Response to Reviewers:

Thanks for the reviewer's comments on our manuscript entitled "A comprehensive study on hygroscopic behaviour and nitrate depletion of $NaNO_3$ and dicarboxylic acid mixtures: Implication for the influence factors of nitrate depletion". The reviewers' comments are helpful for improving the quality of our work. The responses to the comments and the revisions in manuscript are given point-to-point below.

Reviewer #1:

1. In the abstract, the authors suggested that "The HNO_3 release from $NaNO_3$/OA mixtures was observed in both the measurements, owing to the relatively high acidity of OA". What does "the relatively high acidity of OA" mean? Compared with MA and GA, or HNO_3? This should be revised to avoid misunderstanding.

   Author reply: Thanks for the reviewer's suggestion. The relatively high acidity of OA indicated that the acidity of OA was higher than MA and GA, but lower than HNO_3. Indeed, this expression is a bit misleading. Thus, the sentence "The HNO_3 release from $NaNO_3$/OA mixtures was observed in both the measurements, owing to the relatively high acidity of OA" has been revised to "The HNO_3 release from $NaNO_3$/OA mixtures was observed in both the measurements, owing to the relatively higher acidity of OA compared to MA and GA" in the revised manuscript.

2. Line 37: Is there considerable amounts of nitrates present in sea salt aerosols? Or did the nitrate depletion frequently occur in sea salt aerosols?

   Author reply: As known, nitrogen oxides in the atmosphere can undergo heterogeneous reactions with NaCl on the highly reactive surfaces of sea salt particles. The proposed reaction pathways are as follows (Gibson et al., 2006).

$$NaCl(s,aq) + HNO_3(g) \rightarrow NaNO_3\ (s,aq) + HCl(g) \quad (R1)$$

$$NaCl(s,aq) + N_2O_5(g) \rightarrow NaNO_3\ (s,aq) + ClNO_2(g) \quad (R2)$$

$$NaCl(s,aq) + 2NO_2(g) \rightarrow NaNO_3\ (s,aq) + ClNO(g) \quad (R3)$$

   Furthermore, the heterogeneous uptake coefficient (γ) of HNO_3 and N_2O_5 on NaCl particles has been measured to be about $(1.0 \pm 0.8) \times 10^{-3}$ and $(2.9 \pm 1.7) \times 10^{-3}$, respectively

(Hoffman et al., 2003a;Hoffman et al., 2003b). Thus, the chloride in sea salt aerosols can be substituted significantly by nitrate, as observed in field measurements by Kerminen et al. (1998). Coupled with the gas-particle partitioning of dicarboxylic acids, we can infer that nitrate depletion by DCAs would occur frequently in sea salt aerosols.

3. The authors observed the $NaHC_2O_4$ formation in $NaNO_3$/OA mixed system, and then $NaHC_2O_4$ was transformed into $Na_2C_2O_4$ with further nitrate depletion. Whereas, MA was found to produce monosodium malonate as it reacted with nitrate. Why? Please clarify it in the text.

Author reply: Thanks for the reviewer's suggestion. The OA has a pK_{a2} of 4.19, which is lower than that of MA (pK_{a2} = 5.70). This implied that more $C_2O_4^{2-}$ were dissociated from OA than $CH_2(COO)_2^{2-}$ from MA. Thus, the disodium oxalate was mainly formed in $NaNO_3$/OA system, while monosodium malonate was the main product as MA reacted with $NaNO_3$. We have added the sentence "Besides, no disodium salts are observed in the $NaNO_3$/MA system, differing from the $NaNO_3$/OA system, which may be due to the higher acidity of OA (pK_{a2} = 4.19) than MA (pK_{a2} = 5.70)." in Line 270.

4. Line 132: "Likewise, Wang et al. (2017) observed the formation of $NH_4HC_2O_4$ in mixed $(NH_4)_2SO_4$/OA droplets upon drying." So what's the similarity of Wang's study and this work? Did they propose the similar driving force for HC_2O_4- ions formation?

