Responses to Referee 1:

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 new findings on the role ammonia in the formation of SOA from photooxidation of alpha-pinene. Neutralization of carboxylic acid by ammonia in the gas phase is reported as a process of CCN-sized SOA formation. PTR-MS and AMS were mainly used to measure relevant species in gas and particle phase, respectively, and to interpret the measured data for the neutralization. Although this manuscript is unique and concise, there are several main questions to be clarified.
1) In this manuscript key data used to support the process are correlations between organic acids and particulate ammonium. Mixing ratio of ammonia might be a critical factor in the photooxidation of smog chamber. It is not clear about the introduction to a rector bag and mixing ratio of ammonia in the bag. The authors report N/C ratio remained consistent, implying negligible formation of organonitrogen via particle phase reaction. Reaction pathways might be largely dependent on the mixing ratio of ammonia.

Reply:
Both referrers are concerned about the introduction of ammonia and its concentration in this study. We would like to point out that ammonia was not intentionally introduced to the chamber, but it was present as an impurity. Likely sources of ammonia were pressurized air, possible leakage of lab air, and water used for humidification of the chamber. We have added 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".

As we have stated in the manuscript in line 124-128 that we unfortunately lacked the measurement of NH_3 concentration in the chamber but estimated the minimum concentration of NH_3 present from our AMS measurement results, by assuming that the particulate ammonium salt (NH_4^+) was converted from the gas-phase NH_3 (Fig. 1). 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 10ppb (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. We have added the discussion in page 4 in the manuscript.

According to Salonen et al., the detected highest ammonia concentration at Finnish office building is 49 ug m^{-3} (corresponding to 64ppb). This gives an approximatively higher limit for the order of expected ammonia concentration that we can use to perform the following analysis. Based on PTRMS measurements, we estimated the formed organic acid concentration to be about 50-250ppb at the end of our experiments. After comparison of the concentrations to the two species, the ammonia was a limiting species and would be neutralized by the organic acids at the end.

The referee's comments also guide us to recheck the N/C ration in both nucleated and seeded SOA experiments (Fig C1). Regardless of the relatively high noise level of our data, we can see the nearly constant or small time dependent increase in N/C ratio in both sets of experiments. Therefore, line 285 page 8, we have reworded the statement "After SOA are formed, carbonyl group of chemical compounds in SOA particles can also uptake NH_3 heterogeneously to form nitrogen-containing compounds (Zhu et al., 2018; Liu et al., 2015; Updyke et al., 2012; Dinar et al., 2007) and organic ammonium salts (Schlag et al., 2017). However, in this study the N:C ratios measured by AMS remained nearly constant at 0.002 for E0322 and E0326 and 0.004 for E0327 suggesting that the carbonyl-NH_3 heterogeneous reaction could be negligible." to "After SOA are formed, carbonyl group of chemical compounds in SOA particles can also uptake NH_3 heterogeneously to form nitrogen-containing compounds (Zhu et al., 2018; Liu et al., 2015; Updyke et al., 2012; Dinar et al., 2007) and organic ammonium salts (Schlag et al., 2017). Similarly, in this study the N:C ratios measured by AMS

were nearly constant or slightly increasing in two sets of experiments (Fig. C1), suggesting the formation of nitrogen-containing compounds via carbonyl-NH_3 heterogeneous reaction.".

Definitely, we strongly agree with the referee that the accurate measurement of ammonia in the chamber is critical to understand the detailed mechanisms of neutralization of gas-phase organic acids, formation of particulate CO_2^+ and formation of NOC in the specific experiments.
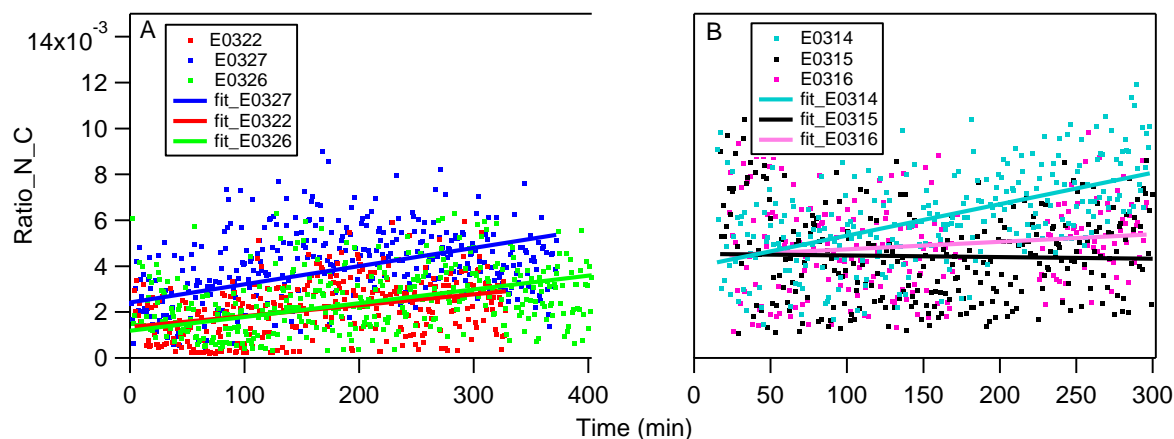

Figure C1. The N:C ratios determined by AMS in (A) the nucleated SOA experiments, and (2) in the seeded SOA experiments.

2) For seeded experiments alpha-pinene concentration was too low compared to nucleation experiments. It is uncertain why such low concentration was used for seeded cases. It makes difficult to clearly show the temporal variation of organic acids. In seeded experiments correlation of organic acids with ammonium are not apparent as much as in nucleation experiments, probably due to lower concentration of alpha-pinene. A result stated in P5, line 181-183 (48.6 times lower concentration of CO2+ for seeded experiment) might be just due to lower initial α-pinene concentration for seeded condition (23 times lower).

Reply:

We agree with the referee that in the seeded experiments αlpha-pinene concentration was about 20 times lower than in the nucleation experiment. The relatively low αlpha-pinene concentration was adopted to mimic an atmospherically relevant monoterpene mixing ratio, for example, in Hyytiälä forest area in Finland (e.g. Kourtchev *et al.*, 2006). We aimed to study if the ammonia plays a similar role as in the high a-pinene concentration case. Meanwhile, in the presence of seed aerosol, the relative low a-pinene can produce detectable amount of secondary organic aerosol (SOA) for the aerosol mass spectrometer (AMS). As the referee pointed out, the correlation of organic acids with ammonium is less obvious in the seeded, low αlpha-pinene concentration experiments compared to the nucleation experiments. Part of reason is that in the seeded experiments, the produced ammonium resulting from organic acid neutralization ($NH_4^+{}_{orgacid}$) is around 40 times less than in the nucleated cases. Such small amount of $NH_4^+{}_{orgacid}$ (at about 0.03 ug m^{-3} level) made the determination to its concentration be noisy by AMS. Hence, its correlation to organic acids is worse in the seeded experiments than in the nucleated SOA experiments. Nevertheless, the results in two sets of experiments are consistent making our conclusion even stronger.

3)

3.1) Figure 3 apparently show the difference in a lag time of CO2+_NH4. It was partly explained that nitric acid delayed its accumulation in high NOx condition. More explanation might be necessary for the delay in low NOx conditions.

Reply:

A lag in time for $CO_2^+{}_{NH4}$ is also observed in the low NO_x conditions, especially in the seeded experiments. The reasons for the observed delay is again affected by the nitric acid arising from the background NO_x photooxidation, where we have observed particulate nitrate formation (Fig C2). The

other reason is that the formation of particulate organic acids was much slower in the seeded experiments compared to the nucleated cases (Fig C3), implying that their reaction with ammonia was also delayed.

Accordingly, we have added the argument in line 189 " In the low-NO_x test, a time lag for $CO_2^+{}_{\_NH4}$ is also observed, especially in the seeded SOA experiments. The delay is caused by the effect of nitric acid arising from the background NO_x photooxidation. In addition, the slower formation of particulate organic acids makes their reaction with ammonia delayed in the seeded experiments compared to the nucleated cases."
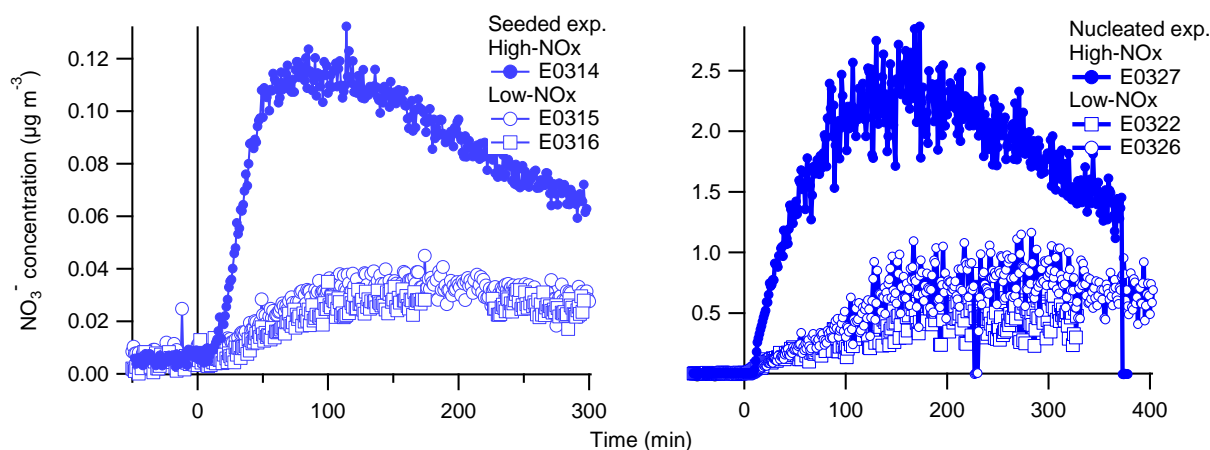

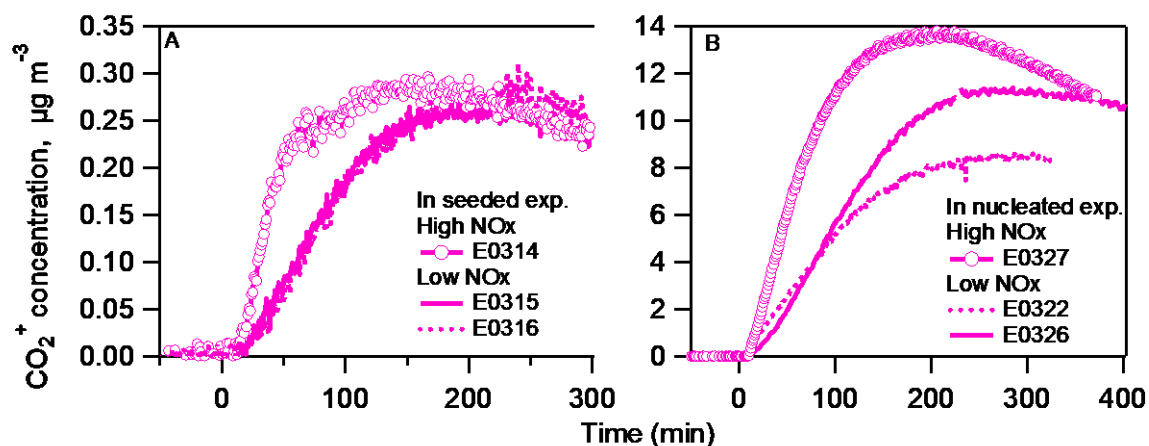Figure C2. The formed nitrate aerosol measured by AMS in the seeded SOA experiment.

