significantly from that of bulk samples. Please extend your manuscript with explicit discussions regarding these issues to prove the significance for atmospheric research.

**Reply:** In addition to this comment (major comment #1), similar concerns have been raised in a few other comments (including major comment #2, part of major comment #3, major comment #4, and specific comment #12) regarding the atmospheric relevance of our VSA results and the comparison between the VSA and H-TDMA measurement. In response to these comments, we have added one section (Section 3.3.1, line 635-665), entitled “**Comparison between H-TDMA and VSA measurements**”. Here we response to these comments and also outline changes implemented in the revised manuscript.

1) Indeed bulk samples, instead of aerosol particles, were used in our VSA experiments. However, thermodynamic principles which govern the equilibrium between water vapor and liquid water in the aqueous solutions are the same for bulk samples and atmospheric particles (we note that particle size may play a role for aerosol particles due to the Kelvin effect, while bulk samples have flat surfaces). More specifically, when RH are higher than DRH, bulk samples (as well as aerosol particles) would be deliquesced to form aqueous solutions, and the water-to-solute ratios would depend on RH. Water-to-solute ratios measured in our work for aqueous solutions formed from the eight compounds, can be used to validate aerosol thermodynamic models which are widely employed to predict aerosol hygroscopicity based on aerosol chemical composition, measured or prescribed.

2) For RH above the DRH, both bulk samples and aerosol particles would become deliquesced to form aqueous solutions; at a given RH, the two types of solutions would have the same concentrations. VSA measured the mass of aqueous solutions while H-TDMA measured the diameter (which could be used to calculate the volume), and therefore the two types of results can be related to each other via solution densities, which also depend on RH. In addition, diameter changes measured by H-TDMA can also be used to validate aerosol thermodynamic models, which can be used to calculate the RH-dependent volume of aerosol particles.

3) When RH is below the DRH, discrepancies are found for the two types of measurements. This is because bulk samples and aerosol particles are of different crystalline state under dry conditions, as we discussed in our original manuscript. For this RH range, H-TDMA results should be used for atmospheric implications since aerosol particles used in H-TDMA measurements are of direct atmospheric relevance. However, the states of aerosol particles at RH below DRH (i.e. before full deliquescence) remain largely unknown. In the revised manuscript ([line 656-665](#)) we have outlined relevant remaining open questions and discussed how they can be addressed in future work.

2. What is the relation between the mass growth factor and mobility growth factor as measured by two independent methods? Extensive works have been performed to measure the hygroscopic growth factor of atmospheric relevant compounds from previous studies. How to compare the mass growth factor obtained by the vapor sorption analyzer with their results and what kind of uncertainties should be taken into account?

**Reply:** In our reply to major comment #1, we have also addressed major comment #2 together. We would kindly refer the reviewer to our reply to major comment #1 for further information.

3. The DRH values of these studied compounds can also be measured by your HTDMA setup. Why the results obtained by your HTDMA did not agree with the ones from the VSA. What is the explanation for the discrepancies? Since the VSA measures the bulk samples, are these results obtained from the VSP measurements applicable in atmospheric research? Could you also please plot the GF-PDF for each compounds measured by the HTDMA? Are there unimode or bimode for your growth factor distributions at different RHs?

**Reply:** 1) The difference in these two types of experiments can be explained by the fact that samples used in the two types of experiments were of different state: samples used in VSA measurement were crystalline, while aerosol particles used in H-TDMA experiments were amorphous. Explanations and discussions have been provided in our original manuscript (line 342-350, page 19, Section 3.1.4; line 488-499, page 26-27, Section 3.2.2); in addition, we have also added a few sentences (line 643-647) in the revised manuscript to further explain such difference and to underscore such differences.

2) Since major comments #1 also raised similar concerns on the atmospheric relevance of our VSA measurements, please refer to our reply to major comment #1 for further details of our discussion on the atmospheric relevance of our VSA results.

3) The size distribution of aerosol particles at different RH are unimode. In the supplementary information of revised manuscript we have provided the size distribution of  $\text{Ca}(\text{NO}_3)_2$  at three RH as an example to illustrate it, since we feel it is not necessary to plot the size distributions for all the eight types of aerosol we studied. In addition, in the revised manuscript we have added one sentence (line 146-149) to summarize the main point regarding size distributions: “Size distributions of all the eight types of aerosol particles, measured using the SMPS, were found to be unimode, as illustrated by Figure S1 (in the supplementary information) in which size distributions of  $\text{Ca}(\text{NO}_3)_2$  aerosols at 4, 50 and 90% RH are displayed as an example.”

4. For the inorganic species you studied, you stated they are important components in mineral dust or sea salt particles. However, for the VSA measurements, you studied their hygroscopic properties of their hydrate forms, while you measured the HGF of these compounds in their anhydrous state using HTDMA. As I see, the hygroscopic properties of these compounds vary significantly

between their anhydrous states and hydrate states (for instance, line 420-421). I feel difficult to relate your results with your introduction and objectives. Which state exist in the real atmosphere? Moreover, which state is hygroscopic and which values should we use for further study? Please clarify and be consistent through your whole manuscript. Otherwise, give your explanations.

**Reply:** In our reply to major comment #1, we have also addressed major comment #4 together. We would kindly refer the reviewer to our reply to major comment #1 for further information.

5. For your conclusion part, it is more like a summary of your results without any atmospheric implications. Please rephrase it and highlight its atmospheric applications.

**Reply:** We fully agree with the referee. In the revised manuscript we have changed the title of Section 4 to “**Summary and Conclusion**”, since this section is more like a summary of our work; furthermore, we have added a new section (Section 3.3.2, line 666-700), entitled “**Atmospheric implications**”, to discuss the atmospheric implications of our work. Please refer to Section 3.3.2 in the revised manuscript for details.

#### **Specific comments:**

1. Line 93-97: These two statements are in conflict with each other.

**Reply:** In the revised manuscript we have rephrased these two sentences (line 98-102) to make what we mean clearer: “However, only a few previous studies explored hygroscopic growth of  $\text{Mg}(\text{CH}_3\text{COO})_2$  and  $\text{Ca}(\text{CH}_3\text{COO})_2$ , **using techniques based on bulk samples** (Wang et al., 2005; Ma et al., 2012; Pang et al., 2015). To our knowledge, hygroscopic growth factors have never been reported for  $\text{Ca}(\text{HCOO})_2$ ,  $\text{Mg}(\text{HCOO})_2$ ,  $\text{Ca}(\text{CH}_3\text{COO})_2$  and  $\text{Mg}(\text{CH}_3\text{COO})_2$  aerosol particles.”

2. Line 128-131: How long is your humidifier and what is the flow rate? And what is the accuracy of your RH measurements, please give its uncertainty.

**Reply:** The flow rate was 300 mL/min, and the residence time in the humidification section was ~27 s, and the accuracy in RH measurement was  $\pm 0.8\%$ . In the revised manuscript, we have provided flow rate information (line 127-128): “After exiting the atomizer, an aerosol flow (**300 mL/min**) was passed through a Nafion dryer...” as well as information on the humidifier and RH measurement (line 131-135): “...the aerosol flow was transferred through a humidification section with a residence time of ~27 s to be humidified to a given RH. **The humidification section was made of two Nafion humidifiers (MD-700-12F-1, Perma Pure) connected in series. The RH of the**

resulting aerosol flow was monitored using a dew-point meter, which had an absolute uncertainty of  $\pm 0.8\%$  in RH measurement as stated by the manufacturer (Michell, UK). After humidification...”

3. Line 139: What do you mean by a particle sample? Did you generate particles and measure the mass of these particles? If not, please rephrase it.

**Reply:** Samples used in the VSA experiments were bulk samples, which can be powdered particles or small crystalline grains. In the revised manuscript (line 160) we have changed “a particle sample” to “a bulk sample” to be more accurate.

4. Line 210-211: What is the possible reason for the deviations?

**Reply:** Since all the other studies agree very well, and the results reported by Apelblat (1992) are always 3-5% higher. This may suggest that the study by Apelblat (1992) could have unknown systematical error. In the revised manuscript we have added one sentence (line 241-242) to explain the possible reason for this deviation: “This may imply that water vapor pressure measurements by Apelblat (1992) could have unknown systematical errors.”

5. Line 222-223: Give proper reference for Eq. 1 in your manuscript, the original source but not only these who also cites it. In addition, which solubility (at which temperature condition) you used for your calculation, as it also depends on temperature.

