Responses to Referee 2:

The authors thank the reviewer for her/his excellent comments. We have modified our manuscript according to the reviewer's comments. All the changes that we have made were saved as a format of "Track Changes" in the manuscript.

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 NH4+. 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.

Reply:

We thank the referee for the positive comments.

Major concerns

1. How did the authors estimate the NH3 concentration in the chamber "by assuming that the particulate ammonium salt (NH4+) was converted from the gas-phase NH3 (Fig. 1)"? Did the authors assume a 1:1 conversion ratio, namely all gas-phase NH3 are converted to NH4+? If so, this assumption is too arbitrary as NH3 is highly volatile. If the authors are introducing the NH3 from the "background gas", I'd suggest at least an estimate of the typical NH3 level (e.g., through a supplementary measurement of typical background NH3 concentration in your lab, or provide the measured NH3 level in the vicinity environments), and do a calculation to check whether all the NH3 would have been depleted by the organic acids at your measured concentration level.

Reply:

We would like to highlight that our estimation gives the lowest boundary for the possible NH_3 concentration. Hence, in our estimation we indeed assumed a conversion ratio of 1:1.

The ammonia was unintentionally introduced to the chamber quite likely with the pressurized air and water used for humidification. Unfortunately, we lacked the ammonia measurement device in our lab. Based on a statistics study by Salonen et al (2009) on the ammonia in 14 Finnish office buildings where there were no specific emission source, the indoor concentrations varied between 1-49 ug m^{-3} with a geometric mean concentration of 14 ug m^{-3} (corresponds 19 ppbV). If we assume that ammonia concentrations in our experiments are on the same order with the highest value reported in Salonen et al. study, we can assume that in the beginning of photooxidation reaction after UV lights were switched on, the ammonia concentration is higher than organic acid concentration, and organic acids should be the limiting species. As photooxidation reactions went on and organic acids formation accumulated in the chamber, their concentration was higher than ammonia, and the ammonia was a limiting species and would be neutralized by the organic acids at the end. However, it is still an open question about the distribution of organic ammonium: how much they are present in the gas phase and how much in the particle phase?

Accordingly, we have added in line these in line92, page 3 that "In two sets of experiments, ammonia was introduced to the chamber as an impurity. The likely sources of ammonia were the pressurized air, possible leakage of the lab air and water used for humidification".

And also in line 126, we added that "The maximum NH_4^+ concentration was in the range of 1.17~1.51 μg m^{-3}, which corresponds to a minimum NH_3 concentration level of 1.6 ~ 2.1 ppbV in our chamber. The NH_3 mixing ratio over continental range is typically between 0.1 and 10 ppb (Seinfeld and Pandis, 2016). A statistics study on the ammonia concentration in 14 Finnish office buildings shows a range of 1-49 ug m^{-3} and a geometric mean concentration of 14 ug m^{-3} (corresponds 19 ppbV) (Salonen et al., 2009). Hence, our method should provide a lowest boundary of ammonia mixing ratio in the chamber."

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

Reply:

The CCN size naturally depends on particle composition, but in general, it is often assumed that atmospheric aerosol particles larger than 100 nm are able to active to cloud droplets. AMS measurement range is 35-1000 nm, and the aerosol mass is centered on the larger sizes, hence we can state that our measurements are in CCN size range. We have now clarified this in line 145, page 4 that "As the measured mass is centered on the larger sizes of AMS measurement range (35-1000nm, Jayne et al., 2000; Zhange et al., 2004), we can state that the measurements represents CCN relevant particle sizes (in general it is often assumed that atmospheric aerosol particles larger than 100 nm are able to active to cloud droplets)."

3. The results seem to suggest that the measured NH4 concentration is more than enough to neutralize the inorganic acids (SO4, NO3 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 CO2+ all comes from organic acids, it should be clarified in the manuscript.

Reply:

We thank the referee for the excellent comment and the next one. The referee is correct that NH_4^+ is sufficient to neutralize the inorganic acids, but not adequate to neutralize organic acids, and it is a limiting species, as we have speculated in the reply to the first general comment.

