

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 reactor 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 line 92, 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 $\mu\text{g m}^{-3}$, 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 $\mu\text{g m}^{-3}$ and a geometric mean concentration of 14 $\mu\text{g m}^{-3}$ (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 $\mu\text{g m}^{-3}$ (corresponding to 64ppb). This gives an approximately 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-NH₃ 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 CO₂⁺ and formation of NOC in the specific experiments.

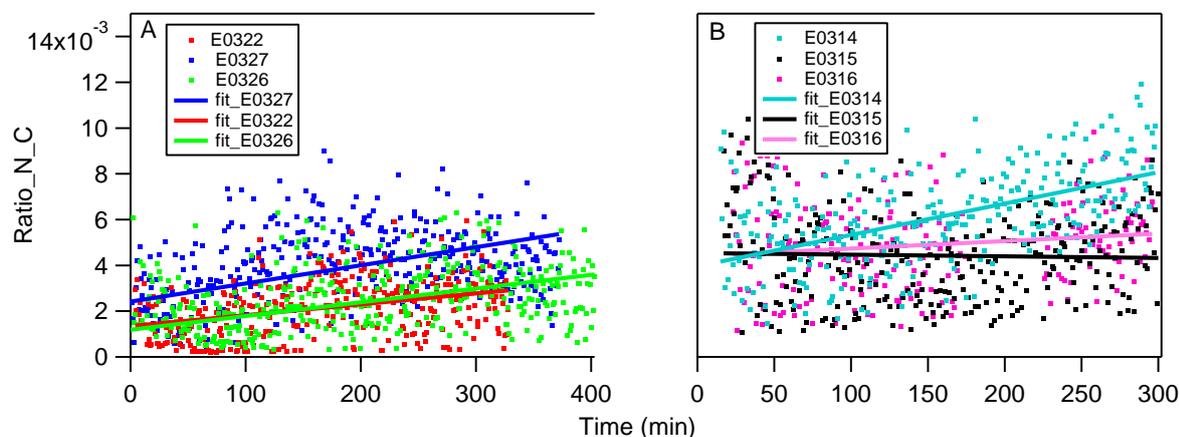


Figure C1. The N:C ratios determined by AMS in (A) the nucleated SOA experiments, and (2) in the seeded SOA experiments.

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 alpha-pinene concentration was about 20 times lower than in the nucleation experiment. The relatively low alpha-pinene concentration was adopted to mimic an atmospherically relevant monoterpene mixing ratio, for example, in Hyytiälä forest area in Finland (e.g. Kourtshev *et al.*, 2006). We aimed to study if the ammonia plays a similar role as in the high α -pinene concentration case. Meanwhile, in the presence of seed aerosol, the relative low α -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 alpha-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 (NH₄⁺_{orgacid}) is around 40 times less than in the nucleated cases. Such small amount of NH₄⁺_{orgacid} (at about 0.03 $\mu\text{g m}^{-3}$ 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 NO_x condition. More explanation might be necessary for the delay in low NO_x conditions.

Reply:

A lag in time for CO₂⁺_{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 CO₂⁺_{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.”

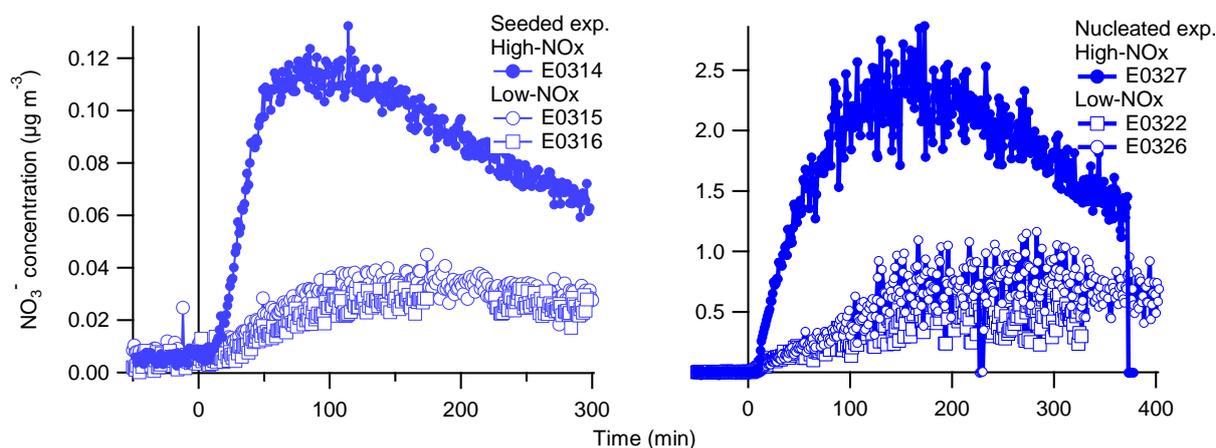


Figure C2. The formed nitrate aerosol measured by AMS in the seeded SOA experiment.

