Review of “Impact of NOx and OH on secondary organic aerosol (SOA) formation from β-pinene photooxidation” by Sarrafzadeh et al.

This manuscript studied the effects of NOx and OH concentration on SOA yield from β-pinene photooxidation based on well-designed laboratory chamber experiments. By adjusting the j(O1D), the authors successfully investigated the individual effect of NOx on SOA yield. The authors showed that the SOA yield from β-pinene photooxidation decreases with increasing NOx while the OH concentration is kept constant. This offers one possible explanation to previously reported non-linear dependence of SOA yield on NOx level. This is an important study on the effects of NOx on SOA formation. However, some discussions in the manuscript are confusing and require clarification. I recommend accepting manuscript after major revisions.

Major comments.

1. Clarification of NOx effects are required.

As stated in the manuscript, NOx can affect SOA yield through various mechanisms (i.e., affect OH concentration, affect RO_2 fate, affect new particle formation, etc). However, the term “NOx effect” is not well-defined and causes confusions in the manuscript. In the manuscript, the impacts of NOx on SOA yield through influencing OH concentration sometimes is treated as NOx effects, but sometimes is not. For example, Page 2 Line 15 stated that “NOx dependencies vary for different NOx conditions”, which implies that the effect of OH is treated as part of NOx effects. However, Page 2 Line 19-21 stated that “After eliminating the effect of NOx induced changes of OH concentrations, the overall effect of NOx on SOA yield was moderate”, where the effect of OH is not treated as part of overall NOx effects. In order to clarify the discussion, I suggest the authors to use “direct effect of NOx” (i.e., effect of NOx on RO_2 fate) and “indirect effect of NOx” (i.e., effect of NOx through influencing OH concentration). Terms “direct effect” and “indirect effect” will be used in the following comments.

2. Are the results in the manuscript helpful to models?

In real atmosphere, if the NOx concentration changes, the SOA yield will change as a result of both direct and indirect effects of NOx. In atmospheric models, which have explicit radical chemistry (like MCM mechanism), the direct and indirect effects of NOx have already been treated separately. In atmospheric models, which do not explicitly treat the RO_2 fate (like global models), the non-linear dependence of SOA yield on NOx is preferable, because it includes the overall (both direct and indirect) effects of NOx. Thus, the results in this study are seemingly not helpful for models. In another words, what suggestions could this study provide to models and how do the authors suggest models to treat the NOx effects on SOA yield?

3. Expand the discussion on the effect of NOx on RO_2 fate.

After eliminating the effect of NOx on NPF and OH concentration, the observation that SOA yield decreases with increasing NOx concentration is caused by NOx effect on RO_2 fate. The authors should expand the discussion on this direct effect of NOx on SOA yield. Also, the authors should comment on why the direct effect of NOx only has a moderate influence on SOA yield. Is this observation surprising since that the products from RO_2+HO_2 and RO_2+NOx are quite different?

Also, the manuscript treated the NOx-induced suppression of NPF as a separate effect of NOx. However, the suppression of NPF is just a reflection of the NOx effect on RO_2 fate and oxidation products. Thus, the suppression of NPF should not be considered as a separate effect.

4. The effect of OH concentration on SOA yield.

Previous studies have investigated the effects of OH exposure (or oxidation extent) on SOA yield (Song et al., 2007; Chan et al., 2007; Healy et al., 2009). For example, Eddingsaas et al. (2012) clearly showed that the SOA yield from α-pinene photooxidation is a function of OH exposure. However, previous studies on the effect of OH concentration on SOA yield are not properly cited in the manuscript. Section 3.1.1 is not novel.

Many previous studies have realized the confounding effect of OH concentration when studying the effects of NOx on SOA yield. For example, Xu et al. (2014) reported the SOA yield of isoprene photooxidation, which is calculated under the same OH exposure, as a function of NOx level. Xu et al. (2014) showed that the SOA yield from isoprene photooxidation has a non-linear dependence on NOx while the OH exposure is kept constant. It is clearly that the direct effect of NOx on SOA yield depends on VOCs.

