Answer to comment of **Referee#2**

on "**Influence of NO2 on secondary organic aerosol formation from ozonolysis of limonene**" by Changjin Hu et al.

Reviewer Comment - OVERVIEW:

In this work, the authors studied the effect of NO_2 on secondary organic formation from limonene. Specifically they conducted chamber experiments with limonene and ozone, and investigated the effect of added NO_2. They followed up with a gas-phase explicit oxidation model (Master Chemical Mechanism) and gas-particle partitioning calculations to corroborate the experimental findings. While the topic explored in this work is relevant to the scope of Atmospheric Chemistry and Physics, the new scientific understanding gained by this work is limited, and there are some major issues with the relevance of the modeling work. I therefore do not recommend publication of this manuscript in ACP.

> **REPLY:**
> Thanks to the referee for the thoughtful comments and valuable suggestions that will contribute without doubt to improve our original manuscript.
>
> The new scientific understanding gained by this work is that the complicated NO_2 effect on SOA formation from ozonolysis of limonene depending on the $[O_3]_0/[VOC]_0$ ratio, different from the generally negative effect of NO on SOA formation, has been observed experimentally. Based on our experimental work, it indicates that a) understanding the overall effect of NOx (NO + NO_2), not only NO as mainly investigated before, on SOA yields is very important, especially for the real atmosphere influenced by both biogenic and anthropogenic sources; b) even the observed aerosol mass or yield are similar, the underground formation mechanism as well as the chemical composition of aerosol particle may be different, indicating the potential different atmospheric or climate effect and different control strategy. Model study based on MCM has revealed further that not only the competition between O_3- and NO_3-initiated oxidation of limonene, but also the competition between RO_2+HO_2 and RO_2+NO_2 (or NO_3) play an important role in the SOA formation of limonene at the presence of NO_2. So it is believed that the work is helpful to answer to what extent can biogenic SOA be controlled when anthropogenic emissions coexists.
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> 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**).

Major comments:

My biggest issue with this paper is whether or not this work advances scientific understanding of SOA mechanisms. Here the authors use explicit mechanisms

outlined in MCM to model SOA formation. The most important lesson from this exercise is that as NO_2 and O_3 concentrations increase, the contribution of NO_3 oxidation increases, leading to higher SOA from limonene + NO_3. It has been shown in many studies (since Griffin et al., 1999) that terpenes + NO_3 have substantially higher SOA yields than OH oxidation. Also work by Fry et al., has shown large contributions of organic nitrate to SOA. It is therefore not surprising that as NO_3 increases, the amount of SOA from limonene + NO_3 increases. Using a model to verify these experimental observations is hardly insightful, as the model is merely a synthesis and a reflection of what the user already understands. I am therefore highly critical about any broader impacts that this work may carry. I do not find this modeling exercise to add any value to the field.

The authors would need to dig deeper and ask more impact research questions. For example, what would be the NO_2 concentration or relative ratios of NO_2/limonene/O_3 that would divide the different regimes (limonene + NO_3 dominated vs limonene + O_3 dominated) and what would be the implications? Would different regions in the world fall under these different regimes?

I also have issues with the use of MCM coupled to gas-partitioning calculations based on vapor pressures, which are in turn calculated by estimation methods that have 1-2 orders of magnitude in error. More important, many processes, such as oligomerization and heterogeneous phase reactions, vapor losses to the walls, are not represented in the model. I understand that there is somewhat of an agreement in SOA yields between the MCM model and experiments, but constraining with yields is hardly the only goal. One suggestion I have for the authors would be to quantify the functional group abundances shown by the FTIR data. It would be very useful to demonstrate the MCM can also successfully predict the abundances of different functional groups, which would make the model much more powerful. I should also stress that a lot of work has been done since Chan et al. (2010) to demonstrate the formation of epoxide intermediates from MPAN that are important for SOA formation. Lin et al. (2013) suggested the role of methacrylic acid epoxide, and Nguyen et al. (2015) and Kjaergaard et al (2012) suggested the role of HMML.

These pathways are quite specific to isoprene, and may not apply to limonene. The authors need to justify how one can extrapolate results from isoprene to limonene. One notable difference between the two systems are the positions of the double bonds. Isoprene has conjugated double bonds, leading to intermolecular reaction mechanisms to ultimately to lead to low-volatility products. It is not clear if limonene would do the same.

I would imagine with the large excess of butanol, butanol would dominate the NO_3 reactivity. Therefore, the reaction of NO_3 with limonene would be minimized. Is the reaction of butanol with NO_3 included in the model? Also, if the main argument is that as NO_2 increases, the role of NO_3 oxidation increases, the authors should demonstrate evidence either experimentally (very difficult) or in the MCM model (easy to show).

I am not sure if there are any specific recommendations or outcomes from this work

for experimentalists or modelers. It seems that message is "the mechanism is complex", but do not offer any suggestions as to how to reduce that complexity, or how to design specific experiments to probe important branches of the mechanisms. These suggestions are absolutely needed to make the modeling exercise worthwhile.

REPLY:

Thank you very much for your comments and useful suggestion.

We agree with the referee that the reaction of limonene + NO_3 contributes substantially to the production of organic nitrate and the formation of SOA formation. However, there was no convincing evidence that the SOA formation yield of limonene + NO_3 is higher than that of limonene + O_3. Although the rate constant of NO_3 + limonene(1.22×10^{-11} cm^3 $molec^{-1}$ s^{-1}) is higher than that of limonene + O_3 ($2.1 \times 10^{-16} cm^3$ $molec^{-1}$ s^{-1}) for several orders (Atkinson and Arey, 2003), and NO_3-initiated chemistry may be more effective at nucleation step, it was found that limonene ozonolysis produced similar eventual SOA mass yield to that of limonene nitrate oxidation at comparable initial concentrations (Fry et al., 2011). As for NO_3 oxidation of limonene, the mass-based yield measured by Hallquist et al at low limonene concentration reacted (10ppb) were 17% (Hallquist et al, 1999). Moldanova and Ljungstrom have also studied NO_3 oxidation of limonene with modeling, and obtained the roughly same SOA mass yield (18%) at the same conditions with the experimental work of Hallquist et al (Moldanova and Ljungstrom, 2000). At the higher particle mass produced (50-400 μg m^{-3}), the SOA mass yield from NO_3 oxidation of limonene was observed to be 20-40% by Spittler et al (Spittler et al., 2006) and Fry et al. respectively (Fry et al., 2011). As for ozonolysis of limonene, SOA mass yields were investigated to be around 20% by Draper et al using a flow-though reaction chamber (Draper et al., 2015), whereas SOA yields were found to range from 47%-69% for the mount of aerosol mass ranging from 28-347 μg m^{-3} at 293K in AIDA simulation chamber (Saathoff et al., 2009). We have also evaluated the percentage of total limonene reacted by NO_3 at 5 hours for Exp. N8-N16 with MCM. As shown in Fig. R1 (the nomenclature Fig. RXXX is used in this reply differentiating from Fig.XXX in main manuscript and Fig. SXXX in supplement), for Exp. N8-N11, the SOA yields increase with the increasing of the percentages of total limonene reacted by NO_3. For Exp. N11-N16, however, although the percentages of total limonene reacted by NO_3 are almost the same (~42%), the SOA yields still increase from N11 to N16. Regarding to the case, even the SOA formation yield of limonene + NO_3 is higher than that of limonene + O_3, the increase of SOA yields from N11 to N16 cannot be attributed solely to NO_3 oxidation of limonene. So it is presumed that it is the joint action of the competition between O_3- and NO_3-initiated oxidation of limonene and the competition between RO_2+HO_2 and RO_2+NO_2 (or NO_3) that results in the variation of SOA mass yields at the presence of NO_2 from this work.
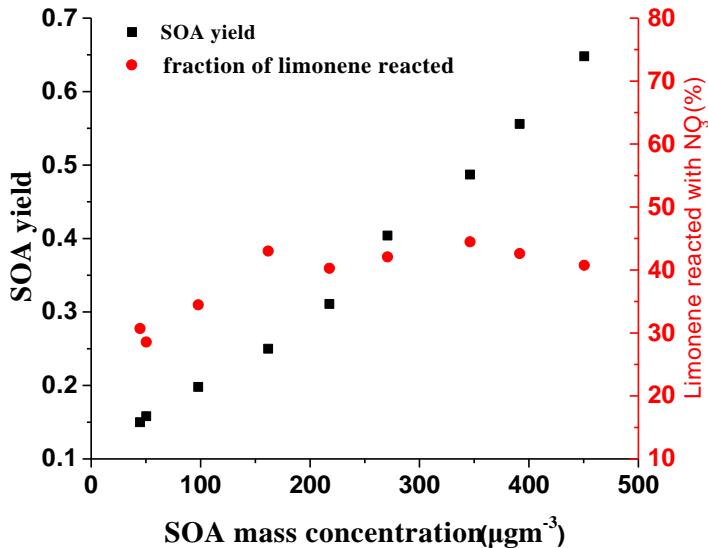
Figure R1. The fraction of the limonone reacted with NO_3(model study) and the corresponding SOA yields (experimental work) for Exp. N8-N16.

