Review of Shuaishuai Ma et al.

In this work by Shuaishuai Ma, Qiong Li and Yunhong Zhang, the water uptake and nitrate/nitric acid depletion of laboratory particles are studied experimentally and evaporation rates estimated with a kinetic model. The authors employed ATR-FTIR and vacuum FTIR methods to study their particles deposited on substrates exposed to different relative humidities (RH). The main focus is on the spectroscopic signatures of nitrate species, nitrate salt formation, and other phase changes when 1:1 mixtures of $NaNO_3$ and dicarboxylic acids (DCAs) undergo RH cycles.

Overall, this work is very interesting and within the subject area of this journal. The manuscript is also well structured and for the most part well written (a few English phrasing issues will need to be addressed).

I have one major comment and many minor ones (see below) that the authors should address to clarify which processes are backed by direct evidence and which ones are based on assumptions or inferred rather indirectly.

Major comments

1. My main concern is with the presentation and interpretation of several of the results with regard to the loss of nitrate from the particles/droplets via evaporation of HNO_3. As the title indicates, nitrate depletion is a key interest of this work, yet most of the data provided does not appear to show direct evidence for nitrate depletion via HNO_3 loss to the gas phase – contrary to what is stated in the abstract (line 15) and the Results and Discussion section.

   The measurements provided characterize the composition and spectral features of nitrate and DCA species in the condensed phase(s) of deposited particles. However, unless I missed it, HNO_3(g) is not measured, nor is the mass of nitrate in the particle phase tracked. If there is substantial loss of nitrate, the particles should change in nitrate content and overall mass. Moreover, the loss of nitrate would likely be accompanied by a loss of water. As pointed out in the specific comments that follow, there are several instances where statements like "... confirms nitrate depletion and HNO_3 release" are made (e.g. line 133), while the information provided does not directly support this conclusion. For example, the authors seem to equate the formation of liquid or solid $NaHC_2O_4$ as evidence for nitrate depletion. However, it is not discussed why that should be a unique signature of such a process. This reviewer argues that (at least some) dissolved or crystalline $NaHC_2O_4$ could also form in the absence of any nitrate depletion, simply as a result of aqueous solution chemistry and resulting equilibria. I strongly suggest that the authors rectify this issue and provide direct evidence for HNO_3 loss to the gas phase or otherwise clarify that their interpretation depends on certain assumptions about the relevant processes taking place.

   To be clear, I also consider nitrate depletion via HNO_3 to be a plausible hypothesis and a likely explanation for the findings from this work. However, what is missing is quantitative evidence and/or clarity in the discussion in support of this hypothesis.

Specific comments

2. Title: phrasing of "Implication for the influence factors of nitrate depletion" needs language improvement and perhaps a more direct link to aerosols. Consider replacing by "implications for nitrate depletion in tropospheric aerosols".

3. Line 15: make statement consistent with the data provided (see my major comment).

4. Line 19: “... potentially indicating the transformation of amorphous solids to semisolid NaNO3; ...”; consider: or the dissolution of $\mathrm{NaNO_3}$ into a liquid DCA + Water rich phase?

5. Line 39: define abbreviations like DCA, ATR-FTIR and OA at first use in the main text (aside from the abstract).

6. Line 42: there are several directly relevant studies on hygroscopicity and surface tension effects that could be cited here; e.g. Peng et al. (2001, 10.1021/es0107531), Ovadnevaite et al. (2017, doi:10.1038/nature22806), Hodas et al. (2015, doi:10.5194/acp-15-5027-2015).

7. Line 43: “It is well known that the displacement of strong acids, i.e., HCl or HNO3, by weak organic acids, e.g., DCAs, is not thermodynamically favoured in bulk solution”. This statement requires citation of a relevant reference. Note that even if the thermodynamic equilibrium is favouring the left hand side of reaction (R1), there will be some amounts of HCl or $\mathrm{HNO_3}$ dissolved and if gas phase exchange is possible, there will be a continuous loss of the right hand side, consuming the reactants of R1 over possibly long time (depending on bulk vs. small aerosols). Therefore, given that in an aqueous phase, $\mathrm{NaNO_3}$ will be present mostly in the form of $\mathrm{Na^+}$ and $\mathrm{NO_3^-}$, some NaA(aq) (or solid) and/or $\mathrm{Na^+}$ and $\mathrm{A^-}$ may be present even in the absence of any evaporation of $\mathrm{HNO_3}$.

