General Comment from Anonymous Referee #1

Li et al. report for the first time the hygroscopic measurements of MBTCA-inorganic system using Raman spectroscopy. The reactions involving HCl(g) release were discussed using the speciation of COOH and COO^-, and related to the hygroscopic curves obtained by the optical imaging of the nominal particle size. This work would be an important increment to our knowledge of SOA hygroscopicity, but the current version is not ready for publication in ACP because of a number of issues as shown below.

Response: We thank the reviewer very much for the careful evaluation and valuable comments for our work. Here we provide the response to the reviewer's comments. The final revision will be made later based on two reviewers' comments.

Specific comments from Anonymous Referee #1 (comments are in italic)

** The abstract is rather long. I suggest the authors to make the text more concise by focusing more results and their interpretation.*

Response: The abstract will be revised in a more concise way as much as possible respecting the reviewer's comment.

** Lines 82-83: It is not clear how MBTCA can accelerate the new particle formation. The authors mentioned that MBTCA is extremely low volatile and one of the SOA components, i.e., one of the particulate compositions. Are you saying that preexisting aerosols enhance the new particle formation?*

Response: As described in the papers (Donahue et al., 2013; Elm, 2019), MBTCA can nucleate the sulfuric acid vapor or provide polar functional groups to form and grow molecular clusters through hydrogen bonds, which promote the new particle formation. However, as this sentence is not directly related to our work, it would be omitted without deteriorating the context.

** Line 127: I don't agree with the author's statement that RMS can provide the chemical compositions. RMS detects chemical functional groups of a molecule of interest.*

Response: The reviewer is correct, and the sentence will be modified as "RMS can provide information on chemical functional groups, water contents, molecular interactions, and phase states of the aerosol particles".

** Lines 170-173: It is useful if the authors show the experimentally measured hygroscopic curves of NaCl together with the thermodynamic model prediction.*

Response: The hygroscopic curve of NaCl (as shown below) will be put into the supporting information as Fig S2.

** Why were deposited and levitated particles examined in this study. The authors need to elaborate the necessity of using levitated particles.*

Response: The deposited particles (~6.5 μm in average in this study) may have some influences from the collecting substrate such as a facilitated heterogeneous nucleation, which can be eliminated in the levitation system due to the substrate-free and contactless properties. However, the particles in the levitation system are generally large in size (~80 μm in average in this study), which is less atmospherically relevant. And thus the analysis of the particles in both systems was expected to give more detailed information on the hygroscopic behavior of MBTCA aerosols. The information will be elaborated in the revised text.

** In Figure 2, the authors need to explicitly define the type of MBTCA particles. How do types 1-3 of the particles differ?*

Response: The types of the particles were classified as, "type 1: with prompt efflorescence around ~50% RH during dehydration; type 2: with gradual efflorescence around ~35% RH during dehydration; type 3: with gradual efflorescence around ~37% RH during humidification", based on their different behavior when efflorescence occurred.

The different efflorescence behavior was attributed to different nucleation mechanisms: heterogeneous nucleation for types 1 and 2 particles, and homogeneous nucleation for type 3 particles.

MBTCA powders (98% purity, Toronto Research Chemicals, TCR), which was used for making the MBTCA solution, has intrinsic unknown impurity of 2%, and they were used without any purification. When MBTCA powders were dissolved in ultrapure de-ionized (DI) water (18 MΩ, Millipore Direct-QTM) and particles were generated by the nebulization of the aqueous solution using N_2 gas (99.999% purity), impurities were either absent or associated with the droplets.

The impurities existed in types 1 and 2 particles after nebulization, acting as seed crystals to induce efflorescence. Aqueous moieties in particles were reported to effloresce more easily by heterogeneous nucleation in the presence of seeds (Schlenker and Martin, 2005; Li et al., 2014; Gupta et al., 2015). The lower ERH and gradual efflorescence of type 2 compared to type 1 particles might be due to the less amount of impurities. Type 3 particles contain negligible or no seed crystals, and large kinetic barrier and/or diffusional resistance make the formation of the crystal structure difficult owing to the decreasing availability of condensed water during dehydration, so that they did not experience any efflorescence. As type 3 particles account for 70% of all the analyzed one, it seems that MBTCA has slow homogeneous nucleation rate. The information will be explicitly described in the revised text.