It seems that NO_2 effect on SOA formation is related to the $[O_3]_0/[VOC]_0$ ratio. For clarity, two suits of experiments are presented here. Both of Exp. N2 and N10 have similar $[O_3]_0$, $[VOC]_0$ and the $[O_3]_0/[VOC]_0$ ratios (nearly to 1) (see Table 1 in the revised manuscript), where the introduction of NO_2 in Exp.N10 resulted in the decrease of SOA yield compared to Exp. N2. However, for Exp. N7 and N16, the $[O_3]_0/[VOC]_0$ ratios of them are > 5 (Table 1), where the introduction of NO_2 in Exp.N16 resulted in the increase of SOA formation. The experimental work has demonstrated the relationship between the NO_2 effect on SOA formation and the $[O_3]_0/[VOC]_0$ ratio, which results from the two kinds of competitions as aforementioned.

We agree with the referee that the present MCM model is deficient in excluding the important processes during the formation to SOA, such as oligomerization, heterogeneous phase reactions, vapor losses to the walls and so on. Although it should be more deliberate in constraining the SOA yields, it is helpful to understand the explicit chemical mechanism of the gaseous oxidation of VOCs leading to the formation of SOA particles based on model work. It is a valuable suggestion to quantify the functional group abundances based on FTIR analysis. It will be taken into consideration in the future study, such as concentration dependence of functional groups, and the absorptions of nitroperoxy-alkylnitrate compounds (the derivation compounds of NLIMO2 as shown in Scheme 1) (Hallquist et al, 1999). As methacrylic acid (Lin et al. 2013) and HMML (Kjaergaard et al., 2012; Nguyen et al., 2015) are believed as OH adducts, while the large excess butanol has been added into the smog chamber as OH scavenger in this work. So even without regard to the differences of molecular backbone between isopene and limonene, there is hardly any methacrylic acid or HMML produced.

Sure, excess butanol has been added into the smog chamber as OH scavenger, and

the reaction of butanol with NO_3 has not included in the model in this work. Regarding to the rate constant of NO_3 + limonene (1.22×10^{-11} cm^3 molec^{-1} s^{-1}) (Atkinson and Arey, 2003) and that of NO_3 + 1-butanol(1.87×10^{-15} cm^3 molec^{-1} s^{-1}) (Moreno et al, 2003), and the initial concentration of limonene (~125ppb) and 1-butanol(~100ppm), the reaction of NO_3 with limonene would be minimized about 15%. And we have tried to simulate butanol effect on SOA formation under the conditions of $[VOC]_0$=125ppb, $[O_3]_0$=125ppb, and $[butanol]_0$=100ppm at 291K. As shown in Fig. R2, including the reaction of butanol with NO_3 in the model will lead about 12% decrease of the total compounds in aerosol phase (Total mass = M_{ROOHs} + M_{acids} + M_{PANs} + $M_{organic\ nitrates}$).
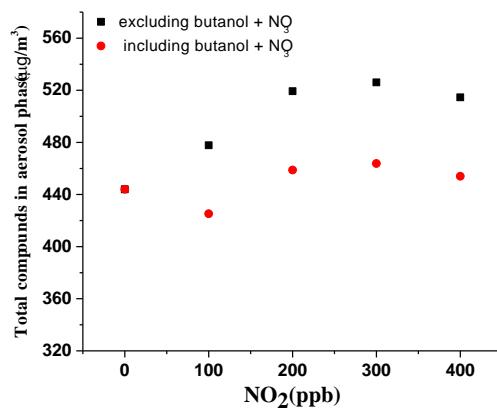
Figure R2. Effect of the reaction of butanol + NO_3 on the particle mass.(● the total compounds in aerosol phase including the butanol + NO_3 in the simulation, same as that shown in Fig 6c in the revised manuscript; ■ the total compounds in aerosol phase excluding the butanol + NO_3 in the simulation)

It's a good suggestion for how to reduce the complexity of the SOA formation mechanism. There are three specific experiments to be planned.
1. Regarding to the case that the precursor limonene was depleted completely at the first 10-20 minutes (Figure 1 in manuscript), to add NO_2 at the 20 minutes (or even longer) later instead of at the beginning will be helpful to exclude or minimize NO_3-initiated oxidation of limonene.
2. Although there were high-resolution mass spectrometric analysis of SOA from ozonolysis of limonene based on ESI (Walser et al., 2008), VUV photoionization aerosol mass spectrometric study based on synchrotron radiation (Pan et al., 2008) is expected meaningful to study the chemical compositions of SOA with or without NO_2.
3. According to the modeling analysis, it seems that when $[O_3]_0$ is 100ppb or below (Figure S5c in supplement), SOA yield will decreases firstly and then increase again with the increasing of $[NO_2]_0$ especially in the low concentration of $[NO_2]_0$. It is believed that the concentration in this levels is more important to field.

CHANGES IN THE REVISED MANUSCRIPT:

Only the main modifications/revisions based on aforementioned reply are listed here, and the other details please find in the point-by-point responses later.

1). Figure 8, as well as Figure S7 and Figure S8 (in the revised supplement), concerning to the fraction of the limonene reacts with O_3 versus NO_3 and the corresponding SOA yields has been added in the revised manuscript. And we have re-written the corresponding paragraph from line 546 to line 568 in **3.4.** part in the revised manuscript, which will confirm that the SOA yield and composition is the combined action of O_3 chemistry and NO_2 chemistry (NO_3 chemistry and direct reaction of NO_2 with the intermediates of limonene+O_3).

Line 546- 568 in **3.4.** part in the revised manuscript:

"*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 LIMBNO3(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 (~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. "
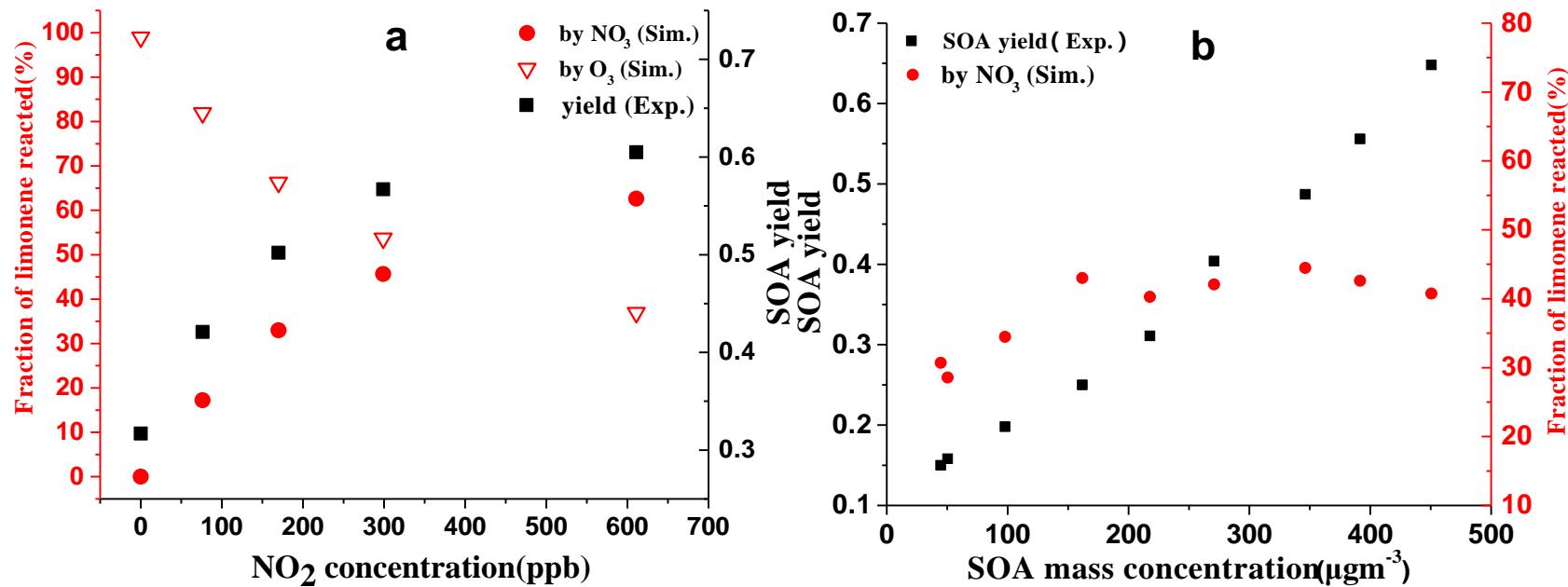
Figure 8. The fraction of the limonene reacted with oxidant (O$_3$ or NO$_3$, model study) and the corresponding SOA yields (experimental work) for Exp. N8-N16(a) and Exp. N17-N21(b).
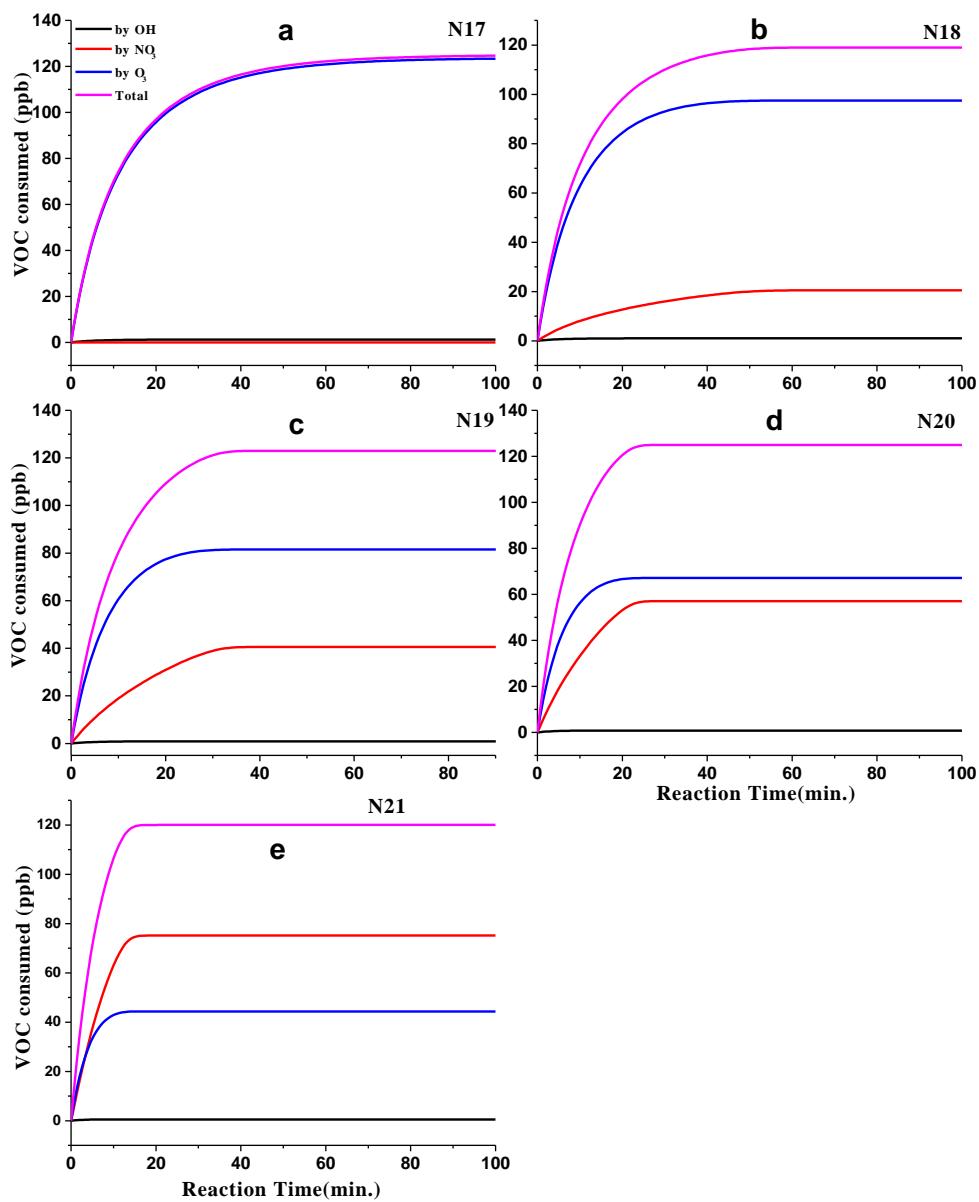
Figure S7. The evolution of the limonene consumed by different oxidants for Exp. N17-N21 (Simulation based on MCM model). In order to show the consuming rate of limonene, only the initial stage of reaction (the first 100 minutes) has been shown here for each experiment.
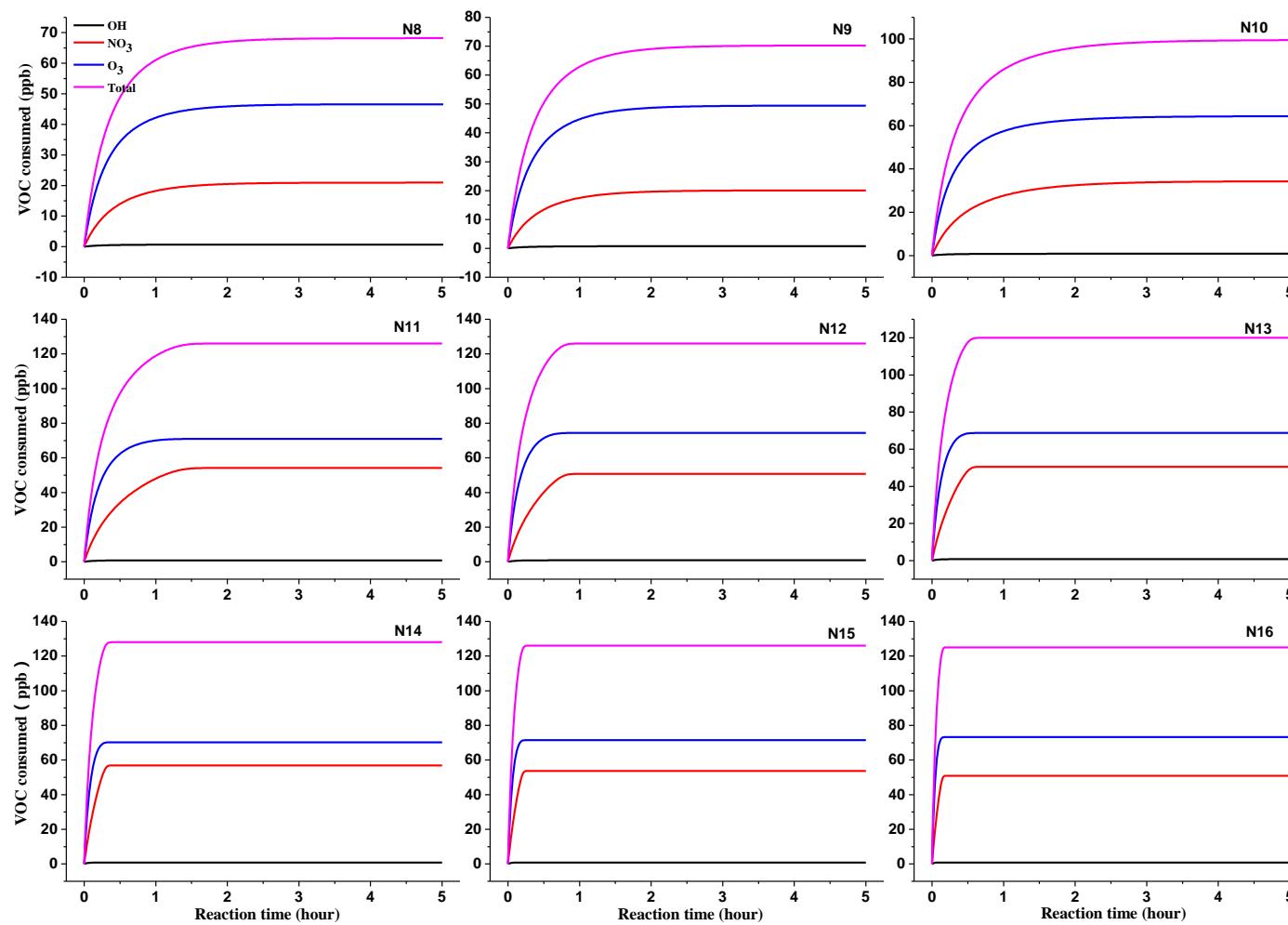
Figure S8. The evolution of the limonene consumed by different oxidants for Exp. N8-N16 (Simulation based on MCM model).

