Response to Reviews

We thank both referees for their constructive comments and suggestions. As far as possible we followed their suggestions and changed the text accordingly. Here, we provide the modifications made in the manuscript as well as our responses to the comments.

To allow better distinguishing between the comments of the reviewers and our responses, the reviewers' comments are written in bold and italic. Additionally, the revised texts are highlighted in yellow in the revised manuscript.

Anonymous Referee #1:

In this manuscript Sarrafzadeh et al. conducted experimental studies of SOA formation from beta-pinene photooxidation. Specifically they controlled the levels of NOx and OH systematically and identified the role of each factor independently. NOx and OH are often coupled and it is generally difficult to separate the individual roles of these 2 species, but the authors have done so successfully and carefully in the work presented here. The end result is that after controlling for OH, NOx (and more likely NO) decreases SOA yield. The authors also investigated the role of NPF in contributing to SOA formation. The experiments are well designed and the results are thoroughly interpreted. I recommend that this manuscript be published in ACP after considering the following minor comments:

- The authors postulate that OH increases SOA yield by accelerating the oxidation and leading to lower volatility products (page 12, lines 7-17). One way to investigate this hypothesis is to compare SOA yields at the same extent of reaction, or OH exposure. This will require repeating the experiments and adjusting the flow rates to achieve the same extent of reaction.

Response: It has been described that SOA yields depend on OH concentrations and the measurements as suggested have already been conducted (see also the comments of reviewer #2). With respect to a dependence of SOA yields on OH concentrations we therefore just confirm what is known from the literature and we see no need to repeat measurements that have already been performed.

- In many instances (such in the abstract pg. 2 line 16-17), the authors mentioned that SOA yields decrease *because of* suppressed new particle formation (NPF). To be more precise, that should be reworded to "SOA yields decrease because of limited available particle surface area."

Response: We agree, in some cases this is a better formulation. We changed the text in the abstract (Page 2, Line 18) and in Page 19, Line 9 of the revised manuscript.

- Also, the section on how to correct for ELVOC in the SOA yields is unclear. More details are needed in page 7 lines 13-20. How are the loss rates of ELVOCs on walls and on particles determined? Are they experimentally determined with CIMS?

Response: Yes, the loss rates of ELVOC were determined by CIMS measurements. We expanded the text written in the manuscript. As the procedure is described in detail in the supplement we tried to keep it as short as possible in the manuscript. The reference to the supplement was placed in the beginning of the paragraph to point to the information in the supplement. The following section has been changed in the revised manuscript (Page 8, Line 14 - Page 9, Line 6):

"Details of the correction method are described in detail in the supplement. Briefly, ELVOCs were measured with a NO_3^--CIMS (Ehn et al., 2014; Mentel et al., 2015). Stopping the ELVOC production by stopping OH production allowed measurement of their decay rates and thus of their lifetimes. In the absence of particles the lifetimes were in the range of 2 to 3 minutes. The lifetimes became shorter with increasing particle surface because of condensation of the ELVOCs onto the particles. Knowