

Interactive comment on “Direct contribution of ammonia to CCN-size alpha-pinene secondary organic aerosol formation” by Liqing Hao et al.

Anonymous Referee #2

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This manuscript reports chamber results of alpha-pinene SOA formation in the presence of ammonia, and suggested that organic acids have a central role in the formation of particle phase ammonium through neutralization. Major arguments supporting this conclusion come from the stoichiometric neutralization analysis, and correlations between gas-phase organic acids and particle-phase NH_4^+ . The experiment looks carefully conducted and calibrated, with interesting results. However, the interpretation of the results is ambiguous and confusing. Although I trust in the data, I'm not convinced by the logic that draws to the conclusions. The following concerns should be addressed before this work can be considered for publication for ACP.

Major concerns

1. How did the authors estimate the NH_3 concentration in the chamber “by assuming C1

that the particulate ammonium salt (NH_4^+) was converted from the gas-phase NH_3 (Fig. 1)”? Did the authors assume a 1:1 conversion ratio, namely all gas-phase NH_3 are converted to NH_4^+ ? If so, this assumption is too arbitrary as NH_3 is highly volatile. If the authors are introducing the NH_3 from the “background gas”, I'd suggest at least an estimate of the typical NH_3 level (e.g., through a supplementary measurement of typical background NH_3 concentration in your lab, or provide the measured NH_3 level in the vicinity environments), and do a calculation to check whether all the NH_3 would have been depleted by the organic acids at your measured concentration level.

2. What on earth is the definition of CCN size in this paper?

3. The results seem to suggest that the measured NH_4 concentration is more than enough to neutralize the inorganic acids (SO_4 , NO_3 and Cl) (Eq. 1), while not enough to neutralize all organic acids (CO_2^+), as “the amount of CO_2^+ required for neutralizing ammonium accounted for the 27.0 ± 3.1 % of total CO_2^+ mass in the nucleated SOA experiments, and 18.7 ± 6.0 % in the seeded SOA experiments”. If so, then ammonia would be the limiting species, the concentration of which should be determined by available total ammonia concentrations. In this case, it is confusing why the NH_4^+ would correlated to gas-phase organic acids. If the authors don't really think the CO_2^+ all comes from organic acids, it should be clarified in the manuscript.

4. Following above question, the good correlations among gas-phase organic acids and NH_4^+ should be expected if the gas-phase organic acids are the limiting species, with total ammonium more than enough to influence the partitioning equilibriums. The results seem self-conflicting.

5. The authors argue that “The reaction of HNO_3 and NH_3 takes precedence over the reaction between organic acids and NH_3 ” (Line 186). Fig. 1 also shows formation of sulfate and nitrate from photooxidation of SO_2 and NO_x . If so, the influences from inorganics should be first excluded in analyzing the correlations of NH_4^+ and gas-phase organic acids (Fig. 5). Instead of AMS NH_4^+ , the difference between measured

NH₄⁺ and that predicted by stoichiometric neutralization analysis of inorganic acid (Eq. 1) should be used (i.e., Free NH₄⁺ = NH₄⁺,meas - NH₄⁺,pre). This is similar concept with the correction of (NH₄)₂SO₄ for the seeded experiment in Fig. 5. How would the correlation look like after this kind of correlation?

Minor concerns

1. There're some typos in the manuscript. For example, Line 59, "updake" should be "uptake". Line 131, "aftert" should be "after". Line 135, there's duplicate periods. The manuscript should be read through more carefully.

2. I'd suggest name the predicted NH₄⁺ differently for that based on Eq. 1 and Eq. 2, i.e. that predicted with / without consideration of CO₂⁺.

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