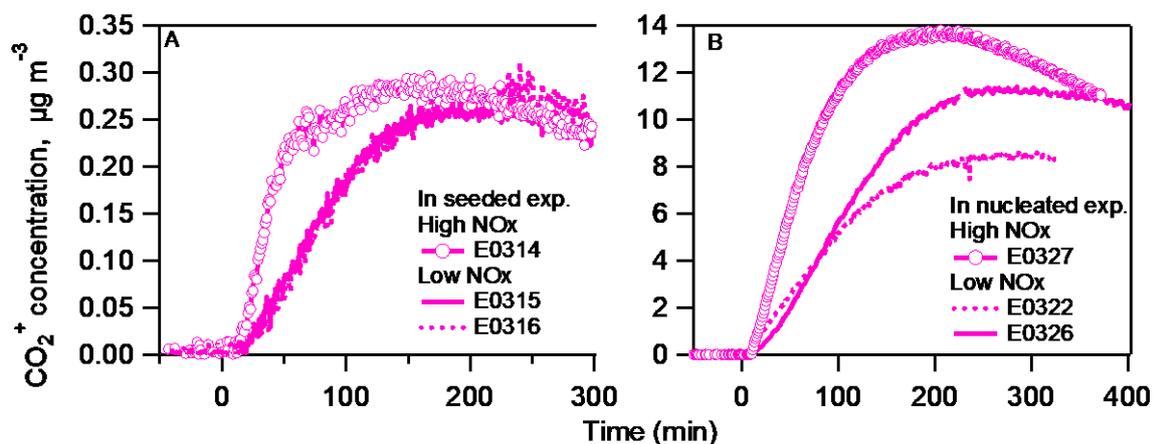


Figure C3. The measured CO₂⁺ ion concentration measured by AMS (A) in the seeded and (B) in the nucleated SOA experiments. CO₂⁺ ion was chosen to represent organic acids. The formation rate of CO₂⁺ in seeded experiments was much slower than in the nucleated cases.

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 NO_x and nitric acids.

Reply:

In the two sets of experiments, the total CO₂⁺ ions account for 2.7% to 7.0% of SOA in mass (Fig. C4). Out of the CO₂⁺ 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 CO₂⁺_{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 $\text{CO}_2^+_{\text{NH}_4}$. The amount of $\text{CO}_2^+_{\text{NH}_4}$ 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.

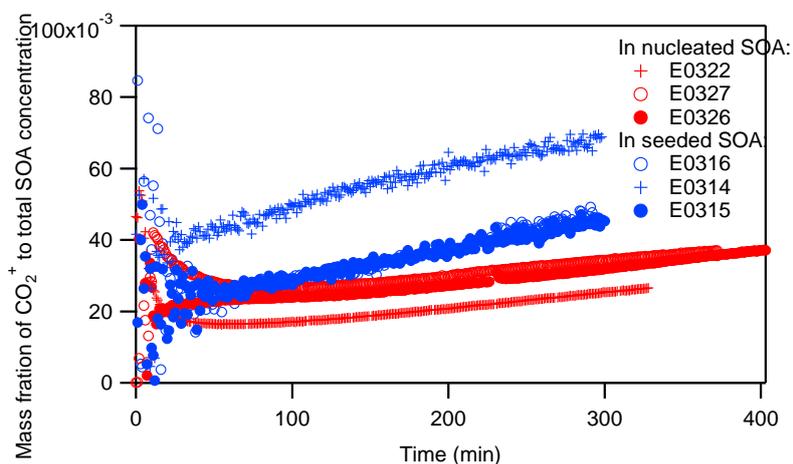


Figure C4. The mass fraction of total CO_2^+ ions to the SOA mass.

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.

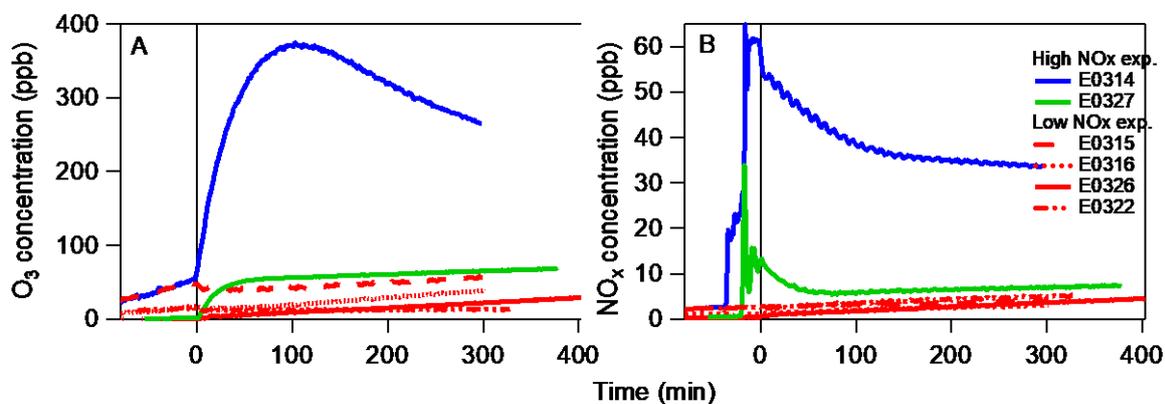


Figure C5. The O_3 and NO_x concentration in the chamber. The high NO_x injection led to high O_3 concentration in the chamber (in blue).

