

## Answer to comment of **Referee#1**

on “**Influence of NO<sub>2</sub> on secondary organic aerosol formation from ozonolysis of limonene**” by Changjin Hu et al.

### **Reviewer Comment - OVERVIEW:**

*This manuscript describes a laboratory and modeling study of SOA formation from the ozonolysis of limonene in the presence of NO<sub>2</sub>. The manuscript is topically relevant to ACP. The authors need to make clearer the unique contribution of this research, and how this manuscript advances the field. Specifically, I have two main criticisms: (1) Are the SOA yield differences meaningful for cases when similar delta SOA is observed with and without NO<sub>2</sub>? (2) Are the resulting changes in SOA yield and composition a consequence of different O<sub>3</sub> chemistry or do they just reflect NO<sub>3</sub> chemistry at high NO<sub>2</sub>? The impact of the research is clearly reduced if the authors are merely reproducing NO<sub>3</sub> oxidation experiments under high NO<sub>2</sub> conditions.*

### **REPLY:**

We appreciate the referee for the constructive comments that will contribute to improve our original manuscript.

Regarding to the importance of understanding the effects of anthropogenic emissions on aerosol formation from biogenic emissions and to what extent can biogenic SOA be controlled (Ng et al., 2017), as well as the situations of high emission of limonene (Guenther et al., 1995, 2000; Griffin et al., 1999) and the increasing tropospheric NO<sub>2</sub> (He et al., 2007), this work has uncovered the underground reaction mechanism of limonene ozonolysis at the presence of NO<sub>2</sub> when anthropogenic and biogenic emissions are entangled together, which is more complicated than that the observed aerosol mass or yield shows.

(1) Firstly, NO<sub>2</sub> effect, not only NO as mainly investigated before (Presto et al., 2005; Kroll and Seinfeld, 2008), on SOA yields has been proved experimentally to be very important, which is more pivotal to real atmosphere (Ng, et al., 2017).

(2) Secondly, even the observed aerosol mass or yield are similar, the underground formation mechanism may be different, for example, different [O<sub>3</sub>]<sub>0</sub>/[VOC]<sub>0</sub> ratio or different NO<sub>2</sub> concentration, which is most important to control strategy.

(3) Thirdly, NO<sub>2</sub> effect on SOA formation from ozonolysis of limonene is not only related to the competition between O<sub>3</sub>- and NO<sub>3</sub>-initiated oxidation of limonene, but also the competition between RO<sub>2</sub>+HO<sub>2</sub> and RO<sub>2</sub>+NO<sub>2</sub> (or NO<sub>3</sub>) following the O<sub>3</sub> initiated oxidation. Under the different [O<sub>3</sub>]<sub>0</sub>/[VOC]<sub>0</sub> ratio, the presence of NO<sub>2</sub> may have different effect on the SOA formation.

So it is believed that this work is helpful to understand to what extent can biogenic SOA be controlled when anthropogenic emissions coexists.

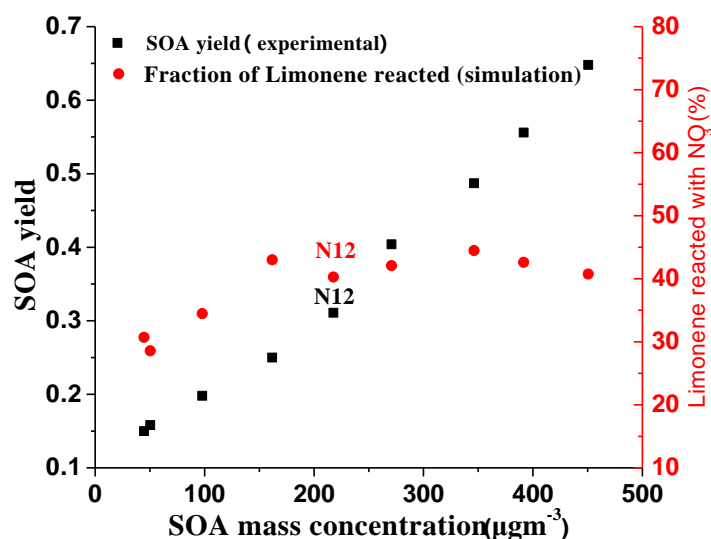
Please find below the point-by-point responses (**in blue**) to each comment (**in**

**black italics**). And we have made corresponding modifications/revisions based on these in the revised manuscript and supplement (the changes are marked **in red**).