8. Line 52: State for what concentration/conditions. Are you comparing at the same RH or the same water content or the same molar concentration of dissolved solutes?

9. Line 58: define the base of the logarithm and perhaps at first use, define the meaning of pK_{a1} formally using molal activities or standard chemical potentials, as appropriate given the values stated.

10. Line 66: what “substrate” is here referred to? do you mean material onto which particles were deposited in laboratory experiments?

11. Line 70: “... the substrate supporting OA droplets would crystallize to form”; do you mean the droplet / OA or really the substrate? Clarify phrasing.

12. Line 70: “OA dihydrate at 71% RH” Is it under conditions of dehumidification? Describe what kind of laboratory experiment you refer to.

13. Line 72: “Pure NaNO3 droplets might not be effloresced...” By “be effloresced” do you rather mean "crystallize" here? Note that effloresced is not necessarily the same as crystalline in the context of amorphous solids as a possibility. Also, clarify under what conditions; here presumably dehydration in an isothermal (and isobaric) experiment.

14. Line 73: “certain RH values” Which ones? Please provide values/ranges.

15. Line 74: Given the stated list of options, how is “highly viscous” different from glassy or semisolid? One could say "highly viscous (i.e. semisolid or glassy), liquid, or mixed-phase (e.g. solid–liquid) mixing states.

16. Line 75: Koop et al. (2011, doi:10.1039/C1CP22617G) would be another key reference to cite here.

17. Line 82: phrasing: “would” or rather “does” it?

18. Line 85: delete “mixture”; it is redundant with solution.

19. Line 92: “... a brief was introduced here”; phrasing.

20. Line 103: “chamber, which could be used to calibrate the ambient RH”; in the context of this description, it is mentioned that water vapor and CO_2 were removed by the vacuum pump. So, how was the RH established in the sample chamber? Is it due to remaining water vapor under low pressure conditions? If so, does that mean that the sample droplets are (potentially) evaporating water alongside with HNO_3 and DCA? The droplets may also outgas dissolved CO_2 during the experiment given the vacuum applied, which might have some effect on the acidity.

21. Line 127: “and anhydrous OA” I suggest to mention that you refer to crystalline anhydrous OA here.

22. Line 131: “... indicative of the $NaHC_2O_4$...”; Is this referring to an actual solid $NaHC_2O_4$ component forming or rather the presence of partially dissociated OA anions ($HC_2O_4^-$) in aqueous solution alongside Na^+? In the latter case, this should not be referred to as $NaHC_2O_4$ since it is not forming a compound of that structure nor stoichiometry. Also, in that case, this does not confirm directly the release of HNO_3, it only indicated the presence of partially dissociated OA. Please discuss.

23. 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. These scenarios confirm the nitrate depletion and HNO_3 release from $NaNO_3$/OA mixtures in the vacuuming process.”
    The provided data and discussion does not uniquely support this conclusion. While HNO_3 evaporation is possible, where is the evidence for it? Oxalate salts could form also without any loss of HNO_3 to the gas phase. For example, $HNO_3(aq)$ could form or, more likely, $H^+(aq)$ and $NO_3^-(aq)$ alongside solid or dissolved OA salts. Please provide evidence or a more nuanced discussion.

24. Line 145: “Likewise, Ma et al. (2013) found that the DRH of NaCl component decreased in both external and internal NaCl/MA mixtures.” How could this be the case in an external mixture (assuming external means (pure) NaCl particles separate from MA particles)?
    Also, worth mentioning in the context of DRH lowering: a lowering of the DRH in particles containing aqueous DCAs is expected from thermodynamic equilibrium theory and has been shown in many other measurements and by means of thermodynamic model predictions, such as those shown for MA or OA and ammonium sulfate by Bouzidi et al. (2020, doi:10.1016/j.atmosenv.2020.117481) and those shown by Hodas et al. (2015, doi:10.5194/acp-15-5027-2015) for mixtures of ammonium sulfate with DCAs and citric acid.