**Reply:** 1) In the revised manuscript (line 255), we have cited two additional references (Wexler and Seinfeld, 1991; Seinfeld and Pandis, 2006) which detailed the process to derive this equation.

2) For this equation to be valid, the solubility and the enthalpy of dissolution are assumed to be constant for the temperature range considered. In the revised manuscript we have added one sentence (line 264-266) to clarify it: “It should be noted that for Eq. (2) to be valid, both the enthalpy of dissolution and the water solubility are assumed to be constant for the temperature range considered.”

6. Line 225: Enthalpy of what? Deliquesce or dissolution?

**Reply:** It should be “enthalpy of dissolution”. We have changed it in the revised manuscript (line 258).

7. Line 246: Could you give proper explanation why WSR increase with a decreasing in temperature.

**Reply:** This is because the dissolution processes are exothermic. In the revised manuscript (line 281-285), we have added one sentences to explain such dependence: “As discussed in Section

3.1.1, the enthalpies of dissolution ( $\Delta H_s$ ) are negative for these compounds, suggesting that their dissolution processes in water are exothermic; therefore, dissolution is favored at lower temperatures and at a given RH, decrease in temperature would lead to increase in WSR in the aqueous solutions.”

8. Line 253, Table 2: How could you get the WSR value for  $\text{Ca}(\text{NO}_3)_2$  at 50% RH, as it did not deliquesce yet according to your previous results in Table 1 (DRH as 60.5%).

**Reply:** The referee is right. We made an error when we calculated WSR for  $\text{Ca}(\text{NO}_3)_2$  at 5 °C, and in fact at 5 °C we could calculate WSR for RH at or above 70%. In the revised manuscript we have corrected this error.

9. Line 258-261: I don't understand the sentences.

**Reply:** In the revised manuscript (line 297-299), we have expanded these sentences to provide further explanation and to increase the readability: “Water activities of  $\text{Ca}(\text{NO}_3)_2$  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  $\text{kg}^{-1}$ , respectively (El Guendouzi and Marouani, 2003). Since water activity of a solution is equal to the RH of air in equilibrium with the solution, it can be derived that the molality concentrations of  $\text{Ca}(\text{NO}_3)_2$  solution were 2.0, 3.5, and 5.0 mol  $\text{kg}^{-1}$  when RH was 71.2, 81.2 and 90.4%; in other words, WSR were found to be 11.1, 15.9 and 27.8 at 71.2, 81.2 and 90.4 % RH, respectively (El Guendouzi and Marouani, 2003).”

10. Line 265: What concentration do you mean here? Bulk solution or droplet? Please be specific.

**Reply:** To be more specific, in the revised manuscript (line 305) we have changed “...the concentrations...” to “...the concentrations of the bulk solutions...”.

11. Line 286: Did you also observe similar phenomena for the other two inorganic compounds for phase transition, as it seems to be according to Fig. 1 in your manuscript.

**Reply:** For compounds investigated in our work, solid-solid phase transition was only observed for  $\text{CaCl}_2$ .

12. Line 311-312: I don't think this is fairly new result as it is still bulk sample. We should always consider size effect as it is atmospheric or at least particle-relevant.

**Reply:** Regarding to our response to this comment, please refer to our reply to major comment #1 for further information.

13. Line 337: What is the stuff after atomizing? Are they in hydrate state or not?

**Reply:** These aerosol particles, generating by atomizing water solutions, are likely to be amorphous. This was explained in line 343-350 in the original manuscript.

14. Line 363-365 and line 379-382: So should we use the dry diameter selected by the DMA (100 nm) or not. If yes, it seems your results did not agree with the ones from Gibson et al., (2006) in line 363-365, but agreed in line 379-382. Please clarify.