(1) *Are the SOA yield differences meaningful for cases when similar delta SOA is observed with and without NO<sub>2</sub>?*

**REPLY:**

By comparing Exp. N1-N7 (without NO<sub>2</sub>) with Exp. N8-N16 (with NO<sub>2</sub>), although they have similar [O<sub>3</sub>]<sub>0</sub> and [VOC]<sub>0</sub>, they have different SOA formation yield. And the most important is that even for the cases when they have similar delta SOA, for example, N3 ( $\Delta M_0=211\mu\text{g}/\text{m}^3$ ) and N12 ( $\Delta M_0=218\mu\text{g}/\text{m}^3$ ) (See Table 1 in the manuscript), they have different reaction mechanism. For N3, all of SOA formed from ozonolysis of limonene, while for N12, there was about 40% limonene reacted with NO<sub>3</sub> (See Fig. R1). Even the exact ratio of SOA formation from NO<sub>3</sub> chemistry was hard to decide, it is believed that there should be organic nitrates in aerosol particles in N12 while there is not any organic nitrates in aerosol particles formed in N3. So, similar delta SOA may have different formation yield; even similar delta SOA have similar formation yield, they have different formation mechanism. For field, different formation mechanism means different sources and different control strategy, which is the most important for pollution or climate.



**Figure R1.** The fraction of the limonene reacted with NO<sub>3</sub> (model study) and the corresponding SOA yields (experimental work) for Exp. N8-N16.

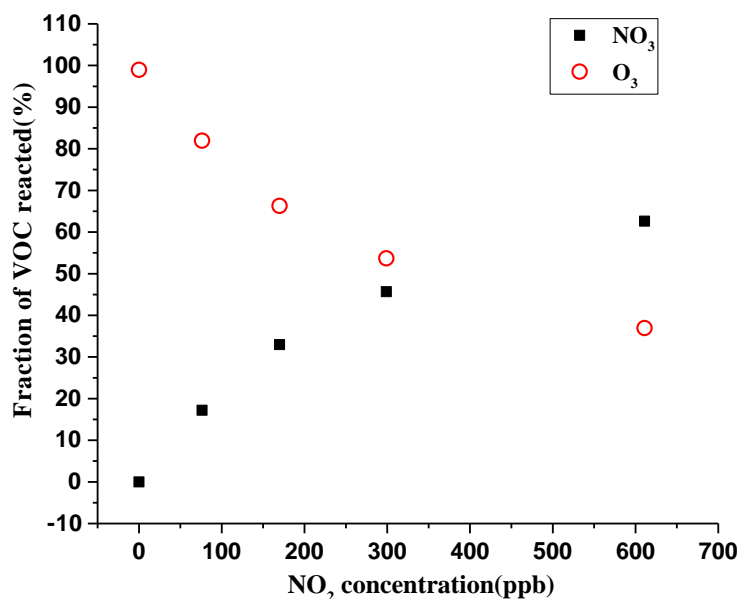
(2) *Are the resulting changes in SOA yield and composition a consequence of different O<sub>3</sub> chemistry or do they just reflect NO<sub>3</sub> chemistry at high NO<sub>2</sub>?*

**REPLY:**

It is believed that the changes in SOA yield and composition is the combined action of O<sub>3</sub> chemistry and NO<sub>2</sub> chemistry (NO<sub>3</sub> chemistry and direct reaction of NO<sub>2</sub> with the intermediates of limonene+O<sub>3</sub>).

As shown in Fig. R1, for Exp. N8-N11, the SOA yields increased in turn from N8 to N11 with the percentages of total limonene reacted by  $\text{NO}_3$  increasing, while they are still lower than the corresponding SOA yields without  $\text{NO}_2$  (Exp. N1-N4, see Table 1). However, it is interesting to find that although the percentages of total limonene reacted by  $\text{NO}_3$  for Exp. N11-N16 were almost the same (~42%), the SOA yields still increased from N11 to N16, and in high  $[\text{O}_3]_0$  conditions, the SOA yields with  $\text{NO}_2$  even are higher than that of without  $\text{NO}_2$  (for example, N16 to N7, see Table 1)). If the  $[\text{VOC}]_0$  and  $[\text{O}_3]_0$ , as well as their ratio ( $[\text{O}_3]_0/[\text{VOC}]_0 \sim 2.4$ ), are fixed (Exp. N17-N21), it can be seen from Fig. R2 that the fraction of limonene reacted with  $\text{NO}_3$  increases monotonically and that reacted with  $\text{O}_3$  decreases monotonically with the increasing of  $\text{NO}_2$ . Under this kind of conditions, the SOA yield first increases rapidly, and then levels off or decreases at last according to the increasing of  $\text{NO}_2$  (See experimental work shown in Fig.3, and modeling work in Fig. S5c). Based on mechanism analysis, it is believed that in very high  $\text{NO}_2$  level, the increase of PANs and nitrates cannot compensate the decrease of ROOHs and acids in aerosol phase with the increase of  $\text{NO}_2$ , which indicates again the competition between  $\text{NO}_3$ - and  $\text{O}_3$ - initiated oxidation.