2). The future work, which is presumed to reduce the complexity of the SOA formation mechanism, are listed at the end of the **Conclusions** in the revised manuscript. (see the following)

"*Despite that the influence of NO2 on SOA formation from ozonolysis of limonene has been proved to be resulted from the competition between O3 initiated and NO3 initiated chemistry, as well as that between RO2+HO2 and RO2+NO2 (or NO3) following O3 chemistry, the questions as to what extent and on what chemical components of NO2 effect in lower concentration similar to field related are still to be resolved. So based on this work, the experimental study concerning to the following aspects are expected:*

1. Delay introducing NO2 after the initiation of the ozonolysis reaction in smog chamber instead of at the beginning will be helpful to avoid or minimize the initial competition from NO3-initiated oxidation of limonene.

2. Study on the chemical compositions of SOA with or without NO2 using soft-ionization AMS technique, such as VUV photoionization aerosol mass spectrometric study based on synchrotron radiation (Pan et al., 2008), is helpful.

3. According to the modeling analysis (Figure S5c in supplement), NO2 effect on SOA formation under low concentration of [O3]0 and [NO2]0 is meaningful to the field."

3). Fig.2 and Fig. 4 in the revised manuscript have been revised according to the referee's suggestion.
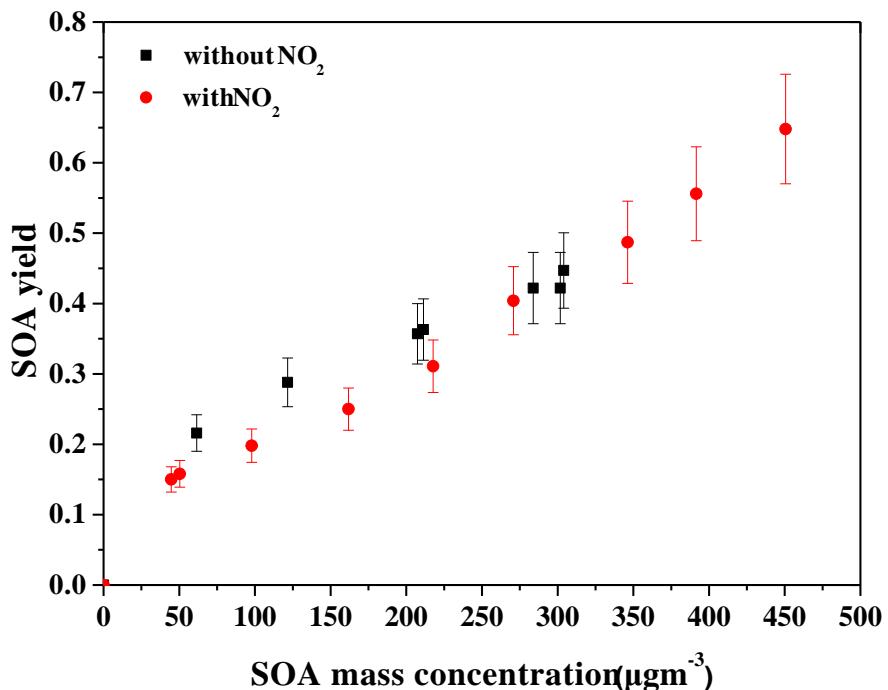
Figure 2. Aerosol yield for the limonene/O_3/NO_2 system for the initial terpene mixing ratios of ~ 125 ppb with NO_2 (~250 ppbv) or without NO_2. Each data point represents an individual experiment, and has an estimated uncertainty of $\pm$ 15%.

We have added 1:1line 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."
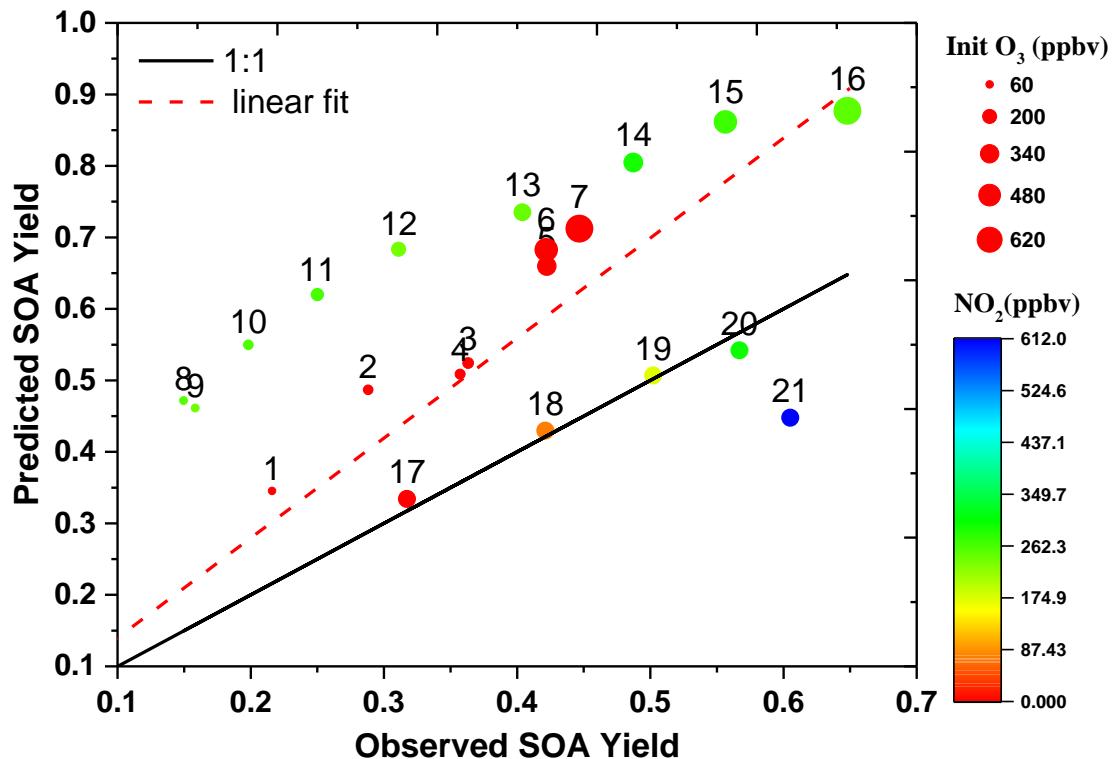
Figure 4. Comparison of the observed SOA yield and the predicted SOA yield for all the smog chamber experiments. The sizes of the data points represent the corresponding initial O_3 levels of the simulated experiments, and the color scale represents corresponding initial NO_2 levels. The solid black 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)

4). There are many other small modifications/revisions, please find in the following.

References:

Atkinson, R. and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: A review. Atmos. Environ. 2003, 37, Supplement No. 2, S197–S219, 2003.

