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Reply on RC1

Hoang Duong Do et al.

Author comment on "Water uptake and the gas-particle partitioning of nitrate aerosols" by
Hoang Duong Do et al., Atmos. Chem. Phys. Discuss.,
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Our responses are written in bold. Changes made in the manuscript according to referee's comments are indicated in red. Thank you for reviewing our paper. Some of referee's comments are helpful. But we feel that all of experiments and discussions were not fully reviewed. The referee focuses on reviewing the section 3.1, 3.2, and 4 (line 301-302 and 310-311) while our key findings are discussed in the section 3.3 and 3.4. Besides, most of our key points seem to be misinterpreted. Therefore, we would like to take this opportunity to clear our points and arguments in this paper, so we can provide a better understanding of our work to the referee.

This paper investigates through H-TDMA experiments the uptake of water onto pure ammonium sulfate and ammonium nitrate particles, mixtures of the two, and then with an added organic species (glyoxal). The experimental data are compared to two thermodynamic models, ISORROPIA and E-AIM.

The paper claims to identify three issues with thermodynamic models:

- *They do not consider the period when a particle may have not yet reached the DRH and so the particles are dry, but most thermodynamic models are run in the metastable mode which assumes the particles are deliquesced. (See comment below on applicability of experiments to the real atmosphere; whether particles are ever dry in the ambient atmosphere and stable mode applies).*
- *They do not correctly predict DRH for mixtures. (If particles are always deliquesced, is this still a significant issue?)*
- *They do not include contribution of organic species to particle water. (This has been discussed for other locations in some detail and is not noted in this paper, see example Guo et al. <http://www.atmos-chem-phys.net/15/5211/2015/>)*

Identifying these three issues is not the purpose of this paper. We claim that in general these issues have been often overlooked, not carefully considered by field study groups, who use thermodynamic models extensively. These issues are more likely a general guide that those who use thermodynamic models should be aware of. For this reason, we provide these issues in the introduction before discussing our experimental results. Although these issues are not our main

points in this paper, we respond here since the referee made comments on these issues.

(By the way, it is not clear that what the referee #1 means by "they." Do you mean thermodynamic models or field study groups who are using thermodynamic models?)

The first issue: Having a DRH point is the inherent property of inorganic salts. Below a DRH point, inorganic salts exist as dry crystals. This is a just general fact, and people who use a thermodynamic model should be aware of. But the referee claims that particles are never dry, but always wet (deliquescent) in the real atmosphere. We cannot agree with this unless the referee provides compelling evidence. We cannot even imagine the non-existence of dry particles in the atmosphere. We cannot rule out the possibility of the existence of dry ammonium sulfate crystals in the atmosphere. Please note that in this paper we are not arguing the importance of dry crystal inorganic particles in the atmosphere.

The second and third issues are basically the limitation of current thermodynamic models. ISORROPIA-II and E-AIM do not perform very well for the mixed inorganic particles and particles containing organic compounds. These are just facts. Besides, Guo et al., as the referee mentioned, actually estimated ALW due to organic compounds (W_o) using the hygroscopicity parameter (κ) from CCN activities, not from thermodynamic model simulations. Please note that in most cases (including Guo et al that the referee mentioned), the total water is the sum of W_i (inorganic contribution) and W_o (i.e., total water = $W_i + W_o$), but in this paper we present the synergetic effect (i.e., total water > $W_i + W_o$) when inorganic compounds are mixed with glyoxal in aerosols.

For the question: *If particles are always deliquesced, is this (second issue) still a significant issue?* **Our answer is yes.** Even if particles are assumed to be always deliquesced, the concentrations of inorganic species and ALWC predicted by a thermodynamic model in the metastable mode can be wrong. We have shown in the paper that the prediction by the metastable mode did not agree with HTDMA measurements: Fig. S3D and S4D (Metastable Simulation (II) for AN aerosols), Fig. S6A, B, C, D, E, and F (Metastable (I) and (II) for the mixture aerosols of AS and AN with different ratios). This is the reason why we modified thermodynamic model simulations.

Overall, the paper is confusing,

It seems that the confusion arises because 1) the referee believes that the main purpose of our paper is to identify the three issues above in the introduction; 2) all of our experiments and discussions have not been fully reviewed.

The main points of our paper are:

- Nitrate aerosols maintain deliquescence in the entire range of 10-90% RH
- ALWC and nitrates in ammonium-sulfate-nitrate aerosols, which are sulfate rich, simultaneously evaporate.
- In ammonium- sulfate-nitrate-glyoxal aerosols, more ALWC and nitrates form above 50% RH (the total ALWC is greater than the ALWC due to inorganic compounds and ALWC due to glyoxal).

These main points are written in the abstract and in the short summary.

Besides, only section 3.1, 3.2 and 4 seem to be covered in the review. The main point #2 and #3, which were discussed in section 3.3 and 3.4, are key findings in this work, but missing in the review.

and the experimental setup does not mimic actual ambient atmospheric conditions

We conducted HTDMA from 10% RH to 90% RH. Although ammonium nitrate salts are known to have a DRH at 60%, we observed that ammonium nitrate aerosols maintain deliquescence because in our HTDMA system it is difficult to remove water completely at RH 10%. So, we conclude ammonium nitrate aerosols are likely to exist as wet particles at atmospheric conditions (this is our main point #1 listed above). The referee seems to agree with us because the he/she even claims below in the comment that RH cannot be below 10% in ambient conditions. Then, he/she suddenly claims that our RH is not atmospherically relevant. We do not understand this. The hygroscopic growth (the uptake and evaporation of water) and the partitioning behavior of ammonia and nitric acid in the RH range of 10% to 90%, which we observed in this work, should be applicable to the atmospheric conditions. Because ammonium nitrate aerosols are deliquescent in the entire range of RH from 10% to 90%, so it is likely that ammonium nitrate aerosols are deliquescent in the atmosphere. But please note that we do not agree with the referee, who seems to think that any particles in the atmosphere are always deliquescent in 10-90% RH.

and so the conclusions that suggest the thermodynamic models are wrongly applied or deficient may not be justified.

For the best-fit to HTDMA measurements, we had to modify thermodynamic model simulations because the initial simulation results (including the metastable simulation results in Fig S6) without modification were wrong. Therefore, our modification by conducting the linear regressions and including the evaporation of ammoniums, nitrates and ALW clearly justifies our conclusions that suggest the thermodynamic models and wrongly applied or deficient.

The paper needs substantial work.

Not only ammonium nitrate aerosols, but ammonium sulfate-ammonium nitrate aerosols with different ratios, glyoxal aerosols, ammonium sulfate-glyoxal aerosols, ammonium nitrate-glyoxal aerosols, and ammonium sulfate-ammonium nitrate-glyoxal aerosols have been thoroughly investigated using HTDMA and thermodynamic models. Therefore, we believe that we have provided the substantial work. Again, it seems the referee only reviews the discussions regarding ammonium nitrate aerosols. The rest parts (section 3.3 and 3.4) are missing in the review.

This paper should really discuss the classic work of Tang and Munckelwitz on water uptake

by salts. Tang and Munckelwitz report results from single particle levitation experiments, likely some of the earliest and most precise work in this area. As one example publication see, *JOURNAL OF GEOPHYSICAL RESEARCH*, VOL. 99, NO. D9, PAGES 18,801-18,808, SEPTEMBER 20, 1994). There are more.

Thank you for introducing a JGR paper by Tang and Munckelwitz. The hygroscopic behavior of ammonium sulfate aerosols is rather fundamental and it is introduced in the well-known textbook, "Atmospheric Chemistry and Physics" by Seinfeld and Pandis. So, we feel that referencing this textbook is sufficient. The results of our experiment for ammonium sulfate aerosols agree well with the text book. It would be nice if Tang and Muckelwitz's work includes ammonium nitrate aerosols. Unfortunately, they did not conduct for ammonium nitrate aerosols in that JGR paper.