Figure C3. The measured CO_2^+ ion concentration measured by AMS (A) in the seeded and (B) in the nucleated SOA experiments. CO_2^+ ion was chosen to represent organic acids. The formation rate of CO_2^+ in seeded experiments was much slower than in the nucleated cases.

3.2) Very limited amount of CO2+_NH4 was formed roughly at 1/100 of SOA in mass both in nucleation and seeded experiments. Is it caused by limit in the available low MW carboxylic acids, ammonia, or other factors? It is probably associated with the contribution of neutralization and its atmospheric implication due to the omnipresence of NOx and nitric acids.

Reply:

In the two sets of experiments, the total CO_2^+ ions account for 2.7% to 7.0% of SOA in mass (Fig. C4). Out of the CO_2^+ ions, only 27.0 ± 3.1 % and 18.7 ± 6.0 % have participated in the reaction with ammonia in the nucleated and the seeded SOA experiments, respectively. This explains why $CO_2^+{}_{\_NH4}$ is roughly 1/100 of SOA in mass. In our experiments, the ammonia could be a limiting species. The produced low-MW carboxylic acid concentration is about one or two orders of magnitude greater than the high-MW acids. Hence, the reaction between low-MW organic acids and ammonia dominated over the reactions between high-MW acids and ammonia. The vapor pressure of the formed low-MW organic ammonium

salts is in the same order as their parental acids. Therefore, we speculate that a large amount of these low-MW organic ammonium salts were present in the gas phase and a minor amount of ammonium salts have participate on the particulate phase, contributing to CO_2^+_NH4. The amount of CO_2^+_NH4 is assumed to be related to: (1) the photooxidation and ozonolysis capacity in our chamber, which determines the amount of particulate organic acids (total CO_2^+), (2) the relative amount of low- and high- MW organic acids and their physicochemical properties, (3) the relative amount of inorganic and organic acids, and (4) the relative amount of ammonia and total acids. We have added the discussion in line 190 in the manuscript.
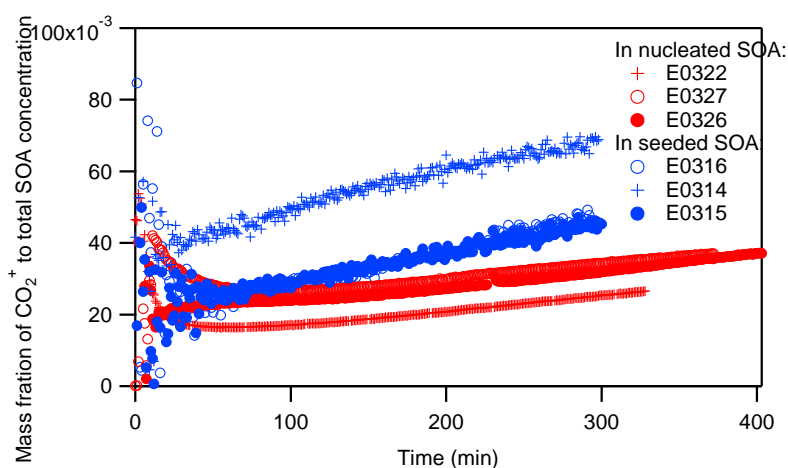

Figure C4. The mass fraction of total CO_2^+ ions to the SOA mass.

4) Although a previous paper (Friedman and Farmer, 2018) also reported the formation of low molecular weight organic acids as observed in this manuscript, little information is available about the formation mechanism of those species. Even a brief introduction of the formation mechanism would be very useful in the understanding of neutralization process.

Reply:

The formation of low molecular weight organic acids remains unclear in the photochemical reaction of α-pinene (e.g.Friedman and Farmer, 2018). It can be speculated that these organic acids were produced as products of stabilized Criegee intermediate associated with ozonolysis of α-pinene and double carbon bond-containing products (Jacob and Wofsy, 1988; Orzechowska and Paulson, 2005). The statement is verified by the fact that we have observed the highest O_3 formation at the highest NO_x/VOC_x initial input in E0314 (Figure C5). In E0314, we also have observed higher concentrations of C1-C5 monoacids corresponding to higher ozonolysis reactivity (Figure C6). The specific formation mechanisms of the organic acids need to be investigated in the future studies. We have included the discussion and the figures C5 and C6 in the manuscript.
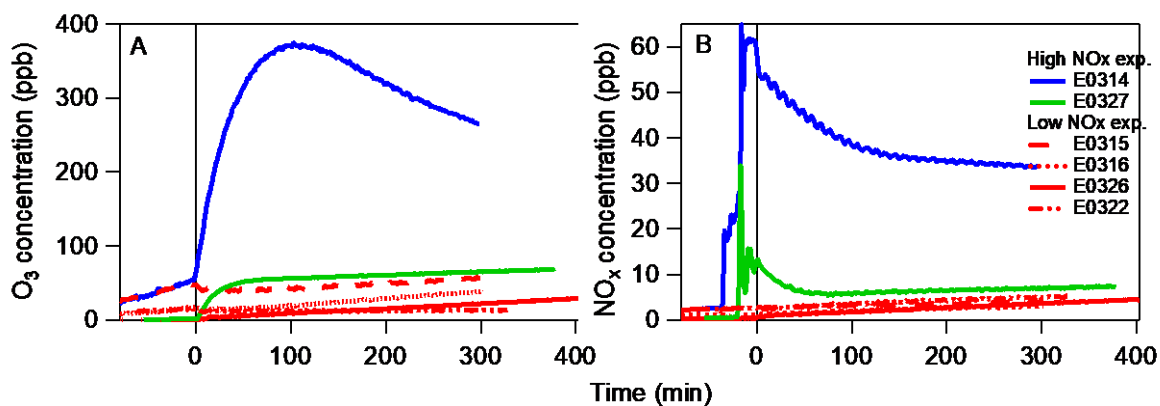

Figure C5. The O_3 and NO_x concentration in the chamber. The high NO_x injection led to high O_3 concentration in the chamber (in blue).
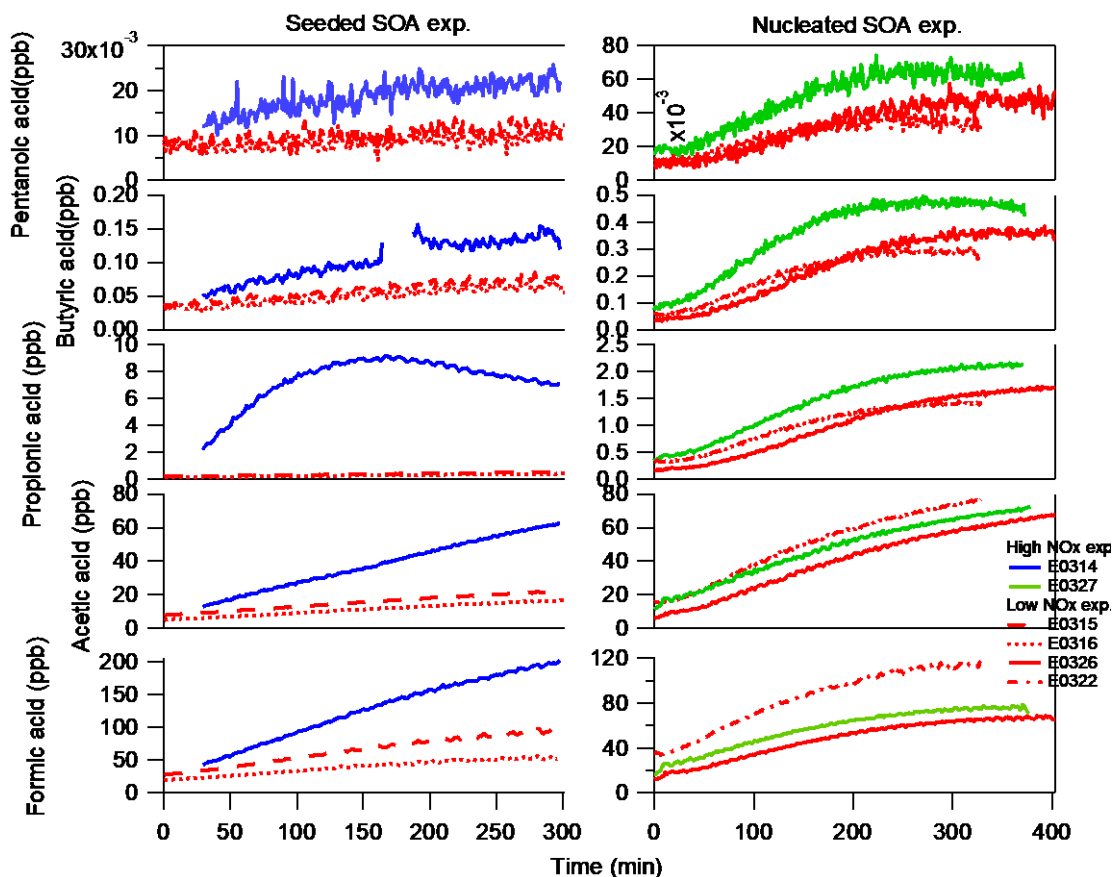
Figure C6. The concentrations of C1-C5 organic monoacid in the seeded (left panels) and nucleated (right panels) SOA experiments. The higher NO_x input in E0314 (in blue) also led to higher ozone formation and eventually led to higher organic acids concentration resulting from ozonolysis reaction. Refer to Fig. C5 and text for more details.

Overall, I would recommend the publication of the manuscript if the authors can address my questions and comments.

Minor comments are show below.

P3, line 89-91: H2O2 was introduced as a source of OH radical. Although OH exposure is presented in Table 1, H2O2 concentration itself is informative for readers.

Reply:

The H_2O_2 concentration is not measured in the chamber. Based on the volume of injected H_2O_2 solution and the chamber volume, we estimated its concentration to be 30ppm. We have added in line91 that "The H_2O_2 concentration was roughly 30ppm estimated from the amount of its injection and the volume of chamber".

P5, line 173, 179: It is curious why chloride ion was added in the estimation of NH4+, since there was no source of chloride in the smog chamber experiments.

Reply:

There was a tiny amount of formed ammonium chloride after UV lights were switched on, e.g. in the nucleated SOA experiment (Fig. C7). Hence, we used it for ammonium estimation.
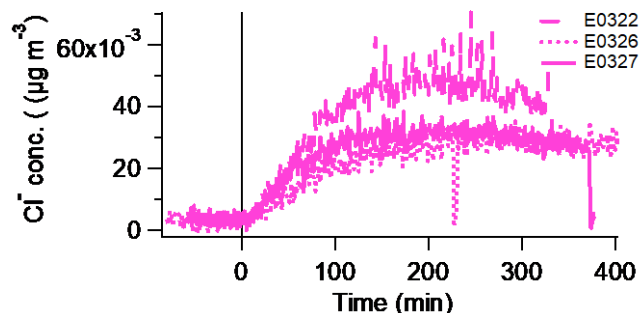
Figure C7. The concentration of chloride measured by AMS in the chamber.

P6, Line 228: "Fig. 4" might a typo of "Fig. 6".

Reply: We have fixed it.

P7, line 270-274: Diacids such as malonic and succinic acids have vapor pressure similar to pinonic acid. Differently from pinonic acid, those diacids showed good correlation with ammonium. This might mean continuous formation of those diacids. It is not clear how these nonvolatile diacids could form in the gas phase until the later part of photooxidation.