There are two ways to isolate the effect of OH exposure. One is holding both OH concentration and oxidation time constant as done in this study. The other one is to vary both OH concentration and oxidation time but keep the OH exposure constant as done in Xu et al. (2014). Can the authors conduct experiments to examine if these two methods result in the same conclusion regarding the direct effect of NOx on SOA yield? For example, in order to achieve the same OH exposure under different NOx levels, the authors can hold j(O1D) constant and adjust the residence time in the reactor.

5. I have serious concerns about the wall loss correction in this manuscript.

Firstly, the wall loss correction algorithm is derived from the loss rate of gas HOMs, but is applied to correct particle masses. This correction is not appropriate considering that HOMs only account for a small mass fraction of total OA concentration (Ehn et al., 2014) and that wall loss rate of HOMs and particles are different. In the SI, the authors briefly mentioned that the wall loss rate of 50-150nm particles is negligible compared to the losses of HOMs. However, the authors should be more quantitative when comparing the rates, instead of only citing Mentel et al. (2009). Although the particle wall loss rate is smaller than HOMs, the mass concentration loss caused by particle wall loss could be orders of magnitude larger than that caused by HOMs wall loss. In another word, in order to justify the wall loss correction applied in the manuscript, the authors need to verify that the mass concentration loss caused by particle wall loss is negligible compared to that caused by HOMs wall loss. Comparing wall loss rate is not enough. In the SI, the authors assume that the Fp is the same between HOMs and semi-volatile species. The authors need to justify this assumption. Many previous studies have investigated the vapor wall loss (Krechmer et al., 2016; Zhang et al., 2014; McVay et al., 2016; Nah et al., 2016), but none of them are cited in the manuscript.

Secondly, the description of wall loss correction methods needs to be expanded and clarified. To name a few,

(1) Although the procedures to calculate incremental yields have been described in Mentel et al. (2009), it is helpful to explain “incremental yields” and the calculation procedure in the manuscript.

(2) Although the wall loss correction procedure has been discussed in the SI, it is helpful to elaborate the discussion in the main text. Especially, how is the correction factor applied to particle mass? Do the authors consider the particle size distribution when apply the correction factor, since the particles with different size has different wall loss rate (Loza et al., 2012).

(3) It is not clear how the authors obtain and apply only one Fp vs particle surface area curve for the correction (Figure S5), since different HOMs have different Fp (Figure S3),

(4) Page 7 Line 20. Why is the procedure only valid for the chamber used in this study?

(5) Page 7 Line 22. Which wall loss correction method does the word “above” refer to?

Thirdly, are HOMs produced under high-NOx conditions? If not, how is the wall loss correction factor obtained for high-NOx experiments?

6. Section 3.2 needs better organization and clarification.

Firstly, in this study, the role of NO/NO_2 ratio in SOA formation is just a reflection of the effect of OH concentration. This needs to be clearly stated, because NO/NO_2 ratio can affect SOA formation through other mechanisms. For example, the NO/NO_2 ratio can affect RO_2 fate and oxidation products (Chan et al., 2010). In fact, section 3.2 can be merged with section 3.1 since section 3.2 still probes the effect of OH concentration, but from another aspect.

Secondly, in section 3.2, the role of NO/NO_2 is probed by comparing high O_3 and low O_3 experiments (figure 5 vs 7 and figure 4 vs 6), instead of within one single figure. This comparison should be clearly stated in the manuscript to avoid confusion. For example, add "by comparing figure 5 and figure 7" in Page 14 Line 11. Also, can the authors merge figure 7 with figure 5 and merge figure 6 with figure 4 to facilitate the comparison?

Thirdly, under the same O_3 concentration (i.e., figure 5), does the NO/NO_2 ratio change with NOx level? Is it possible that the moderate direction effect of NOx on SOA yield is confounded by the varying NO/NO_2 ratio at different NOx level? Can the authors add the NO/NO_2 ratio as a third x-axis in the figures? The authors can potentially probe the effect of NO/NO_2 ratio on SOA yield through affecting the RO_2 fate.

