

1 **Response to Reviewers:**

2 Thanks for the reviewer's comments on our manuscript entitled "A comprehensive study on  
3 hygroscopic behaviour and nitrate depletion of NaNO<sub>3</sub> and dicarboxylic acid mixtures:  
4 Implication for the influence factors of nitrate depletion". The reviewers' comments are helpful for  
5 improving the quality of our work. The responses to the comments and the revisions in manuscript  
6 are given point-to-point below.

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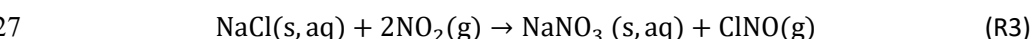
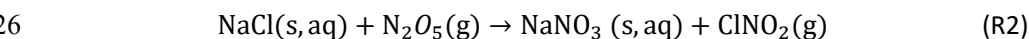
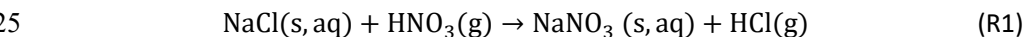
8 **Reviewer #1:**

9 1. In the abstract, the authors suggested that "The HNO<sub>3</sub> release from NaNO<sub>3</sub>/OA mixtures was  
10 observed in both the measurements, owing to the relatively high acidity of OA". What does  
11 "the relatively high acidity of OA" mean? Compared with MA and GA, or HNO<sub>3</sub>? This  
12 should be revised to avoid misunderstanding.

13 **Author reply:** Thanks for the reviewer's suggestion. The relatively high acidity of OA  
14 indicated that the acidity of OA was higher than MA and GA, but lower than HNO<sub>3</sub>. Indeed,  
15 this expression is a bit misleading. Thus, the sentence "The HNO<sub>3</sub> release from NaNO<sub>3</sub>/OA  
16 mixtures was observed in both the measurements, owing to the relatively high acidity of OA"  
17 has been revised to "The HNO<sub>3</sub> release from NaNO<sub>3</sub>/OA mixtures was observed in both the  
18 measurements, owing to the relatively higher acidity of OA compared to MA and GA" in the  
19 revised manuscript.

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

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



28 Furthermore, the heterogeneous uptake coefficient ( $\gamma$ ) of HNO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> on NaCl  
29 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

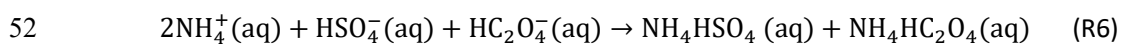
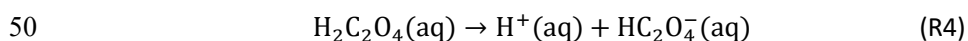
30 (Hoffman et al., 2003a; Hoffman et al., 2003b). Thus, the chloride in sea salt aerosols can be  
31 substituted significantly by nitrate, as observed in field measurements by Kerminen et al.  
32 (1998). Coupled with the gas-particle partitioning of dicarboxylic acids, we can infer that  
33 nitrate depletion by DCAs would occur frequently in sea salt aerosols.

34 3. The authors observed the  $\text{NaHC}_2\text{O}_4$  formation in  $\text{NaNO}_3/\text{OA}$  mixed system, and then  
35  $\text{NaHC}_2\text{O}_4$  was transformed into  $\text{Na}_2\text{C}_2\text{O}_4$  with further nitrate depletion. Whereas, MA was  
36 found to produce monosodium malonate as it reacted with nitrate. Why? Please clarify it in  
37 the text.

38 **Author reply:** Thanks for the reviewer's suggestion. The OA has a  $pK_{a2}$  of 4.19, which is  
39 lower than that of MA ( $pK_{a2} = 5.70$ ). This implied that more  $\text{C}_2\text{O}_4^{2-}$  were dissociated from OA  
40 than  $\text{CH}_2(\text{COO})_2^{2-}$  from MA. Thus, the disodium oxalate was mainly formed in  $\text{NaNO}_3/\text{OA}$   
41 system, while monosodium malonate was the main product as MA reacted with  $\text{NaNO}_3$ . We  
42 have added the sentence "Besides, no disodium salts are observed in the  $\text{NaNO}_3/\text{MA}$  system,  
43 differing from the  $\text{NaNO}_3/\text{OA}$  system, which may be due to the higher acidity of OA ( $pK_{a2} =$   
44 4.19) than MA ( $pK_{a2} = 5.70$ )." in Line 270.