How do the authors handle the possible loss of NH₃ and/or HNO₃ to interior surfaces during the experiments? Since both NO₃⁻ and NH₄⁺ in the particle phase are semi-volatile and surfaces are a sink, there will be continual evaporation of these compounds from the particles. Is this an issue and possible cause for discrepancies with the model predictions?

The technical issue (the loss of ammonia and nitric acid by interior surfaces) should be of no importance because 1) our HTDMA measurements for the hygroscopic growth factor curve for ammonium sulfate aerosols (Figure S1 and S2) agree well with theoretic curves (the stable-mode curves by both ISORROPIA-II (Figure S1) and E-AIM (Figure S2); 2) the evaporation of ammoniums and nitrates is minimum for the AS-AN mixture aerosols containing the most of nitrates (AS: AN = 20: 80; Figure 6); and 3) maximum for the AS-AN mixture aerosols containing the least nitrates (AS: AN = 80: 20; Figure 4).

We discussed with Fred Brechtel, the developer of the HTDMA we used, and added the following in the main text for the technical issue that the referee brought up:

We expect both in the upstream SEMS and the downstream HSEM the loss of ammonia and nitric acid by the interior surfaces in the instrument to be insignificant. In the upstream SEMS, the sample flow eventually makes up the sheath flow, meaning that the gas-phase chemical composition of the sheath flow is identical to that of the sample flow because the PTFE filters are not likely to absorb ammonia or nitric acid. Then, practically no loss of ammonia and nitric acid is expected in the upstream SEMS. In the downstream HSEM, the residence time in the humidifier and DMA of the HSEM is only about 3 second. This means the flow rate is so fast that chemical equilibriums are not likely to change.

Figure 1 schematic is confusing. First, is the gas phase HNO₃-NH₃ reaction important as a source for particle NH₄⁺ and NO₃⁻. If so, state how you know this. I suspect that HNO₃ and NH₃ partitioning is the important route, thus I do not understand the line in the Fig caption that states: thus I do not understand the line in the Fig caption that states: The partitioning of HNO₃(g)-NO₃(p) and NH₃(g)-NH₄⁺(p) can be viewed as the formation of ammonium nitrates(p) by the reaction of ammonia and nitric acid in the gas phase.

The particle phase ammonium nitrates are the products of the gas phase reaction of ammonia and nitric acid. This is well known (and rather fundamental), so we

won't discuss in detail here. We refer the referee to the textbook by Seinfeld and Pandis, "Atmospheric Chemistry and Physics", 3rd Edition p430-432.

For the clarity, we add the following in the caption:

"The partitioning of $\text{HNO}_3(\text{g})\text{-NO}_3(\text{p})$ and $\text{NH}_3(\text{g})\text{-NH}_4^+(\text{p})$ can be viewed as the formation of ammonium nitrates(p) by the reaction of ammonia and nitric acid in the gas phase. Please note that this ammonium nitrates(p) dissociate to ammoniums and nitrates in the aqueous phase."

Second, the red arrow to the particle phase of NH_4NO_3 implies it is a one-way path, yet it is semi-volatile. Is the idea that the NH_4NO_3 formed in the gas phase dissociates in the particle aqueous phase and then these two ions establish equilibrium with their gas phase components?

Yes. We drew a one-way arrow because NH_4NO_3 is already in the particle phase. For clarity, we redrew the schematic diagram. We removed the one-way arrow and $\text{NH}_4\text{NO}_3(\text{p})$. We drew two equilibrium arrows for the partitioning of nitric acid-nitrate and ammonia-ammonium. But we leave the caption above ("Please note that this ammonium nitrate(p) dissociate to ammoniums and nitrates in the aqueous phase").