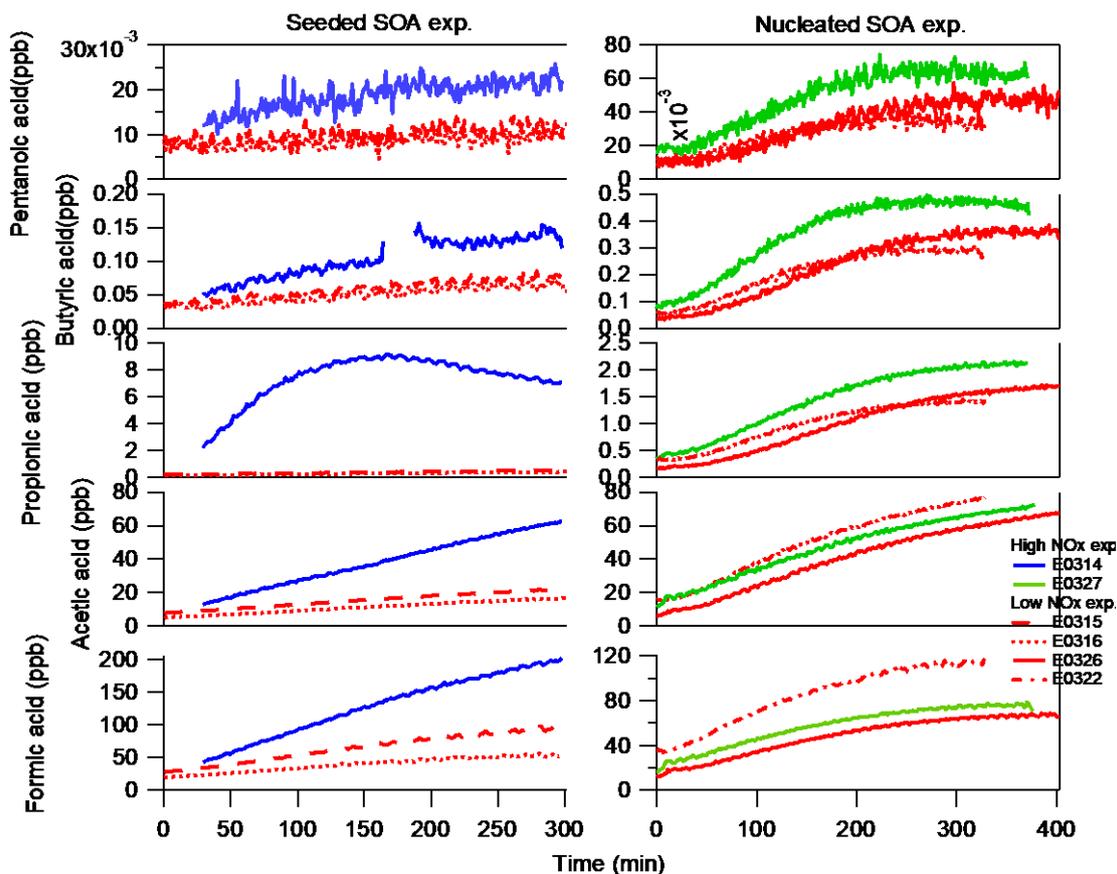


Figure C6. The concentrations of C1-C5 organic monoacid in the seeded (left panels) and nucleated (right panels) SOA experiments. The higher NO_x input in E0314 (in blue) also led to higher ozone formation and eventually led to higher organic acids concentration resulting from ozonolysis reaction. Refer 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 H₂O₂ concentration is not measured in the chamber. Based on the volume of injected H₂O₂ solution and the chamber volume, we estimated its concentration to be 30ppm. We have added in line91 that “The H₂O₂ 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.

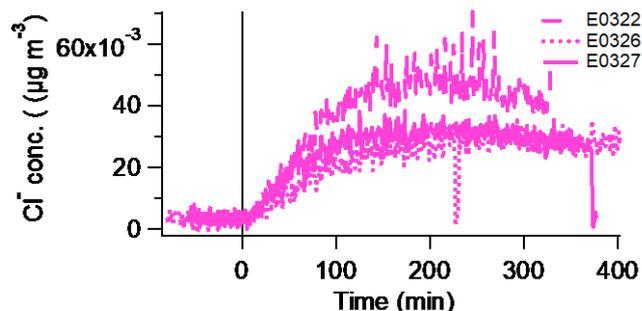


Figure C7. The concentration of chloride measured by AMS in the chamber.

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: *α -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 NH_4^+ is the difference between NH_4^+ ,pre and NH_4^+ ,mea, refer to the text for details.” needs to be clarified. In the text NH_4^+ ,pre and NH_4^+ ,mea are defined, whereas “AMS NH_4^+ ” is not defined. It should be defined clearly in the caption, e.g., NH_4^+ ,mea - NH_4^+ ,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”, “SO₄”, 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.*

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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.

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