We would first make it clear that in our study the NH_4^+ is observed to correlate to the C1-C5 monoacids and two diacids, but not all organic acids, e.g. no correlation to pinonic acid. Fig. C1 shows time series of the particle-phase total $CO_2^+{}_{\_total}$ (green), the ammonium resulting from organic acids ($NH_4^+{}_{\_orgacid}$) , and gas-phase formic acid and pinonic acid in the nucleated SOA experiments. The formic acids was selected to represent the low molecule-weight (MW) organic monoacids, and pinonic acid (molecule weight is 184) was chosen to represent high MW organic acid. We can see that:

(1) The time series of the total particulate organic acids ($CO_2^+{}_{\_total}$ in Fig. C1) is not following the low MW organic acids (formic acid), nor the high MW organic acids (pinonic acid), suggesting that particulate organic acids were not derived from one single type of gas organic acids.

(2) The formation of $NH_4^+{}_{\_orgacid}$ is mainly related to the low MW organic monoacids. We can see that the trend of formic acid formation is consistent with $NH_4^+{}_{\_orgacid}$. In the experiments, we observed a high production of these low MW organic monoacids: their concentrations were about one or two orders of magnitude greater than the concentration of high MW acids. Hence, compared with the high MW acids, the low MW monoacids dominated the reaction with ammonia in the gas phase if we assume similar reaction rate constants $k_{orgacid}$ for both low- and high- MW acids with ammonia ($R=k_{orgacid}\cdot[OrgAcid]\cdot[NH_3]$), and the majority of $NH_4^+{}_{\_orgacid}$ are associated with the low MW monoacids. Therefore, $NH_4^+{}_{\_orgacid}$ is well correlated to the low-MW organic monoacids. We need to point out that although the low MW organic monoacids dominate the ammonia reaction, the formed ammonium salts are still volatile, so we speculate that a large amount of them are present in the gas phase.

(3) Inconsistency between the formation of high MW organic acids and the $NH_4^+{}_{\_orgacid}$. Here we use pinonic acid as an example because it is a high MW organic acid that has been measured in our work. The vapor pressure of pinonic acid is about 4-5 orders of magnitude lower than those of C1-C5 monoacids (Jimenez et al., 2009), and its reactivity to ammonia is more than 500 times lower than that of C1-C5 monoacids. This allows pinonic acid to condense directly on the particle phase before it reacts in large amount with ammonia. These condensed high-MW organic acids are efficient to fragment to form CO_2^+ in AMS, and produced more than 73.0 % and 81.3% of the observed CO_2^+ in the nucleated and seeded SOA experiments, respectively. The remaining CO_2^+ signals (less than 27.0 % and 18.7 %) came from the interaction between low MW organic acids and ammonia. Our analysis is also consistent with other studies showing that the CO_2^+ detected in AMS is caused by the thermal decomposition of the mono-, di-, and poly carboxylic acid groups, and is related to high MW oxygenated organic species (e.g. Zhang

et al., 2005; Alfarra et al., 2004). We still want to point out that the $CO_2^+$$_{_total}$ accounts for 2.7% to 7.0% of SOA mass at maximum in each experiments, and it is very possible that the high-MW organic acids contributed to the majority of these $CO_2^+$$_{_total}$.

So, our above analysis interprets the observation that $NH_4^+$$_{_orgacid}$ correlates well to the low MW organic monoacids, even $CO_2^+$$_{_NH4}$ accounts for only 27.0 % and 18.7 % of the total CO_2^+.