45 4. Line 132: "Likewise, Wang et al. (2017) observed the formation of  $\text{NH}_4\text{HC}_2\text{O}_4$  in mixed  
46  $(\text{NH}_4)_2\text{SO}_4/\text{OA}$  droplets upon drying." So what's the similarity of Wang's study and this work?  
47 Did they propose the similar driving force for  $\text{HC}_2\text{O}_4^-$  ions formation?

48 **Author reply:** Wang et al. (2017) has indicated that OA could react with  $(\text{NH}_4)_2\text{SO}_4$  to form  
49  $\text{NH}_4\text{HSO}_4$  and  $\text{NH}_4\text{HC}_2\text{O}_4$  via the following pathway:



53 In the first step, the OA ( $pK_{a1} = 1.23$ ) was dissociated into  $\text{HC}_2\text{O}_4^-$  and  $\text{H}^+$  ions. Then, the  $\text{H}^+$   
54 reacted with  $\text{SO}_4^{2-}$  to form  $\text{HSO}_4^-$  ions. While in this work, the dissociated  $\text{H}^+$  ions would  
55 interact with  $\text{NO}_3^-$  to produce gaseous  $\text{HNO}_3$ , causing nitrate depletion. After that, the  $\text{HC}_2\text{O}_4^-$   
56 ions further combined with  $\text{NH}_4^+$  to produce  $\text{NH}_4\text{HC}_2\text{O}_4$  in Wang's work, and in this study,  
57 the  $\text{HC}_2\text{O}_4^-$  ions tended to combine with  $\text{Na}^+$  to generate  $\text{NaHC}_2\text{O}_4$ . Besides, the formation of  
58 both  $\text{NH}_4\text{HC}_2\text{O}_4$  and  $\text{NaHC}_2\text{O}_4$  was observed in the drying process in the two studies.

59 Therefore, We proposed that “Likewise, Wang et al. (2017) observed the formation of  
60  $\text{NH}_4\text{HC}_2\text{O}_4$  in mixed  $(\text{NH}_4)_2\text{SO}_4/\text{OA}$  droplets upon drying.”.

61 5. Line 143: As indicated in this work,  $\text{NaNO}_3$  deliquescence proceeds at 46.9%-61.9% RH for  
62  $\text{NaNO}_3/\text{OA}$  mixtures and ~65%-77% RH for pure  $\text{NaNO}_3$ . This implied that  $\text{NaNO}_3$  solids  
63 began to deliquesce at RH significantly lower than its DRH. So is the deliquescence process a  
64 thermodynamic process or a kinetic process?

65 **Author reply:** In our previous work, the  $\text{NaNO}_3$  solids were found to begin to dissolve at  
66 ~63.70% RH during the humidification, which was well below the predicted DRH by EAIM  
67 model (Ma et al., 2021). Meanwhile, the deliquescence behavior of inorganic salt particles  
68 (i.e.,  $\text{NaCl}$ ,  $\text{NaNO}_3$  and  $\text{K}_2\text{CO}_3$ ) has been proved to be a dynamic process, i.e., the particles  
69 would absorb water to form the partially dissolved phase state at RH lower than their DRH,  
70 and then they were deliquesced completely once the DRH was reached (Bruzewicz et al.,  
71 2011;Esat et al., 2018;Ma et al., 2021).

72 6. Line 168: The authors observed phase transition and nitrate depletion of 1:1  $\text{NaNO}_3/\text{OA}$   
73 mixtures in Sec. 3.1, but why did they choose 3:1 mixtures to further investigate the phase  
74 state effect?

75 **Author reply:** As indicated in this work, the final reaction product of  $\text{NaNO}_3/\text{OA}$  system was  
76  $\text{Na}_2\text{C}_2\text{O}_4$ . Thus, we chose 3:1  $\text{NaNO}_3/\text{OA}$  mixtures, in which the amount of reactant  $\text{NaNO}_3$   
77 was in excess according to stoichiometry, to examine whether the liquid OA could be  
78 consumed completely by aqueous  $\text{NaNO}_3$ . Based on this, we indicated that “At ~ 69.2% RH,  
79 the presence of  $1741\text{ cm}^{-1}$  band indicates the excess of liquid OA, suggesting this  
80 displacement reaction tends to reach equilibrium with comparable final concentrations of  
81 “reactants” and “products”.”.

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

84 **Author reply:** Thanks for the reviewer’s suggestion. We have adopted reviewer’s advice and  
85 revised our manuscript accordingly.

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

88 should be presented in the text.

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

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

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

98

99 **Reference:**

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