** Line 230: Please provide the evidence of the phase change at RH = 36.7%. The optical images of type 3 particle in Figure 2 show the morphology change from 34% RH to 36.7% RH, but it does not necessarily mean phase change.*

Response: As shown in the optical image and Raman spectrum in Fig. 2, type 3 particles became irregular in shape during the humidification process, and the overlapped C=O (from COOH) peak at 1660 - 1680 cm^{-1} entirely shifted to 1660 cm^{-1} when the RH was increased from 34% to 36.7%, which indicates the phase change from amorphous/solid-state to solid state. Please also see the content at line 259-261 in the discussion paper, where the explanation has been done. The sentence at line 230 will be modified as, "type 3 particles experienced a sudden morphological change at RH = 36.7% and remained the same until RH = ~85%", for precise expression.

** Lines 250-252: Please clarify if the authors purposely injected impurity in the MBTCA particles. This is related to my earlier question: what is the type?*

Response: The MBTCA powders with intrinsic 2% impurity were used without any purification and no impurity was injected purposely. The information will be clarified in the revised text. Regarding the types of the particles, please see the response above.

** Line 270: It is confusing. The implication is based on the previous study or the current study?*

Response: The sentence will be modified as, “A previous study showed that MBTCA was not hydrated significantly in the ambient atmosphere (Kildgaard et al., 2018), and our results also implied that the MBTCA stay in the air as solids once they effloresced.”, to avoid the confusion.

** In Figure 3, one of the interesting results is the efflorescence at 46.8% RH during the humidification. The explanation for this phenomenon is rather dry. The authors need to elaborate more. It would be also useful if the authors can discuss the repeatability of such a phenomenon.*

Response: Efflorescence during humidification was previously reported for Amazonian rain forest aerosols (Pöhlker et al., 2014) and the laboratory-generated NaCl–$MgCl_2$ mixture particles (Gupta et al., 2015). And thus this phenomenon is not rare and it was claimed that the aerosol particles initially had amorphous or poly-crystalline structures and underwent restructuring through kinetic water and ion mobilization in the presence of sufficient condensed water, resulting in overcoming the kinetic barrier and crystallization during humidification.

Efflorescence during humidification was also observed for type 3 MBTCA particles, in addition to the observation in Fig. 3 for tri-sodium MBTCA particles, which seemed to be attributed to the similar structure to pure MBTCA particles when all three COOH were replaced by COONa. The explanation of “Efflorescence during humidification” will be further explained in the pure MBTCA particles section.

** Based on the chemical reactions the current study has proposed, acidic conditions are preferable for the reactions to proceed. However, Figure 7b shows the higher* *degree of 2 reaction for particles with MBTCA:NaCl = 1:3 than for those with that = 1:1. Particles with the higher abundance of NaCl (MBTCA:NaCl=1:3) are supposed to be less acidic. Do you have any explanation on it?*

Response: The reactions were driven by the liberation of HCl(g), so the increased availability of both dissociated H^+ and Cl^- should facilitate the reaction, which makes the degree of reaction follows the sequence of MBTCA:NaCl = 1:3>1:2>1:1. **We did not say that acidic conditions are preferable for the reactions to proceed, instead we said about "the availability".** The H^+ cannot fully dissociate due to the weak acidic property of MBTCA, and NaCl can be fully consumed only when enough H^+ is provided, so that the reaction was complete only for the mixtures with MBTCA:NaCl = 2:1 in this study.

** Figure 8a exhibits some heterogeneity of elemental distributions for particles with 1:2 and 1:3, which makes me wonder where Raman spectra were obtained. Raman spectra obtained from the edge and the center of the particles would be different.*

Response: The Raman spectra shown in the figures were all obtained in the center of the particles. Actually, the Raman spectra were obtained both at the center and the edge of the particles for comparison during the measurement when the heterogeneity appeared. The reviewer is correct in that the spectra from the edge and the center were different, but only in the intensity since NaCl is Raman inactive. As shown in the figure below (will be put into the supporting information as Fig. S3), the Raman spectra which were obtained from the center and the edge point of an exemplar MBTCA:NaCl = 1:3 particle during the humidification process, corresponds very well after normalization to the CH peak at 1460cm^{-1}. The discussion on the Raman spectra will be given in the revised text.