Overall, I do not understand this aspect of the figure, why is it included, how does it support the findings of the paper?

The partitioning of nitric acid-nitrate, and ammonia-ammonium is the essential part of the figure (It is also a key mechanism in this work). Again, this is well known and the textbook material ("Atmospheric Chemistry and Physics" by Seinfeld and Pandis, 3rd Edition p430-432), so we will not go over details in this work.

Why is SO_2 oxidation by only OH? In Figure 1. Are the authors claiming this is the main route to forming SO_4^{2-} .

Thank you for this comment. "OH" should be "Oxidation" in Figure 1.

The word aerosol means particle within a gas, in many cases in this paper the term aerosol should really be particle or aerosol particle.

We think that "aerosol" is the right word. By definition, aerosols are liquid or solid suspended in the air. Through the atomizer, aerosols were formed. These aerosols reach thermodynamic equilibriums between the gas and particle phase (the partitioning between nitric acid-nitrate and ammonia-ammonium). So, they are indeed within a gas!

Line 179 typo, change all over to over all?

We changed the sentence:

AN aerosols are deliquescent in the entire range of RH (10-90%).

Also, this line is very important and possible explains the discrepancy in Fig 3 for AN. (Note, a similar statement is made later in the paper). The issue is likely that the AN aerosol was never truly dry when exiting the dryers and so the H-TDMA experiments are really for a deliquesced aerosol and the comparison to a dry aerosol in Fig 3a (ISORROPOA stable mode) is not valid. Note that the data does basically agree with Fig 3b which compares to a deliquesced aerosol (ISORROPIA metastable). This point should be made very clear in section 3.2.

This referee's comment regarding Figure 3 does not sound appropriate. In line 179-194, we do claim that AN aerosols are deliquescent in the entire range of RH (10-90%). However, the estimations by the thermodynamic mode in the metastable mode (both ISORROPIA-II and E-AIM) are not right. (They do not match with HTDMA measurements)

In Figure S3D, ISORROPIA-II Metastable (I) is close to HTDMA Measurements. But in Figure S3E and F, concentrations of Ammonium and nitrate are not realistic (too high) between 10% and 30% RH. That is why Metastable Model (II) does not match with HTDMA measurements (Figure S3D).

In Figure S4D, now E-AIM Metastable (II) is close to HTDMA Measurements. But in Figure S4E and F, concentrations of Ammonium and nitrate are not realistic (too low) between 10% and 30% RH. That is why Metastable Model (I) does not match with HTDMA measurements (Figure S3D).

Because simulations by the metastable mode (Metastable (I) and (II)) do not match with HTDMA measurements, we have to modify the metastable mode outputs by the linear regression (S2 Text), and this modified outputs, "AN_{ISO_CORRECTION}" agrees with HTDMA measurements (Figure 3A) and estimates realistic concentrations of ammonium, nitrate and ALW (Figure 3B and C). Again, we discussed this in line 179-194.

Please note that we never claim that AN aerosols can be dry (Please see our main point #1 above). We are not comparing meta-stable mode outputs and stable-mode outputs. ISORROPIA-II Stable (II) in Figure 3 was included as a reference.

I do not understand the following arguments:

Line 301-302 which states; When the fraction of nitrates is small, particles of the ammonium-sulfate-nitrate system will become dry ammonium sulfate aerosols in the RH range of 30 to 70% by evaporating ALWC, nitrates and ammoniums significantly.

Line 310 to 311 which states; a barrier created by ammonium sulfate aerosols that suppress ALWC and nitrate accumulation in the RH range of 30 to 70%.