Reply:

We thank the referee for the insightful comment. The referee is correct to say that this indicates the continuous formation of those diacids in the gas phase at the later stage of photooxidation. Their formation mechanism is unclear for us and might be similar to the low MW monoacid. We rephrased the sentence in line 272-274 "The nice correlations of the gas-phase malonic and succinic acids to the particle-phase ammonium in this study suggest that diacids contribute to the formation of ammonium in both nucleated and seeded SOA experiments." to "The nice correlations of the gas-phase malonic and succinic acids to the particle-phase ammonium study suggest that diacids contribute to the formation of ammonium in both nucleated and seeded SOA experiments. It also indicates the continuous formation of those diacids at the later stage of photooxidation in nucleated and seeded experiments. The formation mechanism of these low molecule-weight diacids remains unclear for us and might be similar to the C1-C5 monoacids.".

P9, Line 316: "affective" might be a typo of "effective".

Reply: we have fixed it.

P15, Table 1: a-Pinene might be a typo of "alpha-Pinene".

Reply: we have fixed it.

P18, Figure 3: In the caption, "SOA" needs to be deleted in ": : : (B) SOA seeded experiments : : :"

Reply: we have fixed it.

P20, Figure 5: In the caption, "the AMS NH4+ is the difference between NH4+,pre and NH4+,mea, refer to the text for details." needs to be clarified. In the text NH4+,pre and NH4+,mea are defined, whereas "AMS NH4+" is not defined. It should be defined clearly in the caption, e.g., NH4+,mea - NH4+,pre. It should be clarified in the caption of figures 6 and 7. It might be better to move the position of "x10-3" to improve the readability in the figure. It is same in figures 6 and 7.

Reply:

Both referees brought up comments on the same question. Following the comment, we have renewed the X-axis with $NH_4^+{}_{\_orgacid}$ in Figs. 5-7 in both nucleated and seeded SOA experiments. $NH_4^+{}_{\_orgacid}$ is the amount of ammonium neutralized by the organic acids.

P21, Figure 6: Readers might expect to see plots of AMS data also as Figure 5.

Reply: we have fixed it.

P22, Figure 7: Readers might expect to see plots of AMS data also as Figure 5.
Reply: we have fixed it.

It is worthy to clearly note in the text that all particulate data were not corrected to wall loss of particulate.
Reply:
We have made it now clear in line 147, page 4 that "Additionally, the organics, nitrate and ammonium aerosols showed similar mass-based size distributions from our AMS measurement (Fig. 4), and internally-mixed aerosol can be assumed in our study, indicating that the aerosol components were lost in a similar rate to the chamber wall. Therefore, no loss correction to the aerosol wall disposition was conducted in this work."

In the figure, axis titles need to be checked to properly note "NH4+", "SO42-", and "NO3-".
Reply: we have fixed all of them.

Reference:
Friedman, B. and Farmer, D.K., SOA and gas phase organic acid yields from the sequential photooxidation of seven monoterpenes, Atmos. Environ., 187, 335-345, 2018.
Jacob, D. J. and Wofsy, S. C.: Photochemistry of biogenic emissions over the Amazon forest, J. Geophys. Res., 93, 1477–1486, doi:10.1029/JD093iD02p01477, 1988.
Kourtchev, I., Giorio, C., Manninen, A., Wilson, E., Mahon, B., Aalto, J., Kajos, M., Venables, D., Ruuskanen, T., Levula, J., Loponen, M., Connors, S., Harris, N., Zhao, D., Kiendler-Scharr, A., Mentel, T., Rudich, Y., Hullquist, M., Doussin J., Maenhaut, W., Back, J., Petaja, T., Wenger, J., Kulmala, M. and Kalberer, M., Enhanced volatile organic compounds emissions and organic aerosol mass increase the oliger content of atmospheric aerosols, Sci. Reports, 6, 35038, 2016.
Orzechowska, G.E., and Paulson, S.E.: Photochemical sources of organic acids. 1. Reaction of ozone with isoprene, propene, and 2-butenes under day and humid conditions using SPME, J. Phys. Chem. A, 109, 5358-5365, 2005.
Salonen, H., Pasanen, A., Lappalainen, S.K., Riuttala, H.M., Tuomi, T.M., Pasanen, P.O., Back, B.C. and Reijula, K.E., Airborne concentrations of volatile organic compounds, formaldehyde and ammonia in Finnish office buildings with suspected indoor air problems, Journal of Occupational and Environmental Hygiene, 6, 200-209, 2009.
Seinfeld, J.H. and Pandis, S.N., Atmospheric chemistryand physics: From air pollution to climate change, 3rd edition, John Wiley & Sons, Inc.,2016.

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."

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 (CO₂⁺), as "the amount of CO₂⁺ required for neutralizing ammonium accounted for the 27.0 _ 3.1 % of total CO₂⁺ 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 NH₄⁺ 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^+.
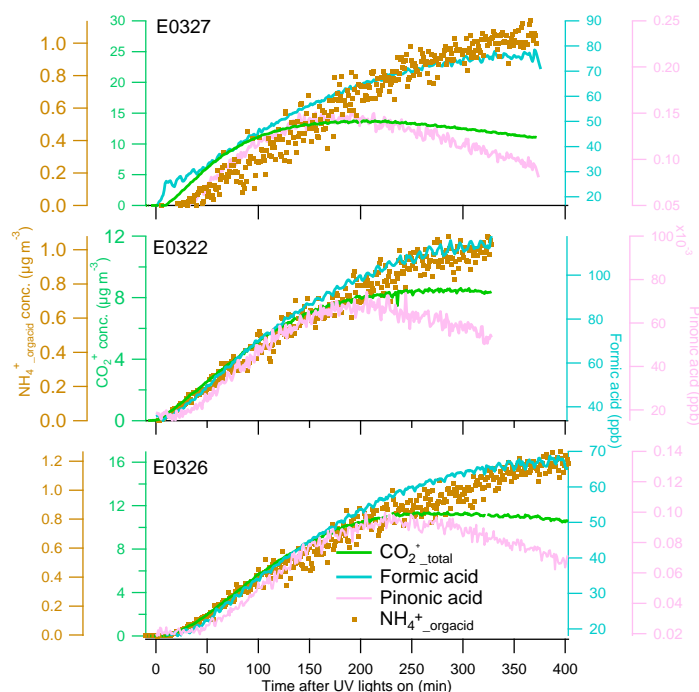

Figure C1. The evolution of time series of the particle-phase total $CO_2^+{}_{\_total}$ (green), the formed ammonium attributed to organic acid neutralization ($NH_4^+{}_{\_orgacid}$), and gas-phase formic acid and pinonic acid in the nucleated SOA experiments. Formic acid is chosen to represent C1-C5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

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Direct contribution of ammonia to CCN-size αlpha-pinene secondary organic aerosol formation

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Abstract. Ammonia (NH_3), a gasous compound ubiquitiously present in the atmosphere, is involved in the formation of secondary organic aerosol (SOA), but the exact mechanism is still not well known. This study presents the results of SOA experiments from the photooxidation of α-pinene in the presence of NH_3 in the reaction chamber. SOA was formed in nucleation experiment and in seeded experiment with ammonium sulfate particles as seeds. The chemical composition and time-series of compounds in the gas- and particle- phase were characterized by an on-line high-resolution time-of-flight proton transfer reaction mass spectrometer (HR-ToF-PTRMS) and a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS), respectively. Our results show that for the aerosol particles in cloud condensation nuclei (CCN) size, the mass concentration of ammonium (NH_4^+) was still rising even after the mass concentration of organic component started to decrease due to aerosol wall deposition and evaporation, implying the continuous new formation of particle phase ammonium in the process. Stoichiometric neutralization analysis of aerosol indicates that organic acids have a central role in the formation of particle phase ammonium. Our measurements show a good correlation between the gas phase organic mono- and di-carboxylic acids formed in the photooxidation of α-pinene and the ammonium in the particle phase, thus highlighting the contribution of gas-phase organic acids to the ammonium formation in the CCN-size SOA particles. The work shows that the gas-phase organic acids contribute to the SOA formation by forming ammonium salts through acid-base reaction. The changes in aerosol mass, particle size and chemical composition resulting from the NH_3-SOA interaction can potentially alter the aerosol direct and indirect forcing and therefore alter its impact on climate change.

1 Introduction

The largest uncertainty in forward projection of global warming is related to our limited knowledge of negative solar radiative forcing associated with aerosols (IPCC, 2013). Formation of secondary organic aerosols (SOA) is one of the main processes that affects the composition and properties of atmospheric aerosols. Formation of SOA occurs through two distinct mechanisms: by increasing the mass of the existing aerosol and through the formation of new particles. Estimate on the SOA formation shows its significance as a source of atmospheric organic aerosol: about 60% of the organic aerosol mass is SOA on the global scale and regionally even more (Hallquist *et al*., 2009; Jimenez et al., 2009; Kanakidou *et al*., 2005). Hence, SOA plays an important role in the direct scattering of solar radiation, cloud formation and precipitation, and visibility reduction, and may also have a direct impact on human health.

Ammonia (NH_3) is ubiquitously present in the atmosphere as a dominant volatile base. The majority of its sources is accounted by emissions from agriculture, livestock, soil and traffic (Huang et al., 2012; Grönroos et al., 2009; Battye et al., 2003). NH_3 governs the neutralization of atmospheric aerosol by reacting with the inorganic acids such as sulfuric acid and nitric acid, leading to transformation of a substantial amount of ammonium sulfate (and

derivatives) and ammonium nitrate (Seinfeld and Pandis, 2016). These inorganic salts play a vital role in contributing to the fine particle matter (PM2.5) and altering the chemical and physical properties of aerosol particles in the atmosphere. The mechanism between NH_3 and the inorganic acids leading to the secondary inorganic aerosol has been well recognized.

A number of studies have shown that NH_3 is one of the key species for the new particle formation through ternary and binary nucleation with water and sulfuric acid (e.g. Lehtipalo et al., 2018; Jokinen et al., 2018; Bianchi et al., 2016; Kirkby et al., 2011; Kurten et al., 2007; Kulmala et al., 2000). The nucleated particles are a significant source of atmospheric SOA particles and subsequent growth to a larger size (>50nm) allows them to serve as cloud condensation nuclei (CCN). However, the role of NH_3 for the CCN-size SOA particles are still rarely studied. A study, conducted more than a decade ago, demonstrated that NH_3 increased the number and volume concentrations of CCN-sized SOA particles from α-pinene-ozone system by 15% and 8%, respectively, (Na et al., 2007). Similar results have also been observed in the photooxidation and ozonolysis of a-pinene SOA experiments that SOA mass yield increased by 13% as a response to NH_3 addition (Babar et al., 2017). Besides, the addition of NH_3 could also promote the SOA formation from photooxidation of vehicle exhaust (Chen et al., 2019; Liu et al., 2015), anthropogenic VOCs (Wang et al., 2018; Huang et al., 2018) and acrolein (Li et al., 2019). The promotion mechanism of NH_3 to SOA formation can be both through base-acid reaction (Schlag et al., 2017; Babar et al., 2017; Rubach et al., 2013; Mensah et al., 2012; Na et al., 2007) and by the NH_3 uptake to the carbonyl group (Zhu et al., 2018; Liu et al., 2015). As a consequence, the changes in particle size and chemical composition could alter the CCN ability and hygroscopicity of SOA particles (Dinar et al., 2008). Moreover, the reaction of NH_3 with SOA decreases the volatility of SOA particle (Paciga et al., 2014), and also results in production of light-absorbing brown carbon compounds that modify the optical properties of the aerosols (Huang et al., 2018; Updyke et al., 2012; Bones et al., 2010). Additionally, the ~~updake~~ uptake of NH_3 by SOA can deplete ambient NH_3 concentrations, causing indirect reductions in the amount of inorganic ammonium salts in particulate matter (Horne et al., 2018). Therefore, the interaction of NH_3 and SOA could alter both direct and indirect aerosol radiative forcing and potentially alter its impact on climate change.

This work presents the results of SOA formation from photooxidation of α-pinene in the presence of NH_3 in the nucleation and seeded experiments. The chemical composition of gas-phase and particle-phase compounds were characterized with a high-resolution time-of-flight proton transfer reaction mass spectrometer (HR-ToF-PTRMS) and a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS), respectively. Our experiments show the formation of ammonium salt (NH_4^+) in the CCN-size SOA particles, and our gas phase measurements indicate organic acids are responsible for their formation. The results will have potential applications in studying SOA formation mechanism and the impact of SOA on climate forcing.

2 Experimental

2.1 Reaction chamber experiments

SOA experiments were conducted in the ILMARI environmental chamber infrastructure in University of Eastern Finland. The experimental system and experimental procedure have been described in details in Leskinen et al. (2015) and Kari et al. (2019a), respectively. The chamber consists of a 29 m^3 Teflon^{TM} FEP film bag. Ultraviolent (UV) lights with a spectrum centered at 340 nm around the chamber enable photochemical reactions. Two sets of experiments were designed (Table 1): (1) SOA nucleation experiments in the absence of seed aerosols; (2) SOA formation experiments in the presence of ammonium sulfate seeds. Prior to each experiment, the chamber was

continuously flushed overnight with laboratory clean air produced by a zero air generator (Model 737-15, Aadco Instruments Inc., USA) and conditioned in a humidifier (Model FC125-240-5MP-02, Perma Pure LLC., USA), aiming at 50 % relative humidity at the typical temperature of 20 °C during the course of each experiment. Independent on the type of experiments (nucleation and seeded), the reactants were added into the chamber in the sequence described below. The $(NH_4)_2SO_4$ (ammonium sulfate, 99 %, Sigma Aldrich) seed was injected to the chamber first. The seed was generated using an atomizer (Topas ATM226, Germany). In two experiments, nitrogen oxide (NO) was added to chamber, and ozone (O_3) was introduced into the chamber to convert NO to nitrogen dioxide (NO_2) to reach the atmospherically relevant NO_2-to-NO ratio of ~ 3 (Kari et al., 2019a). After O_3 and NO_x were fed, 3 µl 9-fold butanol (butanol-d9, 98 %, Sigma Aldrich) was injected to the chamber, from whose consumption the hydroxyl radical (OH) exposure was estimated in each experiment (Kari et al., 2019a). Next, 1 µl and 18 µl of α-pinene (≥ 99%, Sigma Aldrich) were added into the chamber for the seeded and nucleation SOA experiments, respectively, corresponding to concentrations of ~5 ppb and ~100 ppb of α-pinene in the chamber. Last, 5 ml of hydrogen peroxide (H_2O_2, 30 wt. % in H_2O, Sigma Aldrich) was conducted into the chamber by mixing it with purified air flowing at 10 lpm (liter per minute), as a precursor for OH radicals to be generated under UV radiation. The H_2O_2 concentration was roughly 30 ppm estimated from the amount of its injection and the volume of chamber. 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. After all the compounds were introduced into the chamber, the chamber was closed, and the compounds were allowed to stabilize for 15 min. Then the UV lights were switched on to initiate photochemistry.

2.2 Analytical methods and instrumentation

The size-resolved chemical composition and mass concentration of aerosol particles were measured directly with an on-line high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, abbreviated as AMS) (DeCarlo et al., 2006). A detailed description of AMS operational procedure is provided in previous publications (Canagaratna et al., 2007; Jayne et al., 2000). In brief, AMS was operated in V - mode in EI - mode. Calibration of ionization efficiency (IE) followed the standard protocol using dried and size-selected ammonium nitrate particles. The data were analyzed using standard AMS data analysis toolkits (Squirrel V1.62D and Pika V1.22D) in Igor Pro Software (version 6.37, WaveMetrics Inc.). For determining mass concentrations, the default relative ionization efficiency (RIE) values were 1.4, 1.1 and 1.2, for organics, nitrate and sulfate, respectively. The RIE for ammonium was 2.95, as determined in the IE calibration. After a comparison to the volume concentration derived from a scanning mobility particle sizer (SMPS TSI 3081 DMA + 3775 CPC) measurement (Fig. S1), a collection factor of 100 % was applied to determine the aerosol mass concentration in the reported results in this work. The positive matrix factorization (PMF) analysis was performed on the high-resolution mass spectra by using the PMF Evaluation Tool V2.08 (Paatero and Tapper, 1994; Ulbrich et al., 2009). The standard error matrices were processed following the principles of applying minimum error estimate, downweighting weak variables, removing bad variables, and downweighing m/z 44 related fragments (Ulbrich et al., 2009). The PMF was evaluated with 1 to 6 factor. Rotation (Fpeak) varied from -1 to 1 at a step of 0.1.

The concentrations of α-pinene and oxidized organic products were quantified by an on-line high-resolution time-of-flight proton transfer reaction mass spectrometer (HR-ToF-PTRMS, abbreviated as PTRMS) (Ionicon Analytik). A detailed description of the instrument and operation procedure has been provided in Jordan et al. (2009) and Kari

et al. (2019a; 2019b). In brief, the PTRMS instrumental setting were the same as in Kari et al. (2019a). During measurement, the mass calibration was conducted using protonated water isotope signals at m/z 21 and internal instrumental signals of diiodobenzene and its fragment ions (protonated integer m/z 331). The instrumental

120 transmission calibration was conducted using a standard gas mixture containing 8 different VOCs (protonated integers ranging from m/z 79 to m/z 181). The concentration of VOCs were determined according to the principles by Hansel et al. (1995). The selected ions that we are interested in this study are consistent with α-pinene (m/z 136+1), formic acid (m/z 46+1), acetic acid (m/z 60+1), propionic acid (m/z 74+1), pinonic acid (m/z 184+1), butyric acid (m/z 88+1), pentanoic acid (m/z 102+1), malonic acid(m/z 104+1) and succinic acid (m/z 118+1).

125 For supporting information we measured the particle concentration and size distribution in a diameter range of 7-800 nm with an SMPS (TSI 3081 DMA + 3775 CPC) and the concentrations of NO, nitrogen oxides (NO$_x$, Fig. S2), ozone (O$_3$), and sulfur dioxide (SO$_2$, Fig. S2), as well as the relative humidity and temperature inside the chamber. In this study, we lacked the measurement of NH$_3$ concentration in the chamber but estimated it from our AMS measurement results, by assuming that the particulate ammonium salt (NH$_4^+$) was converted from the gas-phase NH$_3$

130 (Fig. 1). 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 10ppb (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.

135

3 Results and discussion

3.1 Time series of aerosol species

After After the UV lamps were switched on, the photooxidation reaction produced oxidized gas-phase compounds and SOA particles in both nucleation and seeded experiments. The time series of mass concentrations of formed SOA

140 (in green) and ammonium (in orange) along with sulfate and nitrate components measured by AMS are presented in Fig. 1. In the nucleation experiments (the left panels in Fig. 1), we observed rapid increase in the SOA mass concentrations after the photooxidation reaction had started. After reaching the maximum concentration of 390 - 476 µg m^{-3}, the SOA concentration declined by 27.9 ± 9.2 % at the end of experiment because of particle deposition on the chamber wall and/or aerosol evaporation. The O:C ratio (oxygen to carbon ratio) of the SOA particles were

145 slightly increased from the initial 0.39 ± 0.015 to the final 0.44 ± 0.01 because of aerosol aging. In a distinct contrast, the mass concentrations of ammonium component were still rising at the stage of decreasing SOA masses. Together taking into account the fact that aerosol wall deposition loss was present resulting in decreasing organic mass (and decreasing sulphate mass in the seeded experiments), our results suggest new production of ammonium salts. The newly formed ammonium can be partly attributed to the co-generated nitrate and sulfate as the photooxidized products

150 of NO and SO$_2$ in the chamber. However, the amount of the two inorganic species can't fully interpret the ammonium and we will elaborate this in more detail in Sec. 3.2 2. Similar phenomena were also observed in the seeded experiments (Fig. 1 and Fig. 2). We need to point out that the lower cutoff diameter of SOA particle is about 35nm for AMS measurement (Zhang et al., 2004), and the majority of the SOA mass is dominated by particles in the Aitken and accumulation modes. Thus the reported results are with SOA in CCN size in this study. Note that as the measured

155 mass is centered on the larger sizes of AMS measurement range (35-1000nm, Jayne et al., 2000; Zhange et al., 2004),

4

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). Additionally, the organics, nitrate and ammonium aerosols showed similar mass-based size distributions from our AMS measurement (Fig. 4), and thus internally-mixed aerosol can be assumed in our study, indicating that the aerosol components were lost in a similar rate to the chamber wall. Therefore, no loss correction to the aerosol wall disposition was conducted in this work.

3.2 Participation of ammoina in SOA formation

3.2.1 Reaction of ammoina with organic acids

To investigate the monotically increasing profile of the ammonium salt in our chamber experiment, we studied the stoichiometric neutralization of formed SOA particles. The approach proposed by Zhang et al (2007) was adopted, in which the ammonium mass concentrations measured ($NH_4^+{}_{,mea}$) in the particles were compared to the stoichiometric ammonium concentrations required ($NH_4^+{}_{,pre}$) to fully neutralize the measured concentrations of SO_4^{2-}, NO_3^- and Cl^-:

$$NH_4^+{}_{,pre} = 18 \times (2 \times SO_4^{2-}/96 + NO_3^-/62 + Cl^-/35.5) \tag{1}$$

where NH_4^+, SO_4^{2-}, NO_3^- and Cl^- represent the mass concentrations (in $\mu g\ m^{-3}$) of the species and the denominators correspond to their molecular weights. The factor 18 is the molecular weight of NH_4^+.

A comparison between the predicted and measured ammonium masses is displayed in Figs. 2 and ~~S2~~S3. In both sets of experiments, the measured ammonium mass concentration was systematically greater than the predicted value. The trend doesn't show a dependence on the presence of NO_x in the chamber. On average, $NH_4^+{}_{,mea}$ is 400 ± 156 % and 21 ± 11 % greater than $NH_4^+{}_{,pre}$ at the end of nucleation and seeded experiments, respectively. The large discrepancy between the measured and predicted ammonium concentrations suggested that the current amount of sulfate, nitrate and chloride is insufficient to neutralize the ammonium formed in the particle phase, which indicates that organic component must have played a role in this process. Considering the nature of NH_3 as a base compound, the candidate species of organic compounds are attributed to organic acids.

Since a vast variety of molecular compositions of organic acids may be present in the photooxidation products of a-pinene, it isn't possible to define the amount of individual organic acid required to neutralize the NH_3. Therefore, we use the CO_2^+ ion measured by AMS to represent carboxylic functional group of organic acids. The CO_2^+ is not only considered as a reliable marker of oxygenated organic aerosol (e.g. Zhang et al., 2005), but is also tightly associated with the formation of organic mono- and di-acids shown in laboratory and field measurements (Yatavelli et al., 2015; Takegawa et al., 2007; Alfarra et al., 2004).

Taking into account the contribution of organic acids to ammonium salt, we reformulate Eq. (1) to:

$$\sout{NH_4^+{}_{,pre} = 18 \times (2 \times SO_4^{2-}/96 + NO_3^-/62 + Cl^-/35.5 + CO_2^+{}_{\_NH4}/44)} \tag{2}$$

$$NH_4^+{}_{,pre\_CO2} = 18 \times (2 \times SO_4^{2-}/96 + NO_3^-/62 + Cl^-/35.5 + CO_2^+{}_{\_NH4}/44) \tag{2}$$

where $NH_4^+{}_{,pre\_CO2}$ is the predicted ammonium mass concentration after taking into account contribution of organic acids. $CO_2^+{}_{\_NH4}$ is the mass concentration of carboxylic function group ($-CO_2$) representing organic acids which were required to neutralize the ammonium. The denominator 44 is the molecular weight of carboxylic functional group.

To interpret $NH_4^+{}_{,mea}$, ~~$NH_4^+{}_{,pre}$~~ $NH_4^+{}_{,pre\_CO2}$ should equal to $NH_4^+{}_{,mea}$:

$$\sout{NH_4^+{}_{,pre}}\ NH_4^+{}_{,pre\_CO2} = NH_4^+{}_{,mea} \tag{3}$$

We can estimate the amount of $CO_2^+{}_{\_NH4}$ by combining Eqs. (2-3):

$$NH_4^+{}_{,mea} = 18 \times (2 \times SO_4^{2-}/96 + NO_3^-/62 + Cl^-/35.5 + CO_2^+{}_{\_NH4}^+/44) \tag{4}$$

So, $CO_2^+{}_{\_NH4}=(NH_4^+{}_{,mea}/18- 2\times SO_4^{2-}/96 -NO_3^-/62-Cl^-/35.5) \times44$ (5)

The time series of estimated $CO_2^+{}_{\_NH4}$ over each experiments is shown in Fig. 3. On average, the $CO_2^+{}_{\_NH4}$ concentration required to explain the observed ammonium concentrations was 48.6 times lower for seeded experiments than for the nucleation experiments. Fig. 3 indicates that organic acids participated in reacting with NH_3 much earlier in the low-NO_x test (red and green mark) than in the high-NO_x experiment (blue mark). Based on the time series in Fig. 3, in the high-NO_x test, the time at which the organic acids started to play a role in ammonium formation was delayed by 31 and 100 minutes for the nucleated and seeded experiments, respectively. This observation can be associated to the formation of nitric acid (HNO_3) from photooxidation of NO_x compounds in the high-NOx conditions. The reaction of HNO_3 and NH_3 takes precedence over the reaction between organic acids and NH_3. In the low-NO_x test, a time lag for $CO_2^\pm{}_{\_NH4}$ is also observed, especially in the seeded SOA experiments. The delay is caused by the effect of nitric acid arising from the background NO_x photooxidation. In addition, the slower formation of particulate organic acids makes their reaction with ammonia delayed in the seeded experiments compared to the nucleated cases. In general, the required $CO_2^+{}_{\_NH4}$ accounted for the 27.0 ± 3.1 % of total CO_2^+ mass in the nucleation experiments and 18.7 ± 6.0 % in the seeded SOA experiments. The amount of $CO_2^\pm{}_{\_NH4}$ is assumed to be related to: (1) the photooxidation and ozonolysis capacity in our chamber, which determines the amount of particulate organic acids (total CO_2^+), (2) the relative amount of low- and high- molecule weight organic acids and their physicochemical properties, (3) the relative amount of inorganic and organic acids, and (4) the relative amount of ammonia and total acids, which needs to be thoroughly characterized in the future study.

To further verify our conclusion that organic acids are the drivers of the ammonium formation, we explored the size distribution of organic acids (represented by CO_2^+ ion), ammonium and nitrate at the end of nucleation experiments (Fig. 4). The mode diameters of the three species, determined by performing log-normal fitting on the size distributions, are listed in Table S1. The mode diameter of CO_2^+ ion is about 5-13 nm greater than that of ammonium and nitrate in the three individual experiments. The slight difference in two species mode diameters might be associated with the lower evaporation rate of organic CO_2^+ than ammonium ions on the AMS vaporizer. Anyhow, the similarity in the mode diameters and size distributions of three chemical species suggests that they are internally mixed in the physical phase and are originated from the similar formation sources.

3.2.2 Connecting gas compounds by PTRMS to ammonium ion by AMS

To investigate the organic acid species which may potentially contribute to the ammonium formation in our experiments, ~~we first examined the organic monocarboxylic acids in the gas phase formed in the photooxidaiton of α-pinene.~~ we compared the gas phase organic acids to the particle phase ammonium attributed to the neutralization by organic acids ($NH_4^\pm{}_{,orgacid}$, defined as the difference between $NH_4^\pm{}_{,mea}$ and $NH_4^\pm{}_{,pre}$). We first examined the organic monocarboxylic acids. Fig. 5(a1) shows the correlation between the concentration of butyric acid ($C_4H_8O_2$) (or its isomer) measured by PTRMS ~~and~~and the $NH_4^\pm{}_{,orgacid}$ ~~the particle phase ammonium salts measured~~ calculated ~~by~~ from AMS measurement in the nucleated SOA experiments. The excellent linear correlation (coefficient $R^2 \approx$ ~~0.88~~-0.95) of these two species implies that the formation of butyric acid is associated with the ammonium formation. In addition, we also identified a molecular ion $C_4H_8O_2^+$ in the AMS mass spectrum, which also shows an excellent correlation to the formed ammonium (Fig. 5c1) and thus indicates its simultaneous formation with ammonium ion. The simultaneous observation of the same ion molecules in both gas and particle phases gives us confidence to speculate that this ion is derived from gas-phase butyric acid. The observation suggests a reaction between butyric

235 acid and NH$_3$ which enables the production of ammonium butyrate salts (NH$_4$C$_4$H$_7$O$_2$). The formation of the salts favors the condensation of butyric acid on the particle phase contributing to the observed ammonium ions. Although we can't overlook the fact that ammonium butyrate is severely fragmented inside AMS, it is believed that the detected C$_4$H$_8$O$_2^+$ ion signal is a residual of parental molecule. In the same way, we also explored pentanoic acid (C$_5$H$_{10}$O$_2$) (or its isomer) (Fig. 3b1 and 3d1) and obtained similar results as with butyric acid.

240 A similar comparison has also been made in the seeded SOA experiments (Fig. 5a2-d2). ~~Because of the presence of ammonium sulfate seeds, the ammonium attributed to the organic acids reaction (defined as NH$_{4,orgacid}$) is estimated to be the difference between NH$_4^+$$_{,pre}$ and NH$_4^+$$_{,mea}$. The butyric and pentanoic acids measured by PTRMS were then compared to the calculated NH$_{4,orgacid}$ in the particle phase.~~ We have observed a good correlation of butyric acid to the organic acid-driven ammonium (NH$_4^\pm$$_{,orgacid}$) (r^2 = ~~0.68-0.73~~ 0.76-0.83), and a moderate correlation of pentanonic acid

245 to NH$_4^\pm$$_{,orgacid}$ (r^2 = ~~0.22-0.63~~ 0.27-0.62). Compared with the nucleation experiments, the correlation relationship in the seeded SOA experiments is worse, mainly because the signals in both PTRMS and AMS measurements are weak in the seeded SOA experiments. Similar to the observation in the nucleated SOA experiments, the ion C$_4$H$_8$O$_2^+$ in AMS mass spectrum was also identified to correlate to NH$_4^\pm$$_{,orgacid}$. The ion has the same molecular formula as butyric acid. The concentration of C$_5$H$_{10}$O$_2^+$ of the same molecular formula as pentanoic acid was in a concentration level of

250 10^{-3} ug m^{-3} (Fig. 5d2). Such signal is at the same level as the background noise in AMS measurement, making it challenging to correlate with NH$_4^\pm$$_{,orgacid}$. In general, the results in the seeded SOA experiments are consistent with those in the nucleated SOA experiments, confirming the role of butyric and pentanoic acids in the formation of ammonium salt.

We also extend our study to other four types of gas phase organic acids measured by the PTR-MS. ~~Fig. 4~~ Fig. 6

255 shows the relationship of the formic acid, acetic acid, propionic acid and pinonic acid measured in the gas phase with the ammonium ion measured by AMS. Surprisingly, the gas phase formic acid, acetic acid and propionic acid were in in good agreement with particle phase ammonium concentration with excellent linear correlation coefficients r^2 ≥ 0.95~~0.89~~ in the nucleated SOA experiments and r^2 ≥ 0.72~~0.69~~ in the seeded SOA experiments. The good correlation of gas phase organic acids with the particle phase ammonium salt suggests that theses acids played a role in the

260 formation of ammonium. Formic acid and acetic acid are the most abundant organic monoacids in the atmosphere (Chebbi and Carlier, 1996), whose one significant source is from photooxidation of a-pinene and other alkenes and terpenes (Friedman and Farmer, 2018). Propionic and butyric acids are also other important organic acids in this process (Nah et al., 2018a; Nah et al., 2018b; Chebbi and Carlier, 1996). The formation mechanisms of these low molecular weight organic acids are unclear in the photochemical reaction of α-pinene (e.g.Friedman and Farmer,

265 2018). It can be speculated that they were produced as products of stabilized Criegee intermediate associated with ozonolysis of α-pinene and double carbon bond-containing products (Jacob and Wofsy, 1988; Orzechowska and Paulson, 2005). The statement is verified by the fact that we have observed the highest O$_3$ formation at the highest NO$_x$/VOC$_x$ initial input in E0314 (Fig. S4). Therefore, in E0314 we have also observed higher concentrations of C1-C5 monoacids corresponding to higher ozonolysis reactivity (Fig.S5). These low molecular weight monoacids have

270 a vapor pressure of 6.8 ~ 8.1 µg m^{-3} (log$_{10}$(C*)) (Friedman and Farmer, 2018), and are generally considered to be too volatile to be distributed substantially to the particle phase. However, their presence in the aerosol particles is ubiquitous in various areas over the world, although the levels of these monoacids are one or two order of magnitude lower than those in the gas phase (Nah et al., 2018a; Fisseha et al., 2004; Chebbi and Carlier, 1996). A study conducted in a forest-agriculture area in Atlanta showed that the acetic acid and formic acid are the second and third richest

275 water-soluble organic acids in the particle phase and their molar fractions to the total individual acid concentrations

in the particulate phase were 5.8 ± 5.0% and 3.6 ± 3.6%, respectively (Nah et al., 2018a). In addition, the presence of NH$_3$ as a strong base facilitates the shift of the equilibrium of these monocarboxylic acids and NH$_3$ to the particle phase (Barsanti et al., 2009). Under a base environment, a higher molar fraction of formic acid and acetic acid has also been observed in the particle phase (Nah et al., 2018a). These organic acids could exist in the particle phase in chemical forms of ammonium formate, ammonium acetate and ammonium propionate salts (Barsanti et al., 2009; Smith et al., 2008; Becker and Davidson, 1963), and thus contribute to the observed ammonium ions.

In an obvious contrast to the observation of C1-C5 monoacids above, the pinonic acids didn't show a linear correlation with the ammonium at the later stage of the nucleated SOA experiments (~~light~~ pink region, Fig. 6d1), and there was no connection in the seeded SOA experiments. Pinonic acid is a typical first-generation marker product in the photooxidation reaction of a-pinene (Hallquiest et al., 2009). Na et al. (2007) reported that the addition of NH$_3$ to the aerosolized pinonic acid in an environmental reactor led to dramatic increase in both number and volume concentrations of pinonic acid. They attributed the observation to the reaction between NH$_3$ and pinonic acids. However, the lack of positive correlation between the pinonic acid and ammoniums can be caused by several reasons in this study. Firstly, the vapor pressure of pinonic acid is about 4 ~ 5 orders of magnitude lower than those of C1-C5 monoacids (Jimenez et al., 2009), so pinonic acid can condense on the particle phase independent on NH$_3$. Meanwhile, the concentration of pinonic acid accounts for less than 1% of the total mono-acids based on the PTR-MS results. Hence, the contribution of pinonic acid to the formed ammonium was estimated to be less than 1%, considering that the acidity strength of pinonic acid is similar to other C1-C5 monoacids (acid dissociation constant (pKa) of pinonic acid is 4.8 (Howell and Fisher, 1958), close to the pKa values of formic acid (3.75), acetic acid (4.75), propionic acid (4.86), butyric acid (4.83) and pentanoic acid (4.84) (Lide, 2007)). Therefore, after α-pinene was completely consumed and pinonic acid formation had ceased in the gas phase (pink region, Fig. 6), the rapid condensation of pinonic acid on the particle phase or chamber wall causes a non-linear correlation of pinonic acid to ammonium. Secondly, the gas-phase pinonic acids could be further reacted away by OH radicals, which also contributes to the non-linear observation. Field experiment has shown the relatively low atmospheric PM concentrations of pinonic acid measured in summer because of the consumption of pinonic acid by OH radicals (Szmigielski et al., 2007).

Analogously, the scattering plots for the gas-phase organic dicarboxylic acids and particle-phase ammonium salts are shown in Fig. 7. We chose malonic acid and succinic acid as representative organic diacids, two of the most abundant dicarboxylic acids measured in the atmospheric aerosols (Chebbi and Carlier, 1996). ~~The nice correlations of the gas phase malonic and succinic acids to the particle phase ammonium in this study suggest that diacids contribute to the formation of ammonium in both nucleated and seeded SOA experiments.~~ The nice correlations of the gas-phase malonic and succinic acids to the particle-phase ammonium study suggest that diacids contribute to the formation of ammonium in both nucleated and seeded SOA experiments. It also indicates the continuous formation of those diacids at the later stage of photooxidation in nucleated and seeded experiments. The formation mechanism of these low molecule-weight diacids remains unclear for us and might be similar to the C1-C5 monoacids.

Our results qualitatively demonstrate that in the photooxidation of α-pinene, the presence of NH$_3$ drives the gas-phase mono- and dicarboxylic acids to the particle phase and promotes the SOA mass concentration in the CCN size. Previous studied have shown that the presence of NH$_3$ can significantly enhance SOA formation from the a-pinene/ozone/photooxidation system because of the interaction of NH$_3$ with gas-phase organic acids (Na et al., 2007; Babar et al., 2017), which is consistent with our results. Carboxylic acid is one of the key species in determining SOA physico-chemical property. Our results may prompt us to reconsider the pathway of gas phase organic acids involving

in SOA formation in the atmosphere, whether they directly participate partitioning between the gas and particle phases, or they undergo secondary conversion via reaction with NH_3 before they condensate on the particle phase in the atmosphere. ~~After SOA are formed, carbonyl group of chemical compounds in SOA particles can also uptake NH_3 heterogeneously to form nitrogen-containing compounds (Zhu et al., 2018; Liu et al., 2015; Updyke et al., 2012; Dinar et al., 2007) and organic ammonium salts (Schlag et al., 2017). However, in this study the N:C ratios measured by AMS remained nearly constant at 0.002 for E0322 and E0326 and 0.004 for E0327 suggesting that the carbonyl-NH_3 heterogeneous reaction could be negligible.~~ After SOA are formed, carbonyl group of chemical compounds in SOA particles can also uptake NH_3 heterogeneously to form nitrogen-containing compounds (Zhu et al., 2018; Liu et al., 2015; Updyke et al., 2012; Dinar et al., 2007) and organic ammonium salts (Schlag et al., 2017). In this study the N:C ratios measured by AMS were nearly constant or slightly increasing in two sets of experiments (Fig. S6), suggesting the formation of nitrogen-containing compounds via carbonyl-NH_3 heterogeneous reaction. The interaction of NH_3 and SOA affects the cloud condensation nuclei (CCN) and hygroscopic growth of SOA particles and may have a potential impact on climate change (Dinar et al., 2007).

3.3 Ammonium relevant to PMF-solved SOA component

PMF analysis on the high-resolution organic mass spectra resolved the organic component to two factors in the nucleation experiments: MO-OOA (more oxidized oxygenated organic aerosol) and LO-OOA (less oxidized OOA). The oxidation level of MO-OOA is represented by an O:C ratio of 0.47 in this study, which is close to the value of 0.48 for MO-OOA determined in New York City in Summer (Sun et al., 2012). Its time series shows a good correlation to the measured gas-phase monocarboxylic and di- acids such as butyric and succinic acids. The second factor LO-OOA is featured by an O:C ratio of 0.38. Its time series is related to the gas-phase oxidant products such as pinonaldehyde. The mass spectra profiles and time series of the two factors are shown in Fig. ~~S3~~S7. In this study, the formation of ammonium salts is consistent with MO-OOA factor and also organic mono- and di- acids (Fig. 8). A higher oxidized organic factor is usually associated with the formation of organic mono- and di-acids. These results further suggest that the ammonium has a close relation to the organic acids. Our observation is in agreement with the study by Schlag et al. (2017) where they showed by field data that NH_4 is associated with a more oxygenated organic aerosol factor.

4 Conclusions

The SOA experiments were carried out from photooxidation reaction of α-pinene in the presence of NH_3 in a $29m^3$ indoor simulation chamber. Experiments were designed for SOA formation in the presence of ammonium sulfate seeds and at the absence of seed aerosols. The chemical composition and time-series of compounds in the gas- and particle-phase were characterized by an on-line high-resolution time-of-flight proton transfer reaction mass spectrometer (PTRMS) and a high-resolution time-of-flight aerosol mass spectrometer (AMS), respectively.

After the precursor α-pinene was consumed in the chamber, the mass concentration of organic aerosol in CCN-size was decreased because of aerosol wall deposition or evaporation, the ammonium concentration was still rising, suggesting the continuous formation of ammonium. AMS results showed that organic acids were required to neutralize the observed ammonium salt. The CO_2^+ ion was selected to represent organic acids. 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. The good correlation of organic monocarboxylic acids (such as formic acid, acetic acid, propionic acid, butyric acid and pentanoic acid (or their isomers)) in the gas

phase to the ammonium salts further qualitatively confirms an ~~affective~~ effective role of organic acids for the ammonium formation. The same conclusion is also applied to the organic dicarboxylic acids such as malonic and succinic acids. In addition, the formed ammonium salts correlated well to the more-oxidized oxygenated organic aerosol (MO-OOA), which is consistent with the conclusion that organic acids contributed to the observed particulate ammonium.

Our work firmly shows the direct contribution of NH_3 to the CCN-size SOA formation through the organic acids-base reaction. The increase in SOA mass and the change of chemical composition due to NH_3-SOA interaction could change the hygroscopocity, CCN ability and optical property of aerosol particles, which may alter the aerosol impact on climate change and need to be studied in the future.

Code/Data availability.

The data included in this paper can be obtained by contacting the authors.

Author contribution.

LH, EK, AL and AV designed and conducted the experiments. LH and EK performed the data analysis with contributions by DW and AV. LH and AV wrote the paper with contributions from all co-authors.

Competing interests.

The authors declare that they have no conflict of interest.

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Table 1 Initial experimental parameters and results in two sets of experiments

	Exp. ID	α-Pinene (ppb)	NO_x (ppb)[1]	R.H. (%)	Temp (°C)	AS seed surface[1] ($\mu m^2/cm^3$)	OH exposure (#/cm^3 s)	ΔNH_4[2,3] mass ($\mu g\ m^{-3}$)	SOA [3] mass ($\mu g\ m^{-3}$)
Nucleation SOA Exp.	E0322	91.7	bg (0.5)	67.2	19.0	bg	1.2e11	1.2	391.8
	E0326	100.9	bg (0.3)	50.5	21.4	bg	1.3e11	1.5	389.7
	E0327	107.2	13.3	51.4	21.5	bg	1.3e11	1.6	476.1
Seeded SOA Exp.	E0314	4.1	61.3	56.2	22.6	3.6e7	1.2e11	0.02	5.5
	E0315	4.2	bg (2.6)	57.2	22.1	4.0e7	1.2e11	0.02	7.5
	E0316	4.8	bg (1.1)	56.5	21.8	2.4e7	1.3e11	0.03	7.7

[1] bg=background concentration inside the chamber.

[2] In the seeded SOA experiment, because of the presence of ammonium sulfate seeds, the maximum mass concentration of newly formed ammonium salt was estimated from the difference between $NH_4^+{}_{,pre}$ and $NH_4^+{}_{,mea}$, refer to the text for details.

[3] The formed aerosol mass at maximum.
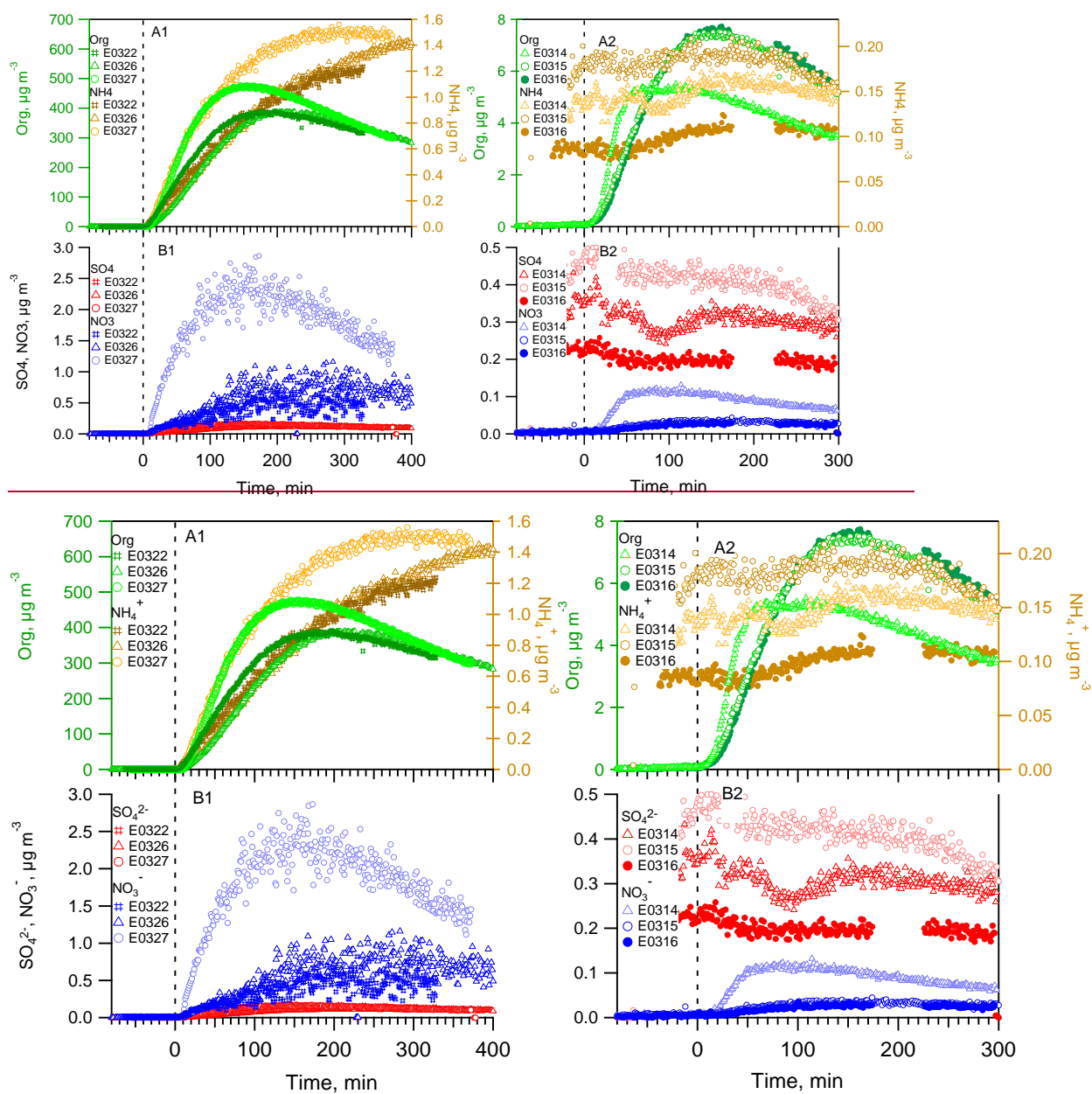
Figure 1. The mass concentrations of organics (left axis), ammonium (top panels, right axis), sulfate and nitrate (bottom panels) as a function of irradiation time in nucleation experiments (left panels) and in seeded SOA experiments (right panels). The irradiation time of 0 min marks the start of photooxidation reactions after UV lights were switched on.