** The levitated particles show the lower reactivity than the deposited particles. The authors ascribed it to less release of HCl and the quenching process, which are too speculative. One more factor I want to point out is the almost one order of magnitude difference of the size between the two particles. It may not affect the reaction rates at a given RH, but it may do the release of HCl. I suggest the authors to discuss the potential size effect on the reactivity difference.*

Response: The default setting of N_2 flow inside the see-through impactor cell and the levitation cell were 4 and 0.2 L·min^{-1}, respectively, so we think that the levitation system is relatively closed compared to the see-through impactor system, which leads to less release of HCl(g). And the quenching process also dramatically decreases the reaction time due to the crystallization of both organic and inorganic compositions. We agree with the reviewer that the larger size of the levitated particles can also limit the release of HCl (Kerminen et al., 1997). The information will be added into the revised text.

** Interestingly, when the authors used the levitated particles, no size decrease (i.e., A/A0 < 1) was observed. The authors need to explain it. The size decrease observed with the deposited particles was attributed to the structural rearrange in the main text, but we may be seeing the effect of substrate.*

Response: We think why the shrinkage of the particles before deliquescence was not captured for the levitated particles can be because the size of the particles (~80 μm in average in this study) is too large to observe the structural rearrangement. And the 2-D optical images of the particles were used for plotting the hygroscopic curves even though the particles were levitated, which might lead to some missing information on the 3-D level. We agree with the reviewer that the substrate can also affect the shrinkage. Especially, the hydrophilic substrate (such as Si wafer used in this study) seems to favor this phenomenon (Eom et al., 2014). The information will be added into the revised text.

References

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Figure S2. Hygroscopic curve of pure NaCl particles. The transition RHs recorded during humidification and dehydration processes are marked with arrows in the hygroscopic curves.

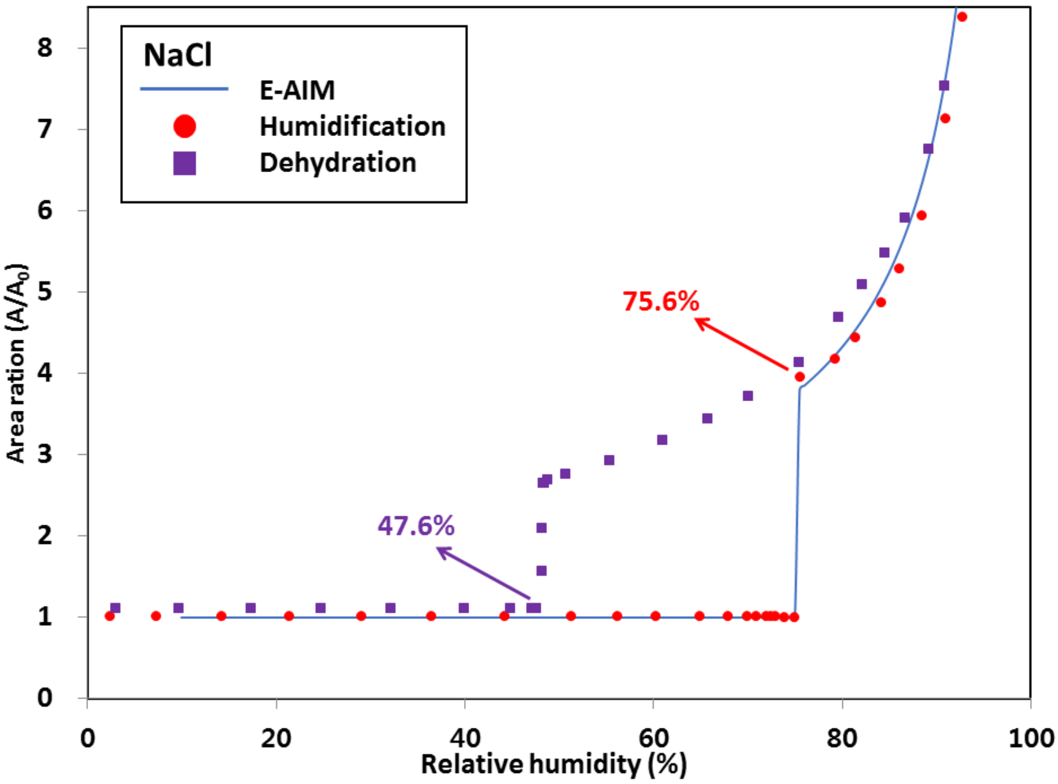

Figure S3. Comparison of Raman spectra of an exemplar particle (MBTCA:NaCl = 1:3) obtained at the center and edge of the particle before and after normalization to the CH peak at 1460 cm^{-1} during humidification (H) process at RH = 5.9% (end of dehydration) and RH = 73.8% (just before deliquescence).