So, it is seemed that neither  $\text{O}_3$  chemistry nor  $\text{NO}_3$  chemistry can result in the changes in SOA yield and composition alone.



**Figure R2.** The fraction of limonene reacted with the different oxidants according to the changing of  $\text{NO}_2$  (simulation for Exp. N19-N21).

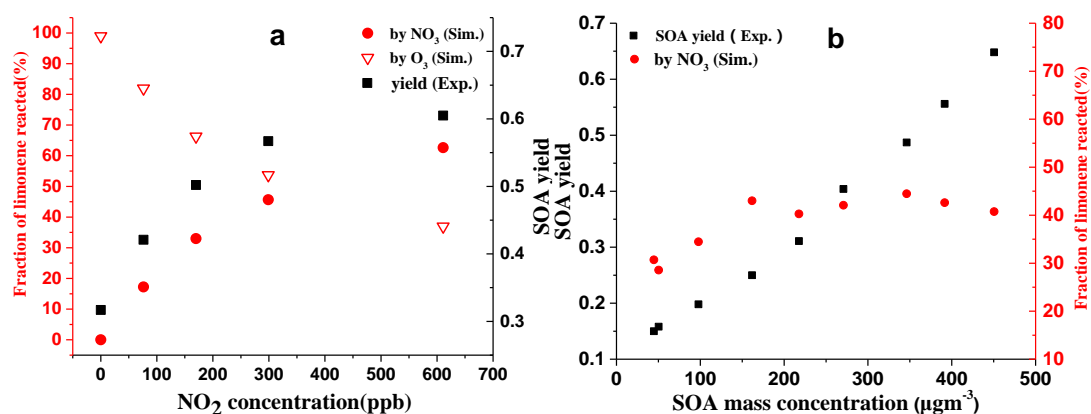
#### CHANGES IN THE REVISED MANUSCRIPT:

Based on Figure R1 and Figure R2 here, Figure 8 concerning to the fraction of the limonene reacts with  $\text{O}_3$  versus  $\text{NO}_3$  and the corresponding SOA yields has been added in the revised manuscript, and the original fraction of limonene reacted with different oxidants for Exp. N8-N21 has been shown in Figure S7 and Figure S8 in the revised supplement (See the revised supplement). And we have re-written the

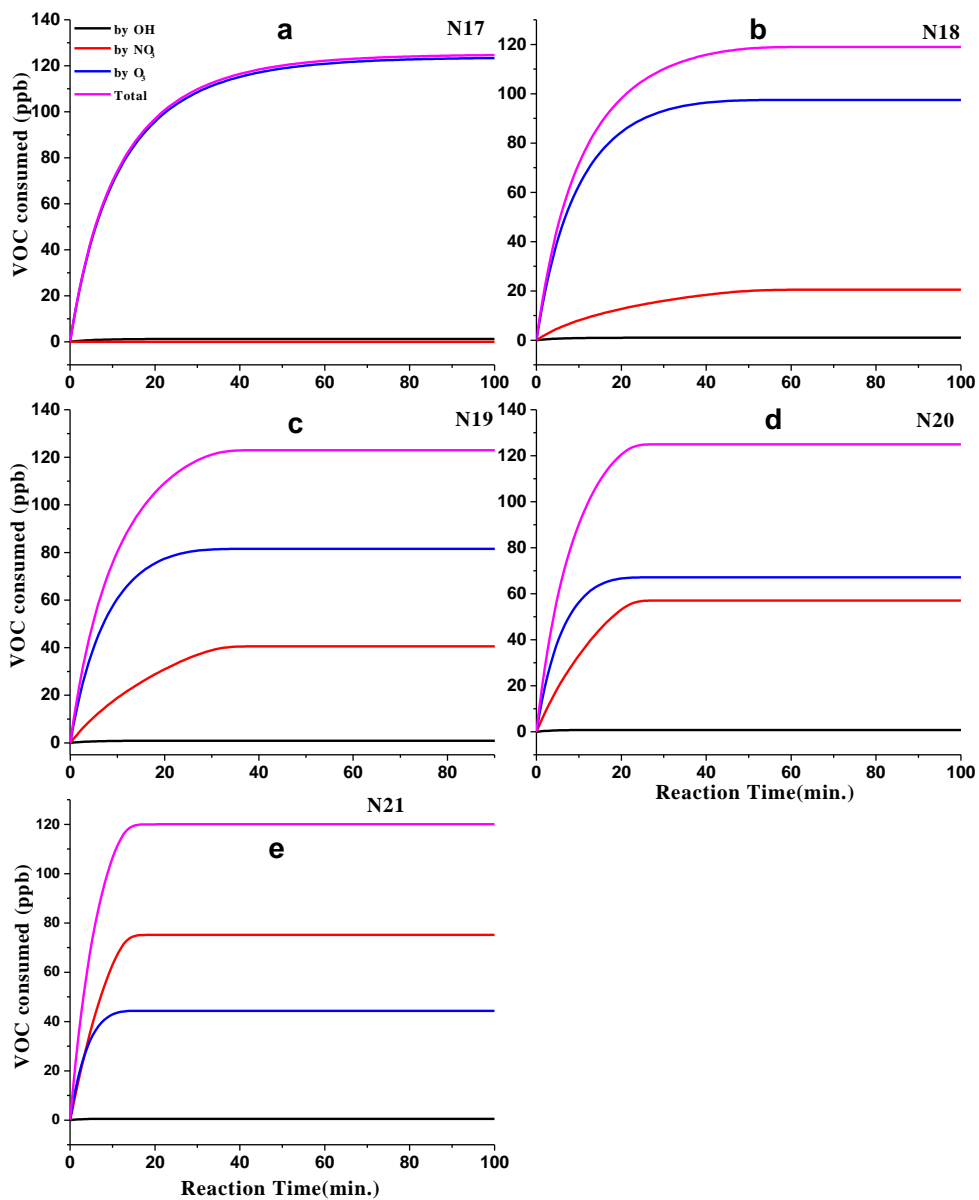
corresponding paragraph from line 546 to line 568 in 3.4. part in the revised manuscript as the following:

"For example, given the fixed  $[VOC]_0$ ,  $[O_3]_0$  and their ratio ( $[O_3]_0/[VOC]_0 \sim 2.4$ ) for Exp. N17-N21, it can be found that the fraction of limonene reacted with  $NO_3$  increases monotonically with the increasing of  $NO_2$ , and the observed SOA yield also increases accordingly under the same conditions (Figure 8a and Figure S7). It is believed that in this case,  $NO_3$ -initiated oxidation of limonene can produce some condensable organic nitrates, such as NLIMOOH and LIMBNO<sub>3</sub>(Figure 7), which compensate the decrease of ROOHs and acids in aerosol phase leading to the increase of SOA formation. In fact, large amounts of organic nitrates have also been observed experimentally as the major reaction product of limonene oxidation by  $NO_3$  (Spittler et al., 2006; Fry et al., 2011), which substantiates the observation in this work.

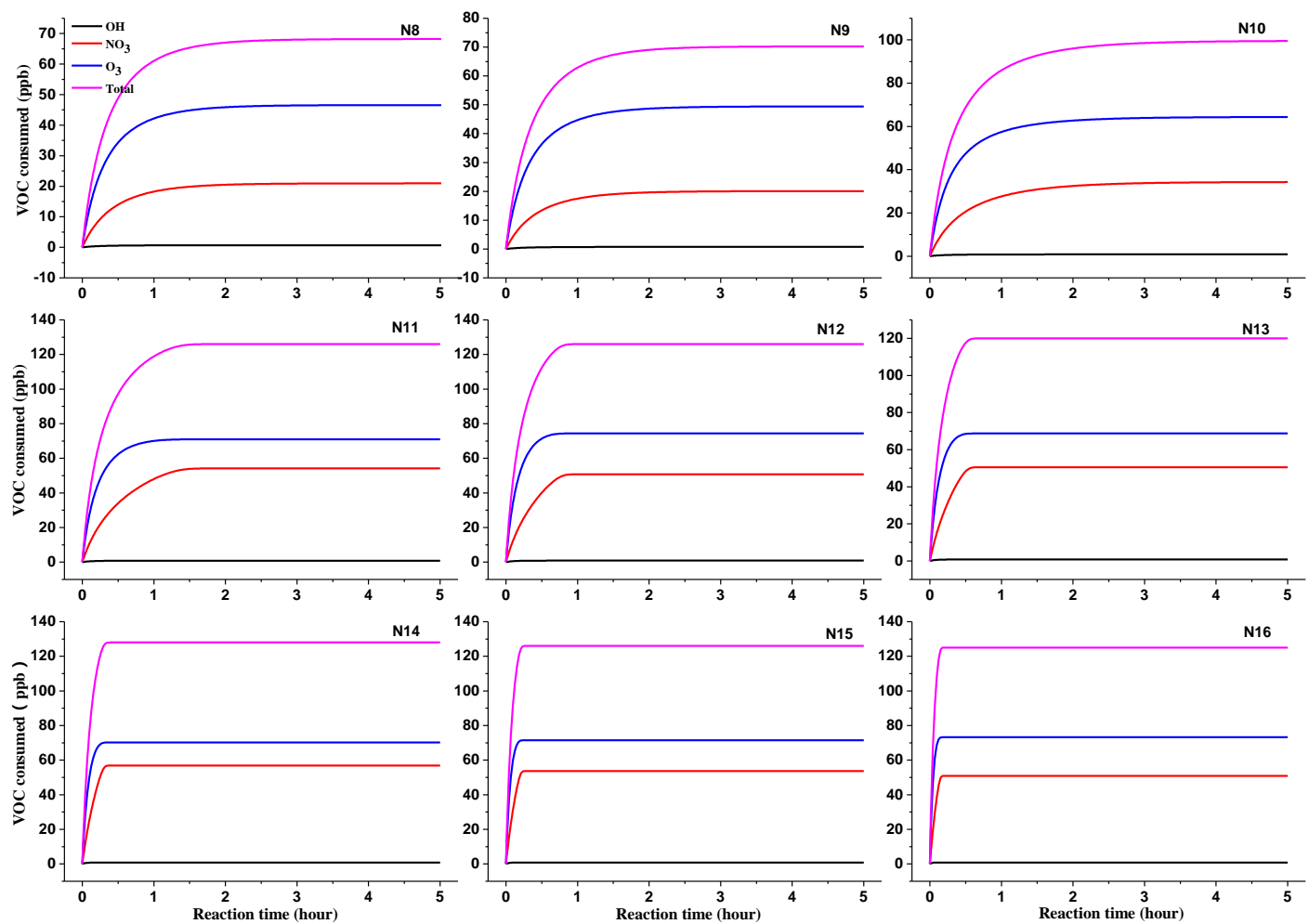
However,  $NO_2$  effect on SOA formation is embodied not only in the initial competition between  $NO_3$  and  $O_3$  oxidation. As shown in Figure 8b and Figure S8, although the SOA yields increased with the increasing of the percentages of total limonene consumed by  $NO_3$  for Exp. N8-N11, it is interesting to find that the SOA yields still increased from Exp. N11 to N16 even the percentages of total limonene reacted by  $NO_3$  were almost the same ( $\sim 42\%$ ). It is worthy to point out that despite increasing in turn from N8 to N11, the SOA yields in N8-N11 are lower than the corresponding SOA yields without  $NO_2$  under the similar  $[O_3]_0$  and  $[VOC]_0$  conditions(Exp. N1-N4, see Table 1). On the contrary, in high  $[O_3]_0$  conditions, the SOA yields with  $NO_2$  (Exp. N14-N16) are even higher than that without  $NO_2$  (Exp. N5 - N7, see Table 1). So it is presumed that  $NO_2$  (or  $NO_3$ ) also participates in participation in the production of PANs and nitrates following ozonolysis of limonene. "