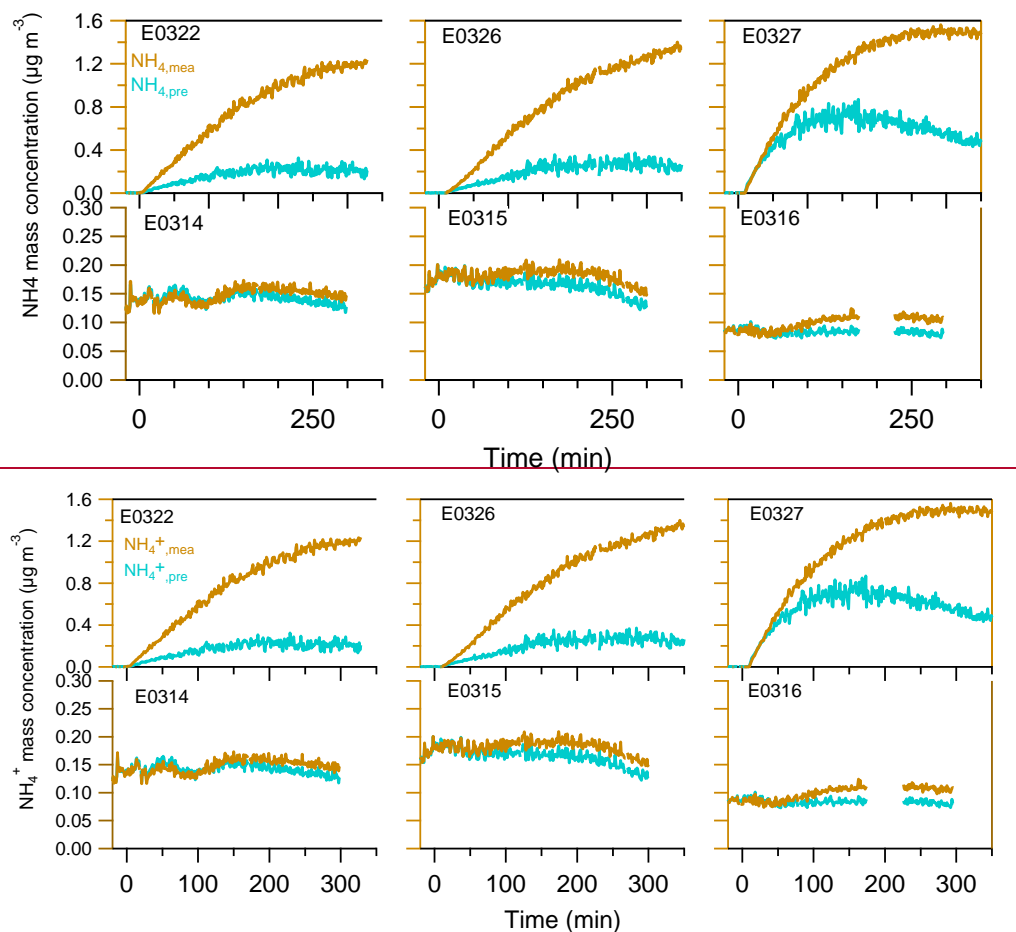**Figure 2**. The time series of measured and predicted ammonium in the nucleated SOA (top panels) and in the seeded SOA experiments (bottom panels).
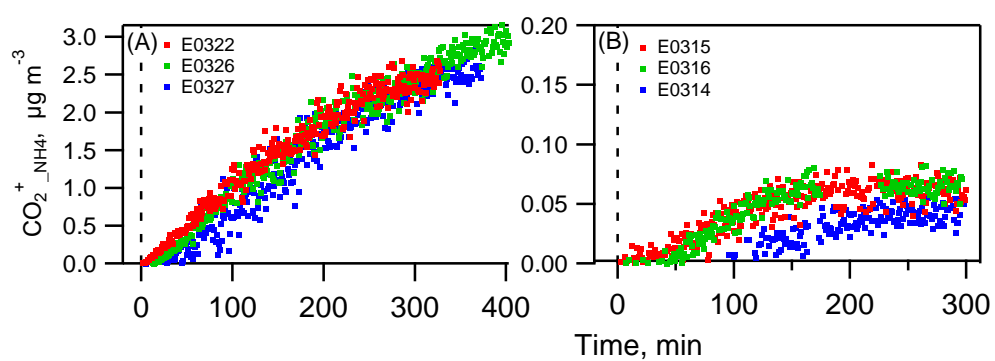
Figure 3. The estimated amount of organic carboxylic acid needed to fully neutralize SOA particles (CO_2^+_NH4). CO_2^+ group is chosen to represent organic acids. (A) nucleation experiments (B) ~~SOA~~ seeded experiments. The time zero marks the beginning of photooxidation reactions when UV lights were switched on.
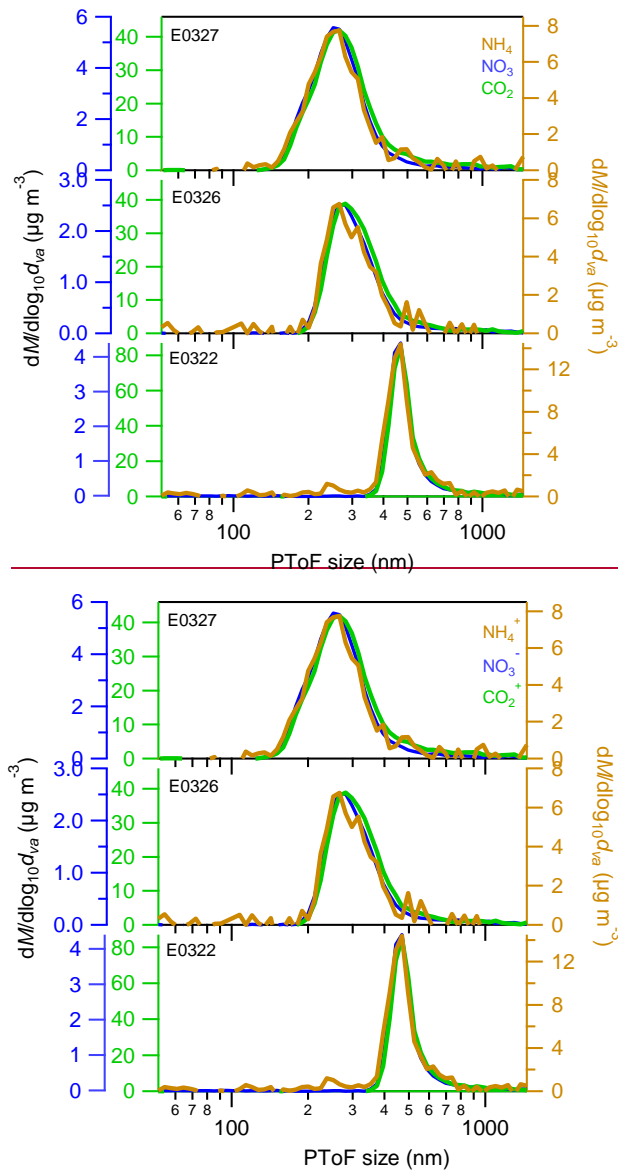
Figure 4. The averaged 30-minute size distribution of organic acids (represented by CO_2^+ ion measured by AMS), nitrate and ammonium in the last 30 minutes prior to the end of the nucleated SOA experiments.
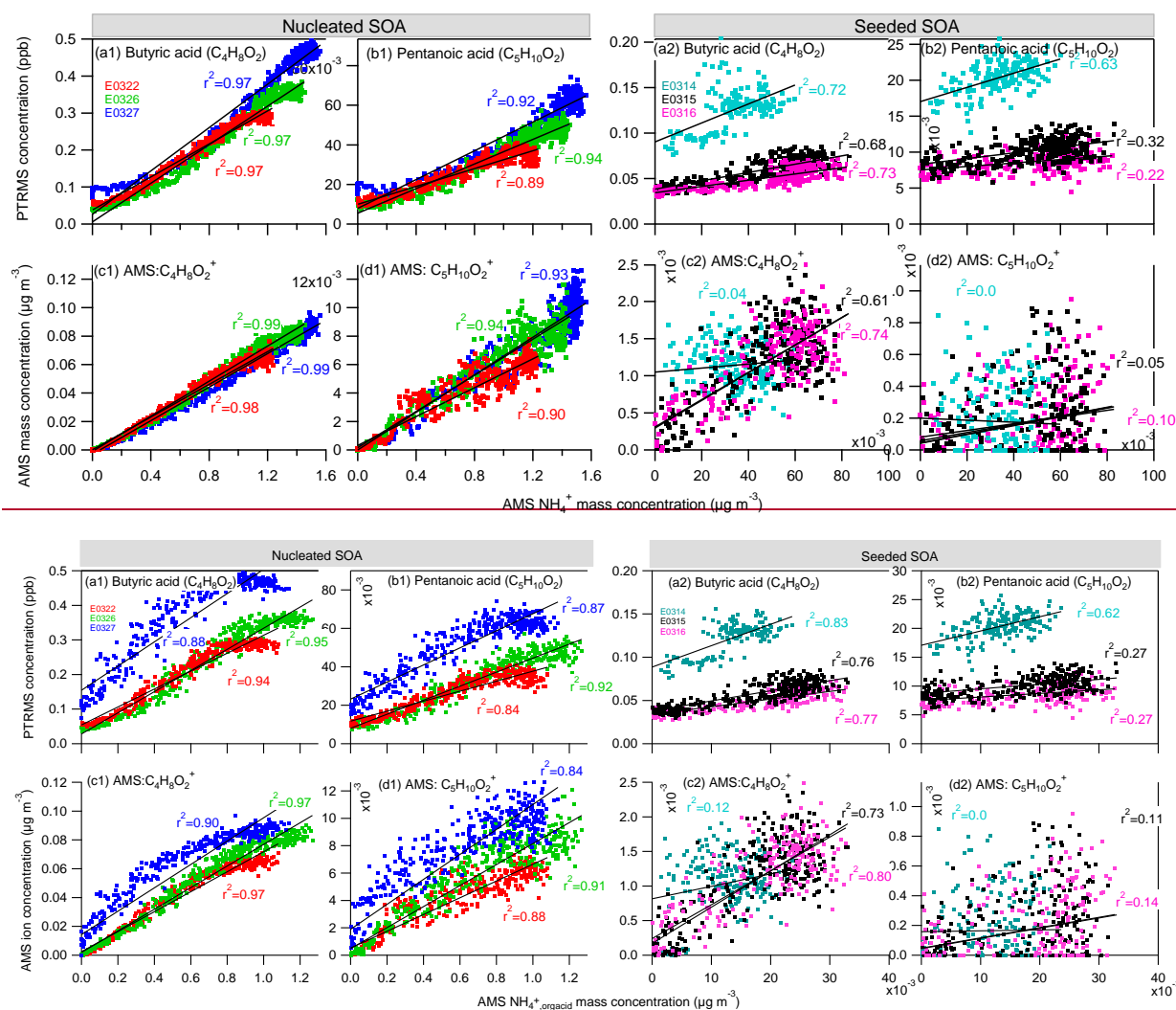
Figure 5. The comparison of measured ~~compounds~~ organic monoacids in the gas phase by PTRMS and the
ammonium attributed to the neutralization by organic acids ($NH_4^{\pm}{}_{,orgacid}$) in the particle phase by AMS in the nucleated
SOA (left four panels) and seeded SOA experiments (right four panels). Top panels: Linear correlation between
butyric ($C_4H_8O_2$) and pentanoic ($C_5H_{10}O_2$) monoacids measured by PTRMS ~~measured~~ and the $NH_4^{\pm}{}_{,orgacid}$ ~~the
ammonium~~ by AMS; Bottom panels: Linear correlation of two fragmental ions $C_4H_8O_2^+$ and $C_5H_{10}O_2^+$ to the
$NH_4^{\pm}{}_{,orgacid}$ ~~ammonium measured~~ by AMS. Note that the two fragmental ions have identical ion molecular formula to
those of butyric and pentanoic acids. ~~In the seeded SOA experiments, the AMS NH_4^+ is the difference between
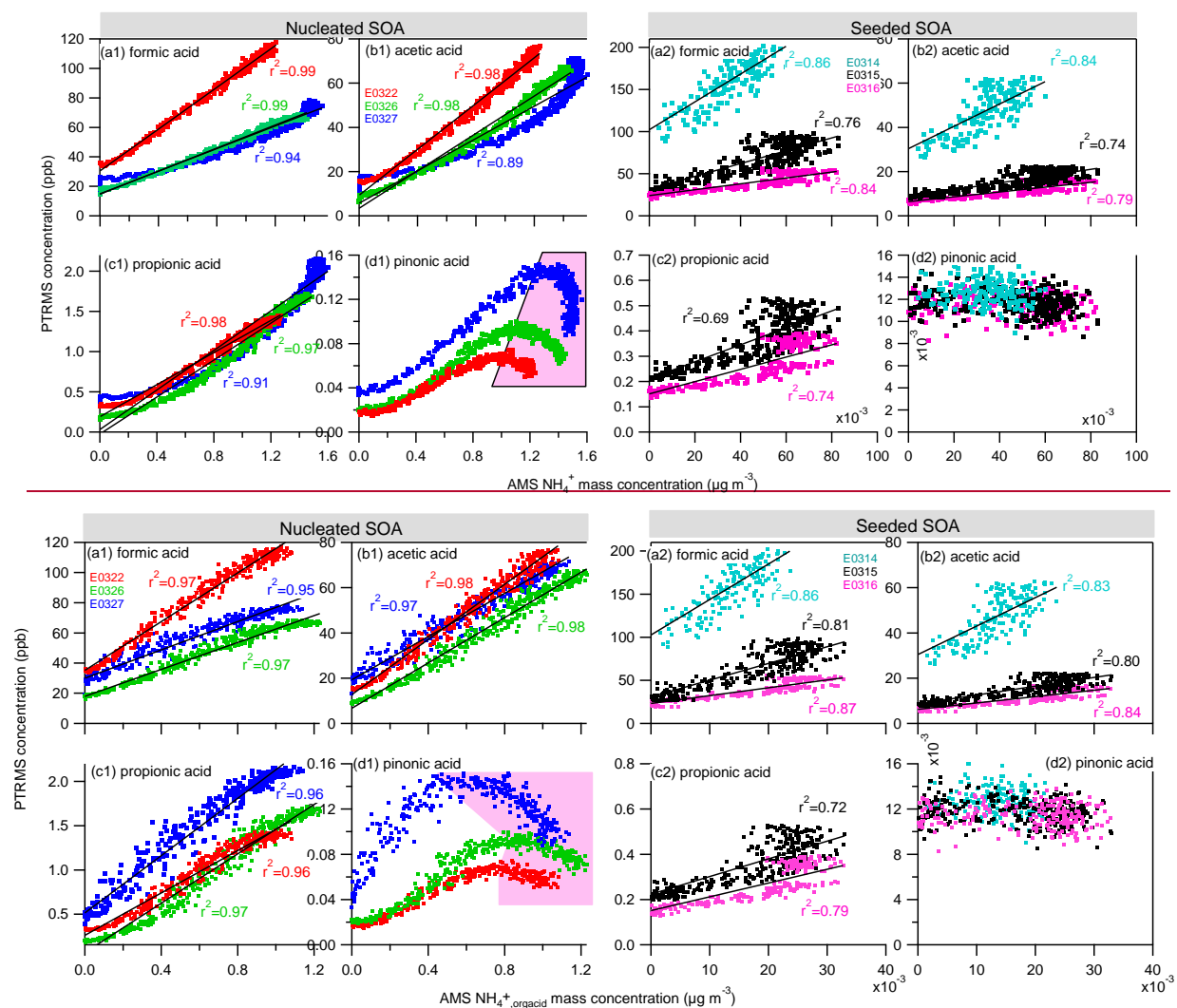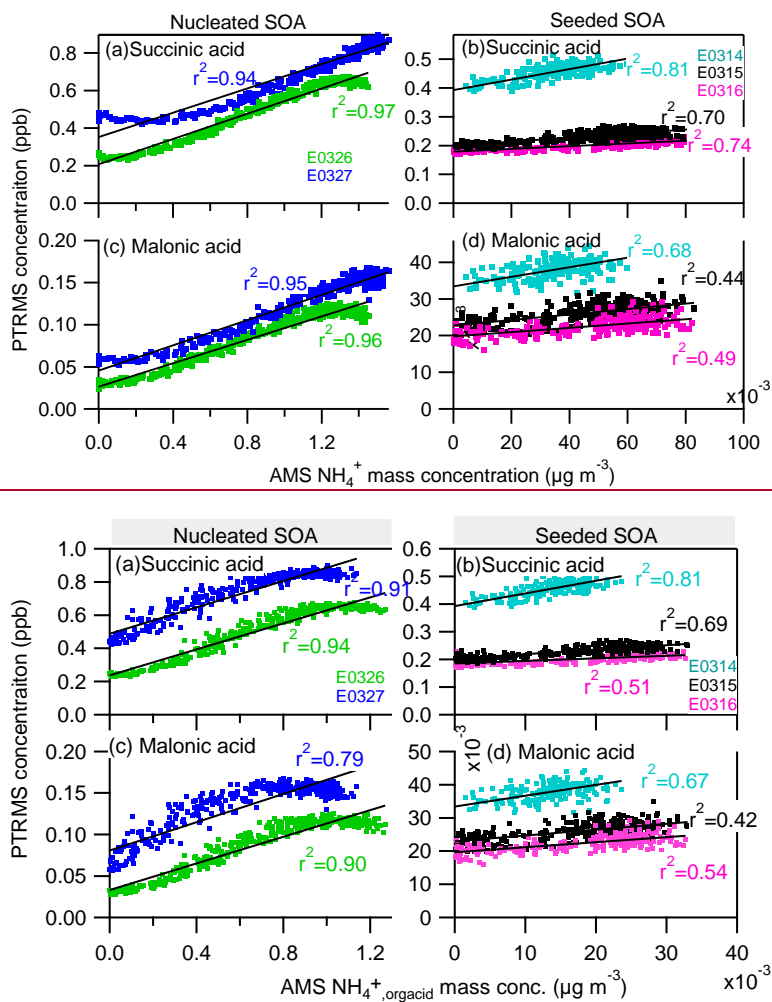$NH_4^+{}_{,pre}$ and $NH_4^+{}_{,mea}$, refer to the text for details~~.