25. Line 146: “Note that the OA dihydrate and crystalline Na2C2O4 cannot be deliquesced due to their very high DRHs ...”. A note: the process of deliquescence, as more clearly observed in binary (water + 1 solute) systems, should not be confused with partial (gradual) dissolution in multicomponent, multiphase systems. Therefore, please clarify the sentence. At present it is misleading. While crystalline substances like OA and Na2C2O4 may not fully dissolve, it should be noted that in the presence of an aqueous phase a solid–liquid equilibrium will be established (given enough time) and some amount of OA and Na2C2O4 will be in the dissolved state, forming a saturated aqueous solution with respect to the pertaining crystalline phase or phases; see, e.g. the discussion by Hodas et al. (2016, doi:10.5194/acp-16-12767-2016).

26. Line 155: “Upon hydration, the water content at high RH is far below that upon dehydration, ...”
    This statement needs further clarification. It seems only to make sense when the dehydration refers to dehydration from an initial state of completely dissolved particles at very high RH. Of course, one could start dehydration at any RH and then the water content could be higher or lower than when arrived at that state from an initial state of low RH.

27. Line 159: I find Fig. S6 insightful and suggest that this figure and the related discussion be moved to the main manuscript.

28. Line 160: “Besides, as shown in Fig. 1c, the absorbance of 1620 cm^{-1} band assigned to oxalate shows a slight increase at RH as low as 21.2%, implying the nitrate depletion proceeds at relatively low RH.”
    In my opinion, what is missing are observations of the loss of nitrate/HNO_3 from the particles. Do the authors have comparison examples for cases where the gas phase exchange is limited (small gas volume) such that only a small loss could occur and, as a result, the signature in oxalate formation substantially different? Without such observations, or other quantitative measures of loss to the gas phase, the interpretation of the experiments hinges on assuming a nitrate depletion takes place without having the data to confirm it. Please discuss.

29. Line 173: “As RH increases to $\sim 15\%$, the ΔA of ν_{as}(COO-) band exhibits a considerable increase, indicative of the occurrence of nitrate depletion.”
    While indicative as an option, it remains speculative. It is indicative of the partial dissociation of OA in solution. Which is expected to increase with increasing particle water content and, hence, increasing RH.

30. Line 177: “2013). Then, the 1620 cm^{-1} band appears and becomes stronger with time, suggesting $\mathrm{Na_2C_2O_4}$ can be continuously produced at constant $\sim 15\%$ RH.”
    I think this is better evidence for $\mathrm{Na_2C_2O_4}$ formation and associated nitrate depletion, because the system is observed at constant RH, which means it should maintain constant water activity (in sufficiently large particles where the Kelvin effect would not change with evaporation). It may be good to expand the discussion of this piece of evidence.

31. Line 179: “... we can infer the conversion of amorphous $\mathrm{NaNO_3}$ solids to highly viscous semisolids due to the uptake of trace amounts of moisture.”
    Please clarify: semisolids of what? if $\mathrm{NaNO_3}$ dissolves partially and forms a viscous aqueous solution, this should not be called a $\mathrm{NaNO_3}$ semisolid because the formed phase contains other species too.

32. Line 216: Define the R^2 metric.

33. Line 231: “As RH increases to around 15%, amorphous solids are converted into viscous semisolids, ...”. Is there any evidence from the spectra for such a conversion and the approximate viscosity of the phase to classify it as semisolid?

34. Line 261: “... formation of monosodium malonate ...”. Is this for a solid malonate phase or dissolved?

35. Line 266: Clarify: “that the first acid dissociation constant (pKa1) of MA was about 2.83, which was $\sim$ 3 orders of magnitude larger than the second one ...”. 3 orders of magnitude in what? clearly not in pKa. Also, 2.83 is the pKa1 not Ka1 (which the current phrasing implies).

36. Line 270: band assigned to ν_{as}(COO$^-$) of monosodium malonate. Please clarify: why of monosodium malonate and not of the malonate anion? The COO^- functionality does not contain any sodium and in aqueous solution the malonate ion is likely dissociated from Na^+. Is the assigned band specific to the COO- group in crystalline monosodium malonate only?