Draper, D. C., Farmer, D. K., Desyaterik Y., and Fry, J. L.: A qualitative comparison of secondary organic aerosol yields and composition from ozonolysis of monoterpenes at varying concentrations of NO_2, Atmos. Chem. Phys., 15, 12267–12281, 2015.

Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Brauers, T., Brown, S. S., Dorn, H.-P., Dubé, W. P., Fuchs, H., Mensah, A., Rohrer, F., Tillmann, R.,Wahner, A.,Wooldridge, P. J., and Cohen, R. C.: SOA from limonene: role of NO_3 in its

generation and degradation, Atmos. Chem. Phys., 11, 3879–3894, doi:10.5194/acp-11-3879-3894., 2011.

Hallquist, M.; Wangberg, I.; Ljungstrom, E.; Barnes, I.; Becker, K. H.: Aerosol and product yields from NO_3 radical-initiated oxidation of selected monoterpenes. Environ. Sci. Technol., 33 (4), 553−559, 1999.

Kjaergaard, H. G., Knap, H. C., Ørnsø, K. B., Jørgensen, S., Crounse, J. D., Paulot, F., and Wennberg, P. O.: Atmospheric Fate of Methacrolein. 2. Formation of Lactone and Implications for Organic Aerosol Production, J. Phys. Chem. A, 116, 5763–5768, 2012.

Lina,Y. H., Zhang, H., Pye, H. O. T., Zhang, Z., Martha, W. J., Parka, S., Arashiro, M., Cui,T., Budisulistiorini, S. H., Sexton, K. G., Vizuete, W., Xie, Y., Luecken, D. J., Piletic, I. R., Edney, E. O., Bartolotti, L. J., Golda, A., and Surratta, J. D.: Epoxide as a precursor to secondary organic aerosol formation from isoprene photooxidation in the presence of nitrogen oxides, Proc. Natl. Acad. Sci. USA, 110 (17), 6718–6723, 2013.

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Moreno A., Salgado S., Taccone R., Martín P., Cabanas B.: Atmospheric degradation of saturated alcohols: Room temperature rate coefficients for NO3 radical reactions, Atmospheric Environment 96 (2014) 229e235

Nguyen, T. B., Bates, K. H., Crounse, J. D., Schwantes, R. H., Zhang, X., Kjaergaard, H. G., Surratt, J. D., Lin, P., Laskin, A., and Seinfeld, J. H.: Mechanism of the hydroxyl radical oxidation of methacryloyl peroxynitrate (MPAN) and its pathway toward secondary organic aerosol formation in the atmosphere, Phys. Chem. Chem. Phys., 17, 17914–17926, 2015.

Pan, G., Hu, C. J., Wang, Z.Y., Cheng, Y., Zheng, X. H., Gu, X. J., Zhao, W. X., Zhang, W. J., Chen, J., Liu, F. Y., Shan, X. B., and Sheng, L. S.: Direct detection of isoprene photooxidation products by using synchrotron radiation photoionization mass spectrometry. Rapid Commun. Mass Spectrom., 26,189–194, 2012.

Saathoff, H., Naumann, K.-H., Möhler, O., Jonsson, Å. M., Hallquist, M., Kiendler-Scharr, A., Mentel, Th. F., Tillmann, R., and Schurath, U.: Temperature dependence of yields of secondary organic aerosols from the ozonolysis of α-pinene and limonene, Atmos. Chem. Phys., 9, 1551–1577, 2009, http://www.atmos-chem-phys.net/9/1551/2009/.

Spittler, M., Barnes, I., Bejan, I., Brockmann, K. J., Benter, T., and Wirtz, K.: Reactions of NO_3 radicals with limonene and alphapinene: Product and SOA formation, Atmos. Environ., 40, S116–S127, 2006.

Walser, M. L., Desyaterik, Y., Laskin, J., Laskin, A., and Nizkorodov, S. A.: High-resolution mass spectrometric analysis of secondary organic aerosol produced by ozonation of limonene, Phys. Chem. Chem. Phys., 10, 1009–1022, 2008.

Other comments:

- *I was wondering about particle wall loss correction, but did not see it until Supporting Information. It would be useful to mention that wall loss has been corrected in the methods and refer to the supporting information.*

REPLY:

Thank you very much for your suggestion.

CHANGES IN THE REVISED MANUSCRIPT:

We have added "*(ΔM_0, $\mu g/m^3$, wall losses has been corrected, please see the detail of wall loss correction in supplement)*" in Line295-296.

- *I assume there are no seed particles (e.g. ammonium sulfate) added. In that case, vapor wall loss will be an even bigger issue since there is an induction period associated with nucleation. Have the authors tried using ammonium sulfate seed to investigate whether or not SOA yields would be higher?*

REPLY:

Thank you very much for your observation. Referring to the study of Zhang et al (Zhang, et al., 2006), where no seed particles added, and the work of Donahue et al (Donahue et al., 2007), where ammonium sulfate seeds were added in roughly 2/3 of the experiments and no systematic dependence on the presence of inorganic seed aerosol, we haven't tried to added seed particles in this work. It's better to try in the future work.

References:

Zhang, J. Y., Huff Hartz, K. E., Pandis S. N., and Donahue, N. M.: Secondary organic aerosol formation from limonene ozonolysis: Homogeneous and heterogeneous influences as a function of NO_x, J. Phys. Chem. A, 110, 11053–11063, 2006.

Donahue, N. M., Tischuk, J. E., Marquis, B. J. and Huff Hartz, K. E.: Secondary organic aerosol from limona ketone: insights into terpene ozonolysis via synthesis of key intermediates, Phys. Chem. Chem. Phys., 9, 2991–2998, 2007.

- *What is the interference of NOy species in the NOx analyzer? They may affect the NO_2 measurements and skew the model-experiment comparison*

REPLY:

Thank you very much for your observation. In principle, PAN and the other organic nitrates in gas phase produced following the reaction of NO_3 or O_3-initiated limonene at the presence of NO_2 will be the interference for NO_2 measurements, especially for high $[NO_2]_0$ and in the late reaction time. So maybe it's one of the sources for the higher observed NO_2 concentration in the late time (See Fig.1).

CHANGES IN THE REVISED MANUSCRIPT:

We have re-written the corresponding sentence "*The simulation also performs well in predicting changes in NO_2 in general except a little lower than the observed value in the later time, which maybe result from the interference of NOy species produced in chamber during the reaction.* " in Line 270-272.

- *Line 327: why is there an increase in particle number concentration? How reproducible are these increases in mode diameter and number concentration?*

REPLY:

Thank you very much for your observation. It's worthy to point out that what we shown the increasing of the mode diameter and the total concentration in Figure S2 was intercepted from two different experiments at the same time(here was 60minitutes) after the initiation of the reaction in smog chamber. It's believed that given the constant $[O_3]_0/[VOC]_0$ ratio with excess O_3, the increase of NO_2 will lead to the increases in mode diameter and number concentration, thus the mass of the SOA as shown in Fig. 3. Although we have mentioned at the same reaction time in the caption of Fig.3, we agree that it's better to be shown in text.

CHANGES IN THE REVISED MANUSCRIPT:

We have re-written the corresponding sentence "the mode diameter increases from 95 to 107 nm and the total concentration increases from 1.77×10^5 to 2.17×10^5 particles/cm^3 *at the same reaction time (here 60 minutes after the initiation of the reaction)* by adding 298.5 ppbv NO_2 " in Line335-336.

- *In general, the FTIR data show what one would expect. Carbonyl groups (and hydroxyl groups) are what one would expect in SOA, and it has been shown in numerous studies that low-volatility organic nitrates can form in the presence of NOx. Is there any indication from the FTIR data about specific reaction pathways? For example, PANs and organic hydroperoxides would produce peroxy (O-O) groups may give a unique peak in the data.*

REPLY:

Thank you very much for your observation.

We have checked the full range FTIR spectra (600-4000cm^{-1}) again (See Fig. R3, from which Fig. 5 in main manuscript were intercepted). Three spectra (background, with and without NO_2) have been normalized according to the background peak at 1151 cm^{-1}. It is shown that there are peaks at 1720 cm^{-1}, 2800-3000 cm^{-1} corresponding to carbonyl groups and aliphatic C-H respectively, as well as the broad absorption around 3400 cm^{-1} corresponding to hydroxyl both in the case with or without the presence of NO_2. However, it is difficult for us to identify which specific aldehyde (for example, limononaldehyde) or acid (for example limononic acid) just depending on the limited FTIR data. We also tried to identify the existence of peroxy (O-O) groups of PANs or organic hydroperoxides. According to the previous work (Hallquist et al, 1999), if there are -O-O-NO_2 groups, three pairs of peaks according to -O-O-NO_2 and -O-NO_2, including 789 cm^{-1} and 848 cm^{-1}, 1298 cm^{-1} and 1286 cm^{-1}, and 1721 cm^{-1} and 1663 cm^{-1}, should be observed. However, comparing to 848 cm^{-1}(-O-NO_2), the peak at 789 cm^{-1} is too weak. That the peaks at 1298 cm^{-1} and 1286 cm^{-1} are too close is beyond the resolution of the spectra. While the peaks at 1721 cm^{-1} is enough to be observed, it overlaps with the absorption of carbonyl groups. Even the data has been normalized in the following figure and it seems that there is difference between

the intensities with or without the presence of NO_2, it is hard to affirm that there is the contribution from -O-O-NO_2 groups at $1721cm^{-1}$ just depending on the present qualitative spectra. More quantitative FTIR studies will be required.
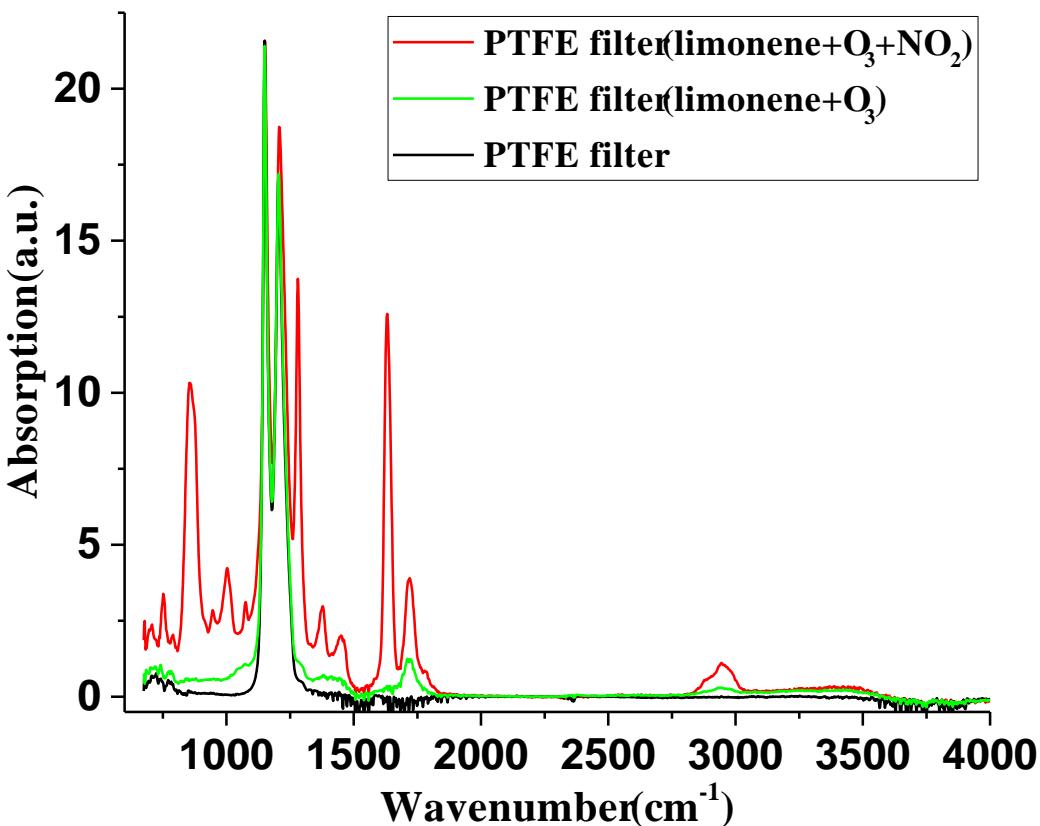
Figure R3. FTIR spectra of the particle products collected with PTFE filters from a high NO_2 experiment (red line), a low NO_2 experiment (green line), and a blank experiment (black line).

CHANGES IN THE REVISED MANUSCRIPT:
We have added the full range FTIR spectra as Figure S6 (same to **Figure R3** shown here) in the revised supplement.

References:
Hallquist, M.; Wangberg, I.; Ljungstrom, E.; Barnes, I.; Becker, K. H.: Aerosol and product yields from NO_3 radical-initiated oxidation of selected monoterpenes. Environ. Sci. Technol., 33 (4), 553−559, 1999.

● *Section 3.3.2: I would take one step back and explore some more basic questions. First, what is the concentration of NO_3 or total NO_3 produced as a function of NO_2 added? Second, what is the fraction of limonene that reacted with O_3 and what is the fraction that reacted with NO_3? These would help support the explanation presented in the conclusions.*

REPLY:
Thank you very much for your useful suggestion.
As in the chamber, NO_3 is produced by the following reactions:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R1}$$
$$NO_3 + NO_2 \rightarrow N_2O_5 \tag{R2}$$
$$N_2O_5 \rightarrow NO_3 + NO_2 \tag{R3}$$

So the change of the concentration of NO_3 is dynamic. The evolutions of NO_3 according to the reaction time in Exp. N19 (left) and Exp. 13 (right) (the conditions of the two experiment please see Table 1 in main manuscript) based on modeling are shown as samples in Fig. R4. During the whole reaction time, the maximum concentration of NO_3 in Exp. 19 is about 0.22 ppb given 300ppb $[O_3]_0$ and 170ppb $[NO_2]_0$, while in Exp. 13, it is about 0.13ppb given 250ppb $[O_3]_0$ and 245ppb $[NO_2]_0$. The evolution of NO_3 in this simulation is similar to that observed using CRDS in the work of Fry et al (Fry et al., 2011). the experimental It seems that the concentration of NO_3 is related to not only the $[NO_2]_0$ but also the $[O_3]_0$.
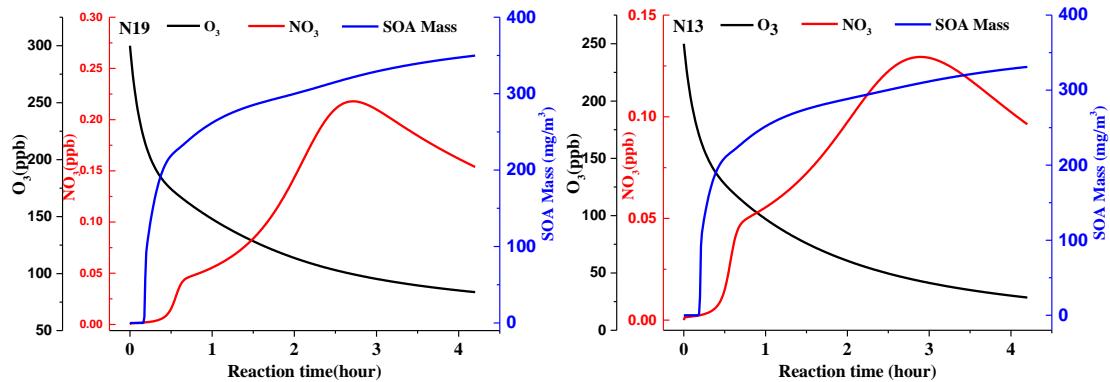
Figure R4. The evolution of O_3, NO_3 and SOA mass in smog chamber.(Simulation for N19 (left)   and for N13 (right))

Given the roughly same $[NO_2]_0$ and $[VOC]_0$ (Exp. N8-N16), the fraction that reacted with NO_3 increased with the increase of $[O_3]_0$ at the low O_3 levels, and then leveled off at the high low O_3 levels (See Fig.R1 in the reply to the major comments). While at the same time, the SOA yield still increases with the increase of $[O_3]_0$ at the high O_3 levels (Fig.2 in main manuscript). If the $[VOC]_0$ and $[O_3]_0$, as well as their ratio ($[O_3]_0/[VOC]_0$ ~2.4) (Exp. N17-N21), are fixed, it can be seen from Fig. R5 that the fraction of limonene reacted with NO_3 increases monotonically and that reacted with O_3 decreases monotonically with the increasing of NO_2. Under this kind of conditions, the SOA yield first increases rapidly with the increasing of NO_2, and then levels off or even decreases at the very high NO_2 level (See experimental work shown in Fig.3, and modeling work in Fig. S5c). The main reason of which is believed that the increase of PANs and nitrates cannot compensate the decrease of ROOHs and acids in aerosol phase at the very high NO_2 level, which indicates again the competition between NO_3- and O_3- initiated oxidation.
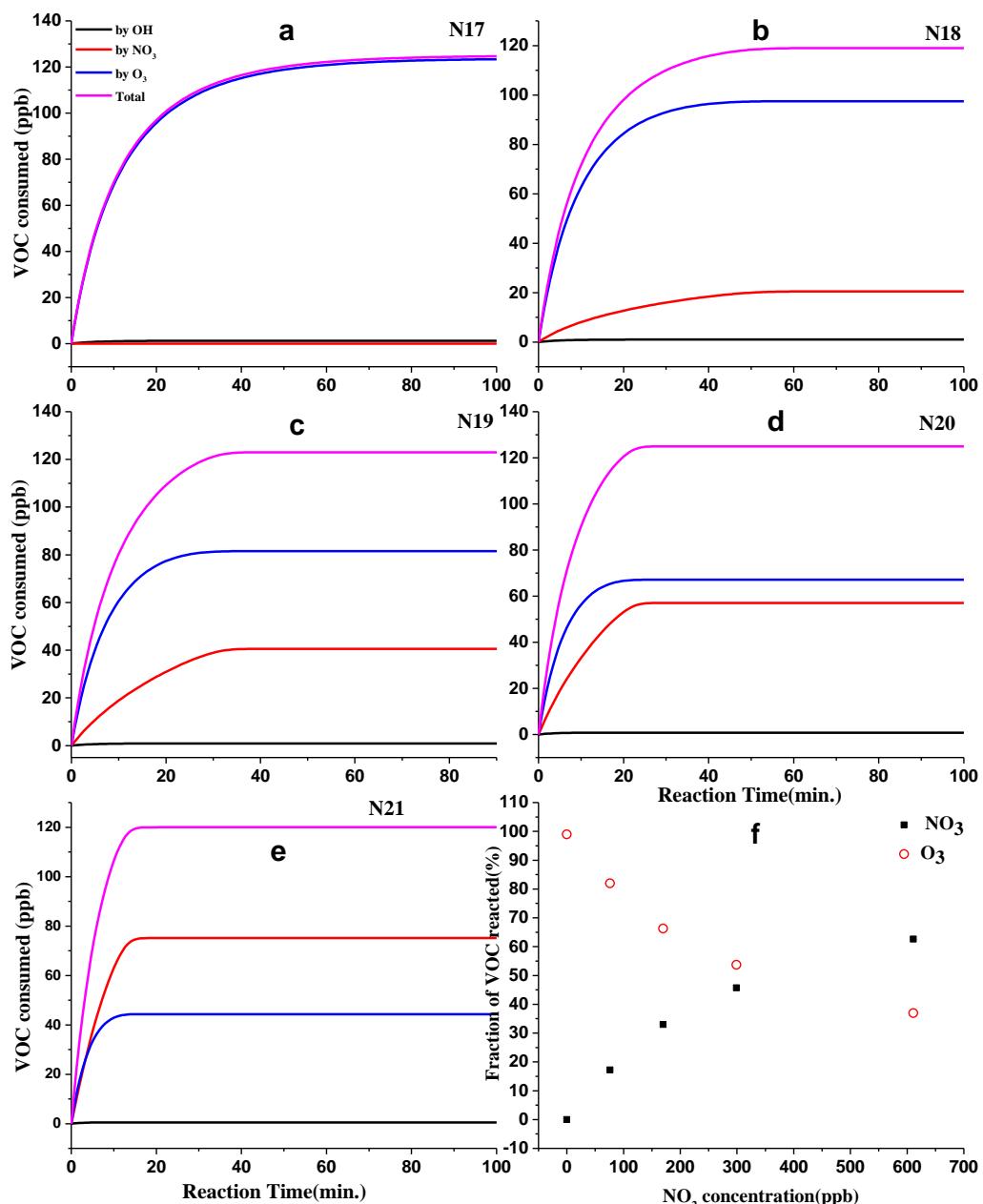
Figure R5. The fraction of limonene reacted with the different oxidants(a-e for Exp. N19-N21) and its change with NO2 concentration(f).

CHANGES IN THE REVISED MANUSCRIPT:

We have added the fraction of the limonene reacts with O_3 versus NO_3 in Figure 8 in **3.4.** in the revised manuscript, as well as Figure S7 and Figure S8 in the revised supplement, and have re-written the corresponding paragraph from line 546 to line 568 in **3.4.** part in the revised manuscript.

References:

Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Brauers, T., Brown, S. S., Dorn, H.-P., Dubé, W. P., Fuchs, H., Mensah, A., Rohrer, F., Tillmann, R.,Wahner, A.,Wooldridge, P. J., and Cohen, R. C.: SOA from limonene: role of NO_3 in its generation and degradation, Atmos. Chem. Phys., 11, 3879–3894,

doi:10.5194/acp-11-3879-3894., 2011.

- *Section 3.3.3: The modeled results about 20 species dominating the particle mass(93-96%) is intriguing. This result may merely be a reflection of what we understand about particle composition, rather than a true representation of the particle composition.The citation stating that a majority of organic nitrates are unidentified (Lines543-544) seems to support the notion that we simply don't have sufficient chemical understanding to model this system explicitly.*

REPLY:

Thank you very much for your useful suggestion.

It seems that we have made a mistake in vocabulary-using, and the word "identified" has confused our original mean. The case is that in our global modeling work, 385 condensable compounds have been examined under the conditions of 125 ppbv $[limonene]_0$ and 300 ppbv $[O_3]_0$. And for each NO_2 level, all of the contributions of the 385 condensable compounds have been investigated. Based on the overall assessment on their the 20 dominant condensable compounds, the 20 top-ranked among the 385 condensable compounds were selected. So it is not that "the 20 dominant condensable compounds were identified" but "were picked out".

CHANGES IN THE REVISED MANUSCRIPT:

We have re-written the corresponding sentences "*By assessing thoroughly their corresponding aerosol mass fractions at 5 different NO_2 scenarios, the top-ranked 20 among the 385 condensable compounds were selected out.* " in Line 499-501, and" *the summation of the contribution from the selected 20 dominant condensable compounds covers 93-96% of the total SOA mass*" in Line 509-510.

Technical comments:

Line 78: "low volatile" should be "low volatility"

REPLY:

Thank you very much for your suggestion.

CHANGES IN THE REVISED MANUSCRIPT:

We have replaced "low volatile" by "*low volatility*".

Line 78: stylistic suggestion "when react with" should be "upon reaction with"

REPLY:

Thank you very much for your suggestion.

CHANGES IN THE REVISED MANUSCRIPT:

We have replaced "when react with" by "*upon reaction with*".

Line 87: "molecular bone" should be "molecular backbone"

REPLY:

Thank you very much for your suggestion.

CHANGES IN THE REVISED MANUSCRIPT:

We have replaced "molecular bone" by "*molecular backbone*".

Line 89: awkward language "a major part from vegetation"

REPLY:

Thank you very much for your suggestion.

CHANGES IN THE REVISED MANUSCRIPT:

We have replaced "is emitted in a major part from vegetation" by "*is one of the major BVOCs emitted by vegetation* ".

Line 99: double bond is unsaturated, saying "unsaturated double bonds" is redundant

REPLY:

Thank you very much for your suggestion.

CHANGES IN THE REVISED MANUSCRIPT:

We have replaced "unsaturated double bonds" by "*double bonds*".