Figure 6. Correlations of <u>the ammonium attributed to the neutralization by organic acids ($NH_4^{\pm}$,orgacid)</u> ~~the measured ammonium ion in the particle phase~~<u>in the particle phase</u> by AMS to the (a) formic acid, (b) acetic acid, (c) propionic acid, (d) pinonic acid in the gas phase measured by PTRMS in the nucleated SOA experiments (left four panels) and in the seeded SOA experiments (right four panels). The light pink area in panel d1 indicates a non-positive correlation regime between two species.
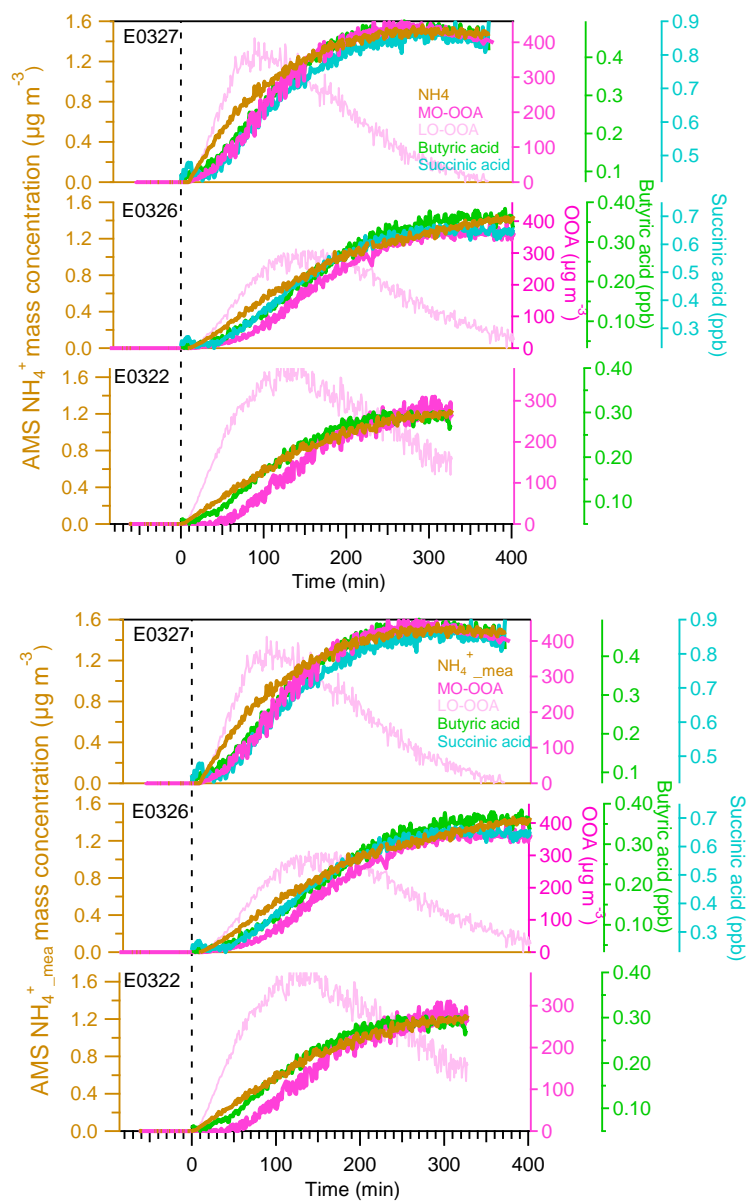
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Figure 7. Correlations of the ammonium attributed to the neutralization by organic acids ($NH_4^{\pm}$,orgacid) in the particle phase ~~measured ammonium ion in the particle phase~~ by AMS to two organic dicarboxylic acids: (a) malonic acid, (b) succinic acid in the gas phase measured by PTRMS. Both of the diacids were not observed in the experiment E0322.

Figure 8. The relevance of particulate ammonium salt to the resolved MO-OOA component by PMF, and to the gas-phase butyric monocarboxylic acid and succinic diacid.