**Figure 8.** The fraction of the limonene reacted with oxidant ( $O_3$  or  $NO_3$ , model study) and the corresponding SOA yields (experimental work) for Exp. N8-N16(a) and Exp. N17-N21(b).



**Figure S7.** The evolution of the limonene consumed by different oxidants for Exp. N17-N21 (Simulation based on MCM model). In order to show the consuming rate of limonene, only the initial stage of reaction (the first 100 minutes) has been shown here for each experiment.



**Figure S8.** The evolution of the limonene consumed by different oxidants for Exp. N8-N16 (Simulation based on MCM model).

## **References:**

- Griffin, R. J., Cocker III, D. R., Flagan, R. C., Seinfeld, J. H., and Dabdub, D.: Estimate of global atmospheric organic aerosol formation from the oxidation of biogenic hydrocarbons, *Geophys. Res. Lett.* 26, 2721–2724, 1999.
- Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, *J. Geophys. Res.-Atmos.*, 100, 8873–8892, doi:10.1029/94JD02950, 1995.
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- He, Y., Uno, I., Wang, Z., Ohara, T., Sugimoto, N., Shimizu, A., Richter, A., and Burrows J. P.: Variations of the increasing trend of tropospheric NO<sub>2</sub> over central east China during the past decade. *Atmos. Environ.*, 41, 4865–4876, 2007.
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- Presto, A. A., Hartz, K. E. H., and Donahue, N. M.: Secondary organic aerosol production from terpene ozonolysis. 2. Effect of NO<sub>x</sub> concentration, *Environ. Sci. Technol.*, 39, 7046–7054, 2005.

## **Specific comments:**

1. *Experimental methods - were these experiments conducted in the dark?*

### **REPLY:**

Sure, these experiments were conducted in the dark. Please see "...21 darkened chamber experiments were carried out at room temperature..." in Line 233 in the revised manuscript.

2. *Figure 2 - I suggest that the authors place error bars on the yield data. Is the difference between NO<sub>2</sub> and non-NO<sub>2</sub> experiments truly meaningful?*

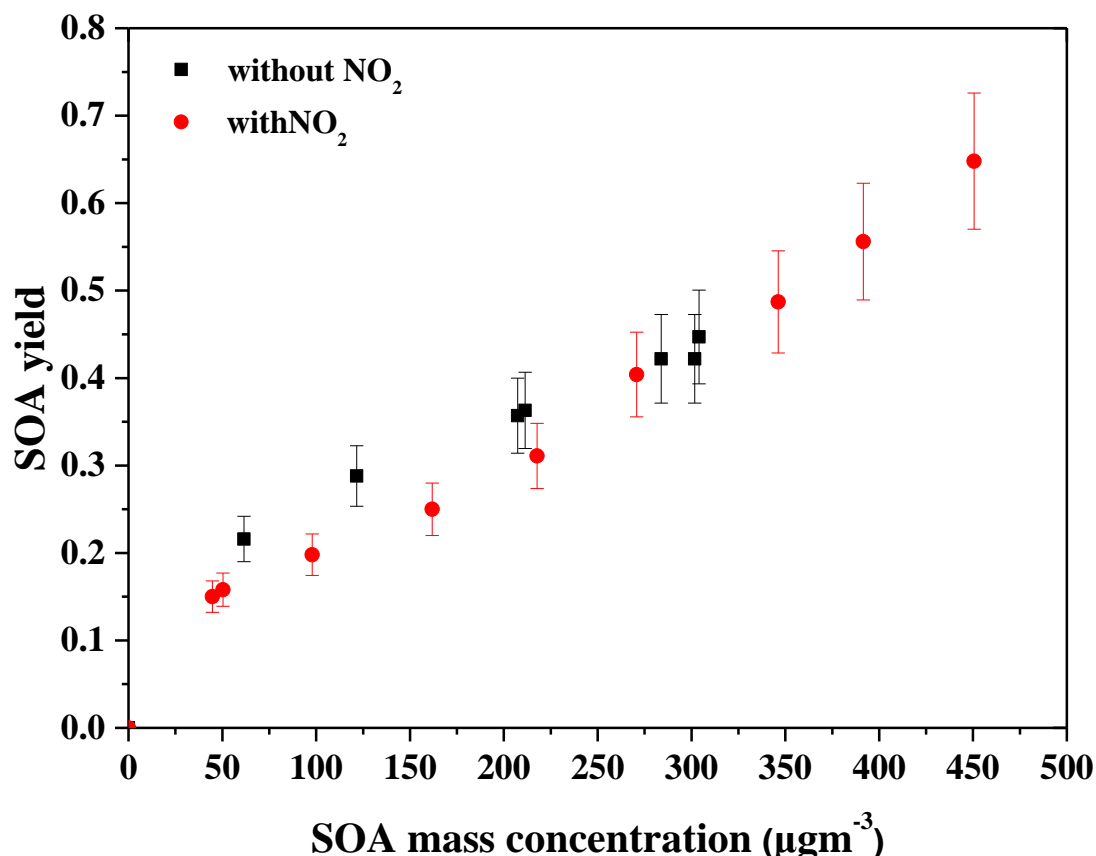
### **REPLY:**

Thank you very much for your suggestion. As aforementioned in the reply to the main criticisms, it is believed that the difference between NO<sub>2</sub> and non-NO<sub>2</sub> experiments is truly meaningful. In compare with that of Exp. N1-N7 (without

NO<sub>2</sub>), the SOA yields for Exp.N8-N16 (with NO<sub>2</sub>) show complicated variation under the similar [VOC]<sub>0</sub> and [O<sub>3</sub>]<sub>0</sub>. Under [O<sub>3</sub>]<sub>0</sub>/[VOC]<sub>0</sub> < 2 conditions (N8-N12), the introduction of NO<sub>2</sub> results in a weak negative effect on the SOA yields compared to that without NO<sub>2</sub>. While at [O<sub>3</sub>]<sub>0</sub>/[VOC]<sub>0</sub> > 2 conditions (N13-N16), SOA yields increase substantially, far exceeding those without NO<sub>2</sub> at a similar mixing ratio of [O<sub>3</sub>]<sub>0</sub> and [limonene]<sub>0</sub>. And it is believed that NO<sub>3</sub> chemistry plays an important role with the introducing of NO<sub>2</sub>. So, the observed difference of SOA yield between NO<sub>2</sub> and non-NO<sub>2</sub> experiments indicates the different source and underground competition between O<sub>3</sub> chemistry and NO<sub>3</sub> chemistry, and the different chemical composition of aerosol particles.