In section 3.3.1 and Figure 4, we discussed the evaporation of ammoniums and nitrates for the mixture of AS and AN aerosols (80: 20) in the RH range of 30-70% (Figure 4). To match HTDMA measurements between 30% RH and 70%

RH, ammoniums, nitrates and ALW have to evaporate. Note that ALW have to evaporate completely (Fig. 4H and I). Thus, in this RH range, we claim that particles will become dry ammonium sulfate aerosols. Yes, there exists small amounts of nitrates in particles in 30%-40% RH and 60%-70% RH. But particles become close to ammonium sulfate aerosols, which tend to be dry below RH 80%. To avoid confusion,

"... will become dry ammonium sulfate aerosols ..." is replaced by

"... will become dry aerosols close to ammonium sulfate ..."

To better explain my confusion, maybe it would work to follow what happens in the atmosphere to an aerosol particle over periods of changing RH (i.e., a diurnal cycle). Say a pure AS particle is somehow formed in the ambient atmosphere (not sure how this would happen, but this is what the experiment simulates). Within one night the RH likely exceeds the AS deliquescent point of about 80% RH, so the particle takes up water, then as the RH decreases the next day the water follows the upper curve of the hysteresis as it dries. Since the RH likely never drops below the crystallization RH of about 37% the particle from now on is always wet, it moves along the upper curve of the hysteresis.

This comment by the referee is confusing. Certainly, RH can drop below 37% in ambient conditions. Once this happens, AS aerosols will become dry again.

The only way it will shift to a dry particle (AS crystal), the lower hysteresis part of the curve, is if the RH drops below the crystallization point sometime during the day, which requires a RH.

This comment is also confusing. Now, the referee argues that RH can drop below 37% RH sometime during the day. This is not consistent with the comment above ("the RH likely never drops below the crystallization RH of about 37% ...). Yes, RH during the daytime is likely lower than RH during the nighttime. But we do not see why RH cannot be below 37% during the nighttime. Besides, the referee did not complete the sentence.

The fundamental question about this work is that the experiments don't seem to mimic the RH levels of what ambient particles experience – they are likely never completely dry (10% RH), which is how they start out in these experiments (I am sure there is never a 10% RH in the ambient boundary layer pertinent to this study).

Except AS aerosols, we never claim that particles are dry at RH 10%. In fact, the most of other aerosols are wet at RH 10%. AN aerosols, the mixture aerosols of AS and AN (80: 20, 50: 50, and 20:80), the mixture aerosols of AS and glyoxal (50: 50), mixture aerosols of AN and glyoxal (50: 50), and the mixture aerosols of AS, AN and glyoxal (50: 50: 20) contain ALW at RH 10% (Please see Figure 3, 4, 5, 6, 7E, 7F, and 8). The referee's statement, "I am sure there is never a 10% RH in the ambient boundary layer pertinent to this study" is confusing. Clearly, RH can be 10%.

The main question is then, would the results of this work change if the particles started off wet (deliquesced)? Or another way to put this, describe the situation where a crystallized

salt exits in the Korean boundary layer so that the use of the metastable mode in the thermodynamic models is incorrect.

Again, except AS aerosols, all other aerosols in our experiments contain ALW at RH 10%. Therefore, the particles started off wet!

In this paper, we are not arguing that metastable mode simulations can be wrong because particles can be dry. We are arguing that metastable-mode simulations (output concentrations of inorganic species and ALW) can be wrong because they do not match with HTDMA measurements quantitatively, so we conducted the linear regression to modify the thermodynamic model simulations. For sulfate-rich inorganic aerosols (mixture of AS and AN aerosols), we demonstrated the evaporation of ammoniums, nitrates, and ALW in the RH range of 30-70% (This is our main point #2). But thermodynamic model simulations (in the metastable mode) did not capture this. Therefore, in addition to the linear regression, we include the evaporation of ammoniums, nitrates, and ALW into the modification for the best-fit to HTDMA measurements. Lastly, although it is not covered in the review, the organic contribution to the hygroscopicity of aerosols is also very important. Here, we demonstrated the synergetic effect of glyoxal on ALW formation in aerosols (This is our main point #3).