37. Line 277: “aqueous $\mathrm{NaNO_3}$” should be “aqueous $\mathrm{NO_3}$.

38. Line 279: “As compared to vacuum FTIR results, we can infer that the heterogeneous efficacy of Ge substrate is much higher than CaF2 windows,...”. It seems unclear whether this is really a substrate effect or rather an effect of the vacuum cell procedures applied.

39. Line 290, Fig. 5: What explains the difference in the normalized water contents comparing panels (a) and (b)? Did you compare the obtained water contents to model predictions of the water content or independent mass growth factor measurements to assess which technique provides more accurate hygroscopic cycles?

40. Line 301: “appears upon hydration, indicating the formation of glutarate sodium salts.” Could you clarify whether this means that a solid crystalline salt phase is forming upon hydration in equilibrium with an aqueous solution?

41. Line 314: “lower temperature of droplets” Is it just the temperature effect or also the drying to much lower effective RH than during the ATR-FTIR measurement cycles?

42. Line 335: Could you discuss in this context whether the size dependence effect is due to the Kelvin effect, leading to a lower water activity and higher pH in smaller particles compared to larger ones exposed to the same RH in the gas phase, or some other effect?

43. Line 346, Eq. (5): check equation; it looks like the p of p_r is missing.

44. Line 358: Eq. (6), for consistency with Eq. (7), consider replacing P by p^*.

45. Line 373: “Therefore, the ambient pressure, dominating the diffusion coefficient of HNO3 in the gas phase, tends to play an important role in nitrate depletion during the transport and aging of atmospheric aerosols.”

This statement is not supported by any quantitative data. How big of a difference is expected in the troposphere? Obviously, one should not directly compare the vaccuum FTIR pressure to realistic tropospheric conditions without accounting for the differences in the ranges of total pressures. If nitrate-containing particles are given hours to days to undergo displacement reactions, the impact of pressure on HNO3 diffusion may be unimportant. Do you have predictions to the contrary?

46. Line 409: "NaNO3 can be treated as a surrogate for a broad class of amorphous or semisolid species existing in atmospheric aerosols,..."
    Please state in what RH range this semisolid state applies. NaNO3 is certainly dissolved and liquid-like in dilute aqueous aerosols at elevated RH (for aqueous NaNO3 viscosity data see e.g. Baldelli et al., 2016, doi:10.1080/02786826.2016.1177163; Lilek and Zuend, 2022, doi:10.5194/acp-22-3203-2022).

47. Line 427: "metastable or liquid-like state..." Please rephrase; metastable and liquid-like characterize two different properties. One related to the supersaturation of aqueous solutions with respect to a certain crystalline phase, while the other refers to a phase state (viscosity related).

Supplement: minor comments

47. SI, lines 20–36: How was that ERH determined? Was it based on just some features of the spectra? Fig. S1a does not seem to indicate any clear signature of efflorescence. Specifically, note that in the absence of severe kinetic limitations, one would expect a sharp change in mass growth factor at the ERH (point of crystallization) of a single-solute particle. Certainly so for a system at equilibrium with the gas phase. Why is that not the case for the systems shown in Fig. S1? Figure S2 shows also no indication of NaNO3 crystallization. Do the authors use the term "efflorescence" for a phase transition other than crystallization? If so, that would be untypical given the common use and meaning of this term and might need clarification in the text.

48. SI, line 40: what about that of a NaNO3 hydrate crystal? Would equilibrium thermodynamics not require that amorphous solids take up some water upon hydration (while single-solute crystalline particles may not)?

49. SI, lines 155–158, 166: these sentences are inconsistent. One is about HCl release, the other about HNO3 but referring to the same study. Please clarify.

50. SI, line 178: molecular weight (or rather molar mass) of water should be stated in $\mathrm{kg\,mol^{-1}}$ to stay consistent with the other units given. Other there will be an incorrect Kelvin effect value.

51. SI, line 188: It should be stated that the true equilibria in aqueous solution involve use of the activities of the species, not the molar concentrations. Also, on line 210, state that self-dissociation of $\mathrm{H_2O}$ is not considered.

52. SI, line 216: given definition of pH; note that this refers only to an approximate, molarity-based pH, as discussed by Pye et al. (2020, doi:10.5194/acp-20-4809-2020). The proper definition of pH involves the molality-based activity of $\mathrm{H^+}$.