**CHANGES IN THE REVISED MANUSCRIPT:**

We have added the error bars in Fig.2 and the corresponding change in figure caption in the revised manuscript as " Each data point represents an individual experiment, and has an estimated uncertainty of ±15%."



**Figure 2.** Aerosol yield for the limonene/O<sub>3</sub>/NO<sub>2</sub> system for the initial terpene mixing ratios of ~ 125 ppb with NO<sub>2</sub> (~250 ppbv) or without NO<sub>2</sub>. Each data point represents an individual experiment, and has an estimated uncertainty of ± 15%.

3. Figure 2, Lines 295-310. The figure shows that the experiments with the highest SOA yield had NO<sub>2</sub>. But I am unconvinced by the argument NO<sub>2</sub> is causing the higher



yields, because it is extremely difficult to compare "paired" sets of experiments (e.g., X ppb limonene and no NO<sub>2</sub> versus X ppb limonene and Y ppb NO<sub>2</sub>).

**REPLY:**

Thank you very much for your observation.

Maybe it's better to give an example here.

It seems that NO<sub>2</sub> effect on SOA formation is related to the [O<sub>3</sub>]<sub>0</sub>/[VOC]<sub>0</sub> ratio. For clarity, two "paired" sets of experiments are presented here. Both of Exp. N2 and N10 have similar [O<sub>3</sub>]<sub>0</sub>, [VOC]<sub>0</sub> and the [O<sub>3</sub>]<sub>0</sub>/[VOC]<sub>0</sub> ratios are nearly to 1 (see Table 1), where the introduction of NO<sub>2</sub> in Exp. N10 resulted in the decrease of SOA yield compared to Exp. N2. However, for Exp. N7 and N16, both of them have similar [O<sub>3</sub>]<sub>0</sub>, [VOC]<sub>0</sub> and the [O<sub>3</sub>]<sub>0</sub>/[VOC]<sub>0</sub> ratios of them are > 5 (see Table 1), where the introduction of NO<sub>2</sub> in Exp. N16 resulted in the increase of SOA formation. Similarly, N5 vs. N14, and N6 vs. N15 can also affirm that the introducing of NO<sub>2</sub> has led to the increasing of SOA yields under the [O<sub>3</sub>]<sub>0</sub>/[VOC]<sub>0</sub> > 2 conditions.

**CHANGES IN THE REVISED MANUSCRIPT:**

We have added the two pair of experiments as example in the corresponding paragraph. "*For example, Exp. N2 and N10 have similar [O<sub>3</sub>]<sub>0</sub>, [VOC]<sub>0</sub> and [O<sub>3</sub>]<sub>0</sub>/[VOC]<sub>0</sub> ratios (~1) (see Table 1), while the introducing of NO<sub>2</sub> in N10 resulted in the decrease of SOA yield compared to N2.*" in line 307-309 and "*For example, N16 has similar [O<sub>3</sub>]<sub>0</sub>, [VOC]<sub>0</sub> and [O<sub>3</sub>]<sub>0</sub>/[VOC]<sub>0</sub> ratios (> 5) to N7 (see Table 1), where the introduction of NO<sub>2</sub> in N16 resulted in the increase of SOA formation compared to N7*" in line 313-316 of the revised manuscript.

4. Line 367 - what drove the temperature difference between the sets of experiments?

**REPLY:**

Thank you very much for your observation.

The case is that the two sets of experiments has been performed in different seasons. N17-N21 were carried in summer season, whereas N1-N16 were carried in winter season. Although with air conditioner in the lab, there was still temperature difference between the two sets of experiments.

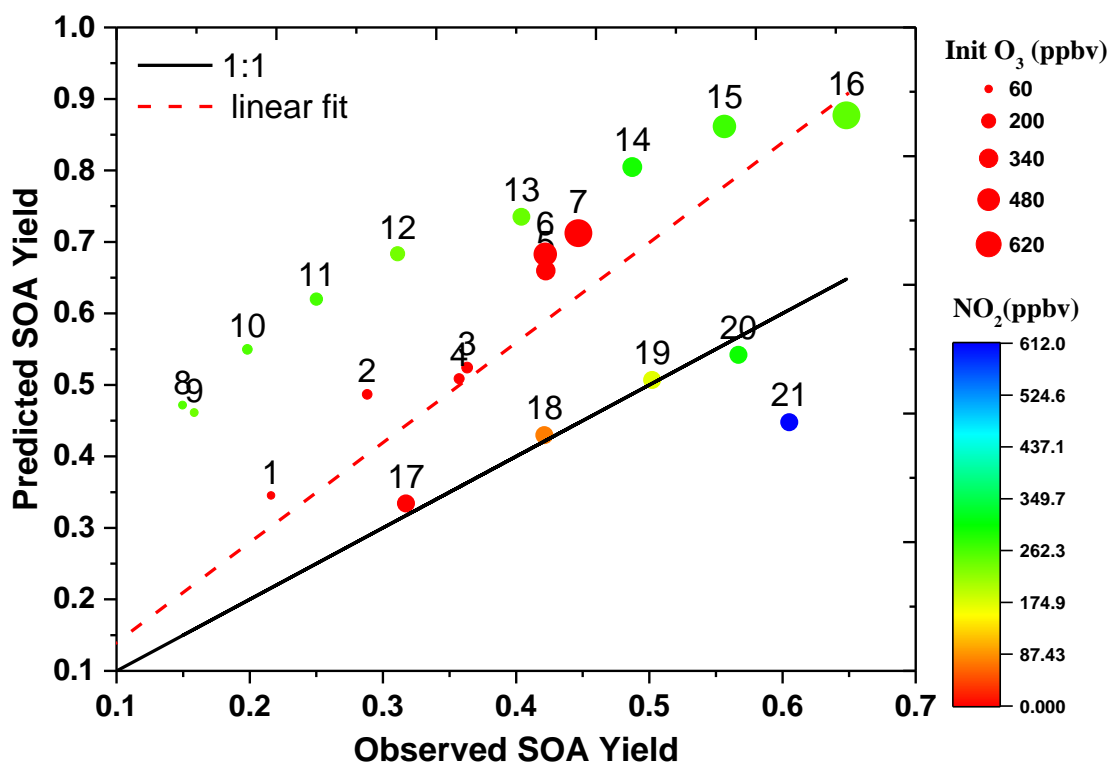
5. Figure 4 would benefit from having a 1:1 line

**REPLY:**

Thank you very much for your suggestion. We agree with you that the linear fit line is not the best way to illustrate the relativity between the predicted SOA yield and the observed SOA yield, so the 1:1 line has been added in new Fig. 4.

**CHANGES IN THE REVISED MANUSCRIPT:**

We have added 1:1 line in new Fig. 4, and revised the corresponding figure caption. We have re-written the paragraph: "It is shown that almost all the data points lie above the 1:1 line and the slope of the linear fit line of the points is 1.4, which indicates that the predicted results are higher than the observed ones."



**Figure 4.** Comparison of the observed SOA yield and the predicted SOA yield for all the smog chamber experiments. The sizes of the data points represent the corresponding initial O<sub>3</sub> levels of the simulated experiments, and the color scale represents corresponding initial NO<sub>2</sub> levels. The solid black line is 1:1 line, while the dash red line is linear fit for all data points. (Number 1-21 above the data points corresponds to Experiment N1-N21 shown in Table 1)

6. The authors should comment on what fraction of the limonene reacts with O<sub>3</sub> versus NO<sub>3</sub> - at least for the endo bond - in the various experiments. It seems like this should be retrievable from the MCM runs.

**REPLY:**

Thank you very much for your valuable suggestion. We agree with you that if the fraction of the limonene reacts with O<sub>3</sub> versus NO<sub>3</sub> is added, the role of the competition between O<sub>3</sub> with NO<sub>3</sub> initiated limonene oxidation on SOA formation will be more explicit. So we have investigated the fractions of the limonene reacts with O<sub>3</sub> versus NO<sub>3</sub> for the experiments (N8-N21) as shown in Figure S7 and Figure S8 in the revised supplement.

**CHANGES IN THE REVISED MANUSCRIPT:**

We have re-written the corresponding paragraph from line 539 to line 561 in 3.4. part in the revised manuscript, and added the fraction of the limonene reacts with O<sub>3</sub> versus NO<sub>3</sub> in Figure 8 in the revised manuscript, as well as Figure S7 and Figure S8 in the revised supplement.

*7. Is scheme 1 new - generated as a result of this work - or reproduced from the MCM? If it is from the MCM, the authors need to clearly state that the Scheme is not their original work. The same applies to Table 2.*

**REPLY:**

Thank you very much for your suggestion. Scheme 1, as well as the contents in Table 2, was reproduced from the MCM.

**CHANGES IN THE REVISED MANUSCRIPT:**

We have labeled " Reproduced from the MCM " in the corresponding place.