Author reply: Wang et al. (2017) has indicated that OA could react with $(NH_4)_2SO_4$ to form NH_4HSO_4 and $NH_4HC_2O_4$ via the following pathway:

$$H_2C_2O_4(aq) \rightarrow H^+(aq) + HC_2O_4^-(aq) \quad \text{(R4)}$$

$$H^+(aq) + SO_4^{2-}(aq) \rightarrow HSO_4^-(aq) \quad \text{(R5)}$$

$$2NH_4^+(aq) + HSO_4^-(aq) + HC_2O_4^-(aq) \rightarrow NH_4HSO_4\,(aq) + NH_4HC_2O_4(aq) \quad \text{(R6)}$$

In the first step, the OA (pK_{a1} = 1.23) was dissociated into $HC_2O_4^-$ and H^+ ions. Then, the H^+ reacted with SO_4^{2-} to form HSO_4^- ions. While in this work, the dissociated H^+ ions would interact with NO_3^- to produce gaseous HNO_3, causing nitrate depletion. After that, the $HC_2O_4^-$ ions further combined with NH_4^+ to produce $NH_4HC_2O_4$ in Wang's work, and in this study, the $HC_2O_4^-$ ions tended to combine with Na^+ to generate $NaHC_2O_4$. Besides, the formation of both $NH_4HC_2O_4$ and $NaHC_2O_4$ was observed in the drying process in the two studies.

Therefore, We proposed that "Likewise, Wang et al. (2017) observed the formation of $NH_4HC_2O_4$ in mixed $(NH_4)_2SO_4$/OA droplets upon drying.".

5. Line 143: As indicated in this work, $NaNO_3$ deliquescence proceeds at 46.9%-61.9% RH for $NaNO_3$/OA mixtures and ~65%-77% RH for pure $NaNO_3$. This implied that $NaNO_3$ solids began to deliquesce at RH significantly lower than its DRH. So is the deliquescence process a thermodynamic process or a kinetic process?

Author reply: In our previous work, the $NaNO_3$ solids were found to begin to dissolve at ~63.70% RH during the humidification, which was well below the predicted DRH by EAIM model (Ma et al., 2021). Meanwhile, the deliquescence behavior of inorganic salt particles (i.e., NaCl, $NaNO_3$ and K_2CO_3) has been proved to be a dynamic process, i.e., the particles would absorb water to form the partially dissolved phase state at RH lower than their DRH, and then they were deliquesced completely once the DRH was reached (Bruzewicz et al., 2011;Esat et al., 2018;Ma et al., 2021).

6. Line 168: The authors observed phase transition and nitrate depletion of 1:1 $NaNO_3$/OA mixtures in Sec. 3.1, but why did they choose 3:1 mixtures to further investigate the phase state effect?

Author reply: As indicated in this work, the final reaction product of $NaNO_3$/OA system was $Na_2C_2O_4$. Thus, we chose 3:1 $NaNO_3$/OA mixtures, in which the amount of reactant $NaNO_3$ was in excess according to stoichiometry, to examine whether the liquid OA could be consumed completely by aqueous $NaNO_3$. Based on this, we indicated that "At ~ 69.2% RH, the presence of 1741 cm^{-1} band indicates the excess of liquid OA, suggesting this displacement reaction tends to reach equilibrium with comparable final concentrations of "reactants" and "products".".

7. Line 231: The 15% RH was only a preset RH value with stepwise increasing RH, so it should be revised to "As RH increases to around 15% (or even lower)".

Author reply: Thanks for the reviewer's suggestion. We have adopted reviewer's advice and revised our manuscript accordingly.

8. Line 287: The authors also observed the chlorine depletion in 1:1 mixed NaCl/MA particles with two different RH changing rates, but a brief discussion about the experimental results

should be presented in the text.

Author reply: Thanks for the reviewer's suggestion. We have adopted reviewer's advice and revised our manuscript accordingly.

9. Line 413-424: I suggest that this paragraph should be rewrote to better illustrate the atmospheric implications of the experimental observations in view of the presence of mineral dust inclusions and so on in atmospheric aerosols, which constantly induce the heterogeneous nucleation of aerosols at relatively high RH.

Author reply: Thanks for the reviewer's suggestion. We have adopted reviewer's advice and rewrote this paragraph to illustrate the atmospheric implications of the influence of efflorescence behaviors of aerosols on nitrate depletion.

Reference:

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