**Reply:** We believe the dry particle diameter (100 nm) should be used to calculate GF measured by Gibson et al. (2006); and if used, our results show relative good agreement with them. In the revised manuscript we have rephrased relevant sentences (line 401-409) to make it clearer: “If the dry diameter selected using the DMA (i.e. 100 nm) was used for calculation instead, GF reported by Gibson et al. (2006) would be ~1.34 at 80% RH and ~1.58 at 85% RH; **compared with our results (1.51±0.02 at 80% RH and 1.62±0.01 at 85% RH), GF reported by Gibson et al. (2006) are ~11% smaller at 80% RH and only ~3% smaller at 85%.** In the second study (Jing et al., 2018), GF were determined to be 1.56 at 80% RH and 1.89 at 90% RH; **compared with our results (1.51±0.02 at 80% RH and 1.79±0.03 at 90% RH), GF reported by Jing et al. (2018) were ~3% larger at 80% RH and ~6% larger at 90% RH.** Overall, our results show reasonably good agreement with the two previous studies (Gibson et al., 2006; Jing et al., 2018).”

15. Extra cautions must be taken by introducing several scientific terms in the manuscript. For instance, in line 221-223. What is the scientific reason to study the temperature-dependence of DRH and its enthalpy value? Please clarify. For instance, in line 258-263, why you studied the water-solute ratio and what is this variable used for? What is the relation between water activity and water-solute ratio? And how you converted it to each other in details?

**Reply:** In the revised manuscript we have added one sentence (line 252-253) to clarify the scientific reason to study temperature dependence of DRH values: “Temperature in the troposphere varies from ~200 to >300 K, and it is thus warranted to explore the effects of temperature on hygroscopic properties of atmospherically relevant particles.”

The water activity of a solution with flat surface is equal to the RH of the air in equilibrium with the solution; therefore, if we know the water to solute ratios as a function of water activity, we can calculate water to solute ratios of aerosol particles and aerosol water content as a function of RH. We have added one new section (Section 3.3, line 634-700) in the revised manuscript, entitled “**Discussion and atmospheric implication**”, to further discuss our experimental results and

their atmospheric implications. Please refer to Section 3.3 in the revised manuscript for more details.

16. Which particle size did you selected during the HTDMA measurements? In Eq. 4 in your manuscript, where is the Kelvin term? Please use the correct formulation and make further comparison. For instance, in line 410-411, which particle size or which supersaturation they selected in their CCN measurements?

**Reply:** The mobility diameter of dry aerosol particles selected using the first DMA was always 100 nm, and in Section 2.2 of the revised manuscript, we have added one sentence (line 145-146) to clarify it.

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.

The dry particles sizes were in the range of 50-125 nm, and in the revised manuscript we have added one sentence (line 471-472) to provide relevant information: “**In previous work which measured CCN activities measured (Sullivan et al., 2009; Tang et al., 2015; Gaston et al., 2017), the dry particle diameters used were typically in the range of 50-125 nm.**”

17. In addition, please rephrase your discussion part and make sound comparisons with the other studies. For instance, line 367-368, GF of  $\text{Ca}(\text{NO}_3)_2$  aerosols was measured to be 1.79 in your work, while Jing et al., (2018) reported it to be 1.89 at 90%RH. In line 387-389, Park et al., (2009) measured the GF of  $\text{CaCl}_2$  to be 1.59 at 90% RH and the measured value from your result was 1.71. There were some differences (around 7%) but not always in good agreement as you stated in the manuscript between your results and the ones from others. Please give proper discussions.

**Reply:** As suggested, in the revised manuscript we have rephrased our discussion when comparing our results with previous work, to make our statement more precise. For example, when comparing our measurement with the two previous studies for hygroscopic growth of  $\text{Ca}(\text{NO}_3)_2$  aerosol particles, the discussion (line 401-409) has been changed to: “If the dry diameter selected using the DMA (i.e. 100 nm) was used for calculation instead, GF reported by Gibson et al. (2006) would be  $\sim 1.34$  at 80% RH and  $\sim 1.58$  at 85% RH; **compared with our results ( $1.51 \pm 0.02$  at 80% RH and  $1.62 \pm 0.01$  at 85% RH), GF reported by Gibson et al. (2006) are  $\sim 11\%$  smaller at 80% RH and only  $\sim 3\%$  smaller at 85%.** In the second study (Jing et al., 2018), GF were determined to be



1.56 at 80% RH and 1.89 at 90% RH; compared with our results (1.51±0.02 at 80% RH and 1.79±0.03 at 90% RH), GF reported by Jing et al. (2018) were ~3% larger at 80% RH and ~6% larger at 90% RH. Overall, our results show reasonably good agreement with the two previous studies (Gibson et al., 2006; Jing et al., 2018).”