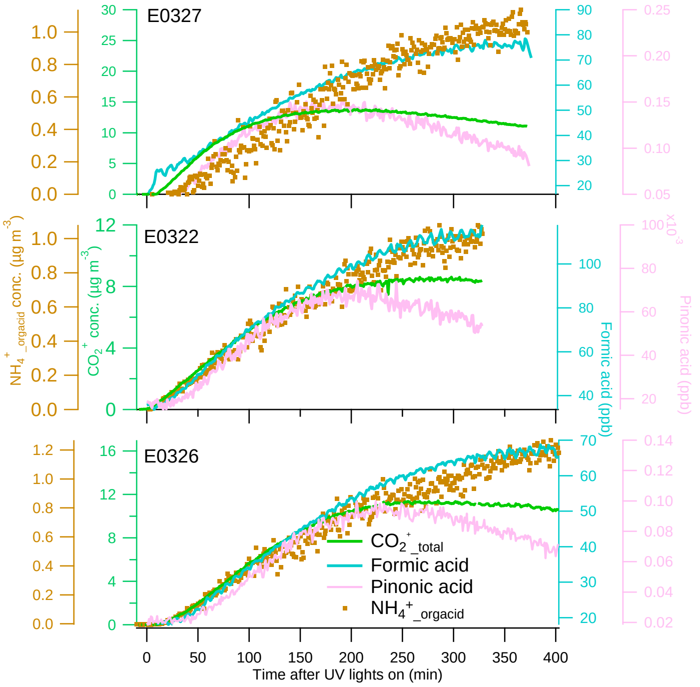

Figure C1. The evolution of time series of the particle-phase total $CO_2^+$$_{_total}$ (green), the formed ammonium attributed to organic acid neutralization ($NH_4^+$$_{_orgacid}$), and gas-phase formic acid and pinonic acid in the nucleated SOA experiments. Formic acid is chosen to represent C1-C5 organic monoacids and pinonic acid as a high molecule-weight organic acid.

4. Following above question, the good correlations among gas-phase organic acids and NH4+ 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.

Reply:

As we have replied to the prior comment, ammonia is the limiting species in our experiments. The majority of $NH_4^+$$_{_orgacid}$ are associated with the low MW monoacids, and the high-MW organic acids contributed to the majority of the observed CO_2^+. Our analysis is consistent with the observation that $NH_4^+$$_{_orgacid}$ correlates well to the low MW organic monoacids.

5. The authors argue that "The reaction of HNO3 and NH3 takes precedence over the reaction between organic acids and NH3" (Line 186). Fig. 1 also shows formation of sulfate and nitrate from photooxidation of SO2 and NOx. If so, the influences from inorganics should be first excluded in analyzing the correlations of NH4+ and gas phase organic acids (Fig. 5). Instead of AMS NH4+, the difference between measuredNH4+ 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?

Reply:

Following the referee's comment, in the nucleated SOA experiments, the sulfate, nitrate and chloride related ammonium was excluded from the $NH_4^+$$_{_mea}$, so only organic acid-related ammonium was used for plotting in Figs. 5-7. The identical analysis protocol was applied in both nucleated and seeded SOA experiments. After we did the analysis suggested by the referee, the correlation coefficients don't change much (table C1). Meanwhile, we also noticed an error in the seeded SOA experiments, that is, we misused ammonium-related organic acids for X-axis in Figs. 5-7; Instead, the correct one should be organic acids-related ammonium. The mistake doesn't affect any of our conclusion, but after correction, the correlation relationship is becoming better in the figures.

Table C1. The correlation coefficients in the new and old figures.

Correlation species	Correlation coefficient (r^2)			
	Nucleated SOA(old)	Nucleated SOA(new)	Seeded SOA(old)	Seeded SOA(new)
Butyric acid vs $NH_4^+{}_{\_orgacid}$ (Fig.5)	0.97-0.97	0.88-0.95	0.68-0.73	0.76-0.83
$C_4H_8O_2^+$ vs $NH_4^+{}_{\_orgacid}$ (Fig.5)	0.98-0.99	0.90-0.97	0.04-0.74	0.12-0.80
Pentanoic acid vs $NH_4^+{}_{\_orgacid}$ (Fig.5)	0.89-0.94	0.84-0.92	0.22-0.63	0.27-0.62
$C_5H_{10}O_2^+$ vs $NH_4^+{}_{\_orgacid}$ (Fig.5)	0.90-0.94	0.84-0.91	0.05-0.10	0.0-0.14
Formic acid vs $NH_4^+{}_{\_orgacid}$ (Fig.6)	0.94-0.99	0.95-0.97	0.76-0.86	0.81-0.87
Acetic acid vs vs $NH_4^+{}_{\_orgacid}$ (Fig.6)	0.89-0.98	0.97-0.98	0.74-0.84	0.80-0.84
Propionic acis vs $NH_4^+{}_{\_orgacid}$ (Fig.6)	0.91-0.98	0.96-0.97	0.69-0.74	0.72-0.79
Succinic acid vs $NH_4^+{}_{\_orgacid}$ (Fig.7)	0.94-0.97	0.91-0.94	0.70-0.81	0.51-0.81
Malonic acid vs $NH_4^+{}_{\_orgacid}$ (Fig.7)	0.95-0.96	0.79-0.90	0.44-0.68	0.42-0.67

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.

Reply:

The typos were corrected and we have read the manuscript 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+.

Reply:

We have changed $NH_4^+{}_{,pre}$ to $NH_4^+{}_{,pre\_CO2}$ in Eq. 2.

Reference

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