Line 170 – 173: is it necessary to cite these papers? It seems like these self citations are here to inflate citation numbers. These papers should only be cited if they help describe the experiment methods. Even so, one citation should be sufficient.

REPLY:

Thank you very much for your suggestion.

CHANGES IN THE REVISED MANUSCRIPT:

Only one paper (Huang et al., 2013), which is helpful to describe the experiment methods, has been kept. Please see Line 172 in the revised manuscript.

Line 175 and 179: what is the difference between dry zero air and purified air?

REPLY:

There was no difference between the "dry zero air" and the "purified air" in this work.

CHANGES IN THE REVISED MANUSCRIPT:

In order to avoid the potential confusion, "*dry zero air*" has been used consistently (Line174, 177 and 182 in the revised manuscript).

Line 181: excessive should be excess. How much butanol is in excess?

REPLY:

Thank you very much for your suggestion. And the concentration of butanol in

smog chamber was around 100 ppm.

CHANGES IN THE REVISED MANUSCRIPT:
We have replaced "excessive" by "*excess*" in Line 179 in the revised manuscript. And the concentration of butanol has been given in parentheses.

Line 187: what is TEI? I assume it is the ThermoFisher NOx analyzer (42i).

REPLY:
Thank you very much for your observation. And TEI is the abbreviation for "Thermo Environmental Instruments Inc", which is the old name of the Thermo Inc.. It's better to use the new name "Thermo Fisher Scientific Inc."

CHANGES IN THE REVISED MANUSCRIPT:
We have replaced "TEI model 42i" and "TEI model 49i" by "*Thermo Fisher Scientific Inc, model 42i*" and "*Thermo Fisher Scientific Inc, model 49i*" respectively (Line 185 and Line 188 in the revised manuscript).

Line 229-230: I am not sure what this statement means. Oligomerization reactions do happen for larger molecules too. Why are they not considered? The SOA yields here are on average around 40%, meaning that there is still a lot of mass that are in the gas phase and can potentially condense upon further oxidation, or oligomerization.

REPLY:
Thank you very much for your observation. Sorry for the unclear expression. We agree with you that oligomerization reactions can happen for larger molecules too. What we wanted to show is that oligomerization reactions, as well as heterogeneous and multiphase reactions, are not included in current model, and only the gas/particle partitioning of condensable organic compound are included. In this case, it was suggested that the compounds with more carbons have the potential to form SOA.

CHANGES IN THE REVISED MANUSCRIPT:
We have re-written the paragraph:
"...in this work *(Xia et al., 2008). And it was suggested that generally the compounds with more carbons have the potential to condense into the aerosol phase (Seinfeld and Pandis, 1998), so* 385 stable species with more than three carbons..." (in Line 230-232 in the revised manuscript)

Line 286: what does typical mean? Is it typical of polluted regions? If so, how much limonene is typically present in high NO2 areas? Limonene has very short lifetimes and therefore may not be present in high concentrations outside of forested areas. One exception could be indoor environments where limonene is used in air fresheners.

REPLY:
Thank you very much for your observation. It seems that the word "typical" has

been inappropriately used here. Our original intention was just to show that the experiments were conducted under two different NO_2 levels.

CHANGES IN THE REVISED MANUSCRIPT:
We have replaced "typical" by "*different*". (in Line 289 in the revised manuscript)

Line 330: form should be from

REPLY:
Thank you very much for your observation.

CHANGES IN THE REVISED MANUSCRIPT:
We have replaced "form" by "*from*". (in Line 338 in the revised manuscript)

Line 347: passways should be pathways

REPLY:
Thank you very much for your observation.

CHANGES IN THE REVISED MANUSCRIPT:
We have replaced "passways" by "pathways". (in Line 355 in the revised manuscript)

Line 368-369: slope does not makes sense. Just because the slope is 1.4 it does not mean yields are overestimated across the board. There is an intercept for the best fit line.

REPLY:
Thank you very much for your observation. The intercept of the linear fit line of the points is 0. And 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 1:1line has been added in new Fig. 4.

CHANGES IN THE REVISED MANUSCRIPT:
We have added 1:1line 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.*" (in Line 375-377 in the revised manuscript).

Lines 415-416: why can NO be ruled out? Is it because of high O_3 and NO_3 levels? What are the measured levels of NO?

REPLY:
Thank you very much for your observation.
As our opinions, there are two reasons that why NO has been minimize in this work. The first is in order to control the initial concentration of NO_2, NO_2 gas

from cylinder has been input another Teflon bag firstly and diluted with zero air (main components of which are N_2 and O_2). Even there was some impure NO in NO_2 cylinder gas, they should be oxidized by O_2 leading to NO_2. The second is due to the high initial concentration of O_3, which will also react with NO even if there is residual. In all the experiments, the levels of NO is under the limit of the NOx analyzer (Thermo Fisher Scientific Inc, model 42i).

CHANGES IN THE REVISED MANUSCRIPT:
We have replaced "However, this reaction pathway can be ruled out at high O_3 conditions." by "*However, this reaction pathway has been minimized under the conditions in this work.*". (in Line 424-425 in the revised manuscript)

Line 419: Ng et al. (2007) does not show PAN formation.

REPLY:
Thank you very much for your observation. Sure, we have made a mistake in referring to the work of Ng et al. (2007). In their work, the formation of relatively low-volatility organic nitrates and isomerization of large alkoxy radicals, not the formation of PAN, were observed.

CHANGES IN THE REVISED MANUSCRIPT:
We have re-written the paragraph: *"...it was confirmed recently that the formation of low-volatility organic nitrates (Ng et al., 2007) or peroxy acyl nitrates (PANs, $RC(O)OONO_2$) (Chan et al., 2010) can contribute certainly to SOA formation at high NO_2 levels...".* (in Line 427-429 in the revised manuscript)

Line 423: awkward language "learn" should be "study"

REPLY:
Thank you very much for your suggestion.

CHANGES IN THE REVISED MANUSCRIPT:
We have replaced "learn" by "*study*". (in Line 432 in the revised manuscript)

Line 448 typo: oxidation

REPLY:
Thank you very much for your observation.

CHANGES IN THE REVISED MANUSCRIPT:
We have corrected. (in Line 458 in the revised manuscript)

Line 484: what does "semi-qualitative" mean?

REPLY:
Thank you very much for your observation. We agree with you that the ambiguous word " semi-qualitative" has been used here.

CHANGES IN THE REVISED MANUSCRIPT:

We have re-written the sentence:" *The simulation result here also supports the FTIR analysis of SOA particles.*" (in Line 493-494 in the revised manuscript)

Line 583: typo in the second set of parentheses

REPLY:
Thank you very much for your observation. We have missed some words after the "except".

CHANGES IN THE REVISED MANUSCRIPT:
We have corrected "*except N17*". (in Line 605 in the revised manuscript)

Line 597: stylistic suggestion: do not start a sentence with actually.

REPLY:
Thank you very much for your suggestion.

CHANGES IN THE REVISED MANUSCRIPT:
We have deleted the word " *actually* ". (in Line 618 in the revised manuscript)

Line 599: what is whenas? Maybe "whereas"?

REPLY:
Thank you very much for your observation and suggestion. We have equated the word "whenas" with "whereas".

CHANGES IN THE REVISED MANUSCRIPT:
We have replaced "whenas" by "*whereas*". (in Line 620 in the revised manuscript)

Figure 2: what are the error bars?

REPLY:
Thank you very much for your observation. The main error of SOA yield is believed to result from the systematic error for measuring [limonene] and the mass of aerosol particles. The accuracy for the detection of limonene with GC-MS was $\pm6\%$, while that for the integrated mass of formed SOA with SMPS system was $\pm5\%$, so the total error of SOA yield is estimated less than 15%.

CHANGES IN THE REVISED MANUSCRIPT:
We have added the error bars in Fig.2 (as aforementioned) and the corresponding change in figure caption.

Figure 4: the red line is not the 1:1 line. For these model-experiment comparison, it would be useful to show a 1:1 line. The best fit line is not useful.

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 1:1line has been added in new Fig. 4.

CHANGES IN THE REVISED MANUSCRIPT:

We have added 1:1line in new Fig.4(as aforementioned), 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.*"