Fourthly, in order to justify that the NO/NO_2 ratio changes with adjusting O_3, the author could simply show the NO/NO_2 ratio for high low O_3 and high O_3 experiments. If the authors want to theoretically prove the argument, the authors need to justify how the reaction of NO with RO_2 can be neglected (Page 14 Line 3).

7. Experiments in the presence of seed aerosol (section 3.4)

The fundamental reason for enhanced SOA yield by adding seed is that seed particles reduce the vapor wall loss. In fact, the lower SOA yield without seed emphasizes the uncertainties/errors in wall loss correction procedures. Thus, the authors should expand the discussion on the wall loss correction uncertainties/errors (i.e., my comment #5). The authors should also comment on why adding seed has larger effect on high-NOx conditions than low-NOx conditions.

Minor Comments.

1. Figure 3. Why does the particle mass have a linear relationship with consumed β-pinene? In another word, why is the SOA yield constant and independent on ΔMo? This contradicts previous studies (Ng et al., 2006; Griffin et al., 1999).

2. Page 2 Line 4. Please change it to "we found increases of SOA yields <u>with increasing NOx</u> as low NOx conditions."

3. Page 2 Line 13. Remove the semi-colon after "both".

4. Page 2 Line 22. Add the discussion why a-p SOA yield decreases with increasing NOx. To avoid confusion.

5. Page 3 Line 21. The dependence of SOA yield on NOx level is different for different VOCs. For larger VOCs, such as sesquiterpenes, SOA yields are largest at high NOx levels (Ng et al., 2007; Kroll and Seinfeld, 2008).

6. Page 4 Line 7. It is not right to state that "organic nitrates are suggested to be relatively volatile…" According to the SIMPOL model (Pankow and Asher, 2008), nitrate functionality can reduce the molecule volatility by the similar magnitude as hydroxyl functionality and hydroperoxide functionality.

7. Page 5 Line 17-18. It is very nice to adjust j(O1D) to adjust [OH]. Please comment on how the adjustment would affect the photolysis of other species.

8. Page 8 Line 2-7. Why is SOA yield determined by the oxidation rate of the BVOC? Eq. (3) seems straightforward.

9. Page 8 Line 14. Why is the low-NOx condition defined as $[NO_x]_0<30$ppb and $[BVOC]_0/[NO_x]_0 > 10$?

10. Page 10 Line 4. Please cite Xu et al. (2014) who studied the effects of NO_x on isoprene SOA yield.

11. Page 10 Line 12. Add "from isoprene" after the word "yield".

12. Page 10 Line 17. It is true that the RO_2 fate changes over the course of experiments in many previous studies, which run the chamber in the batch mode. Is the batch mode or CSTR mode more representative of real atmosphere?

13. Page 12 Line 8. Could be more explicit/quantitative about β-pinene+OH rate vs nopinone+OH rate.

14. Page 12 Line 17. The formation of ELVOCs is mainly from isomerization. Its formation only requires one OH reaction to initiate the reaction (Ehn et al., 2014).

15. Page 15 Line 10-12. Does it mean the direct effect of NOx on SOA yield is related to OH concentration? If the O_3 concentration is even higher, will the decrease in SOA yield become smaller? Why?

16. Page 16 Line 1-2. Why did the authors conclude that "no particle formation at all was observed when $[NOx]_0$ was above 60ppb"? The SOA yield is about 5% when NOx was above 60ppb as shown in Figure 8. Also, in the caption of Figure 8, why is the x-axis not comparable even if α-pinene concentrations are lower?

17. Page 16 Line 15-16. Will the authors observe similar trends between α-pinene and β-pinene systems if the OH concentration is the same?

18. Page 19 Line 9. This sentence could be rephrased to something like "the non-linear dependence of SOA yield on NOx reported in previous studies is due to differing OH concentration."

19. Page 19 Line 10. The mechanism for [OH] dependence has been probed in previous studies (Chan et al., 2007), which should be discussed in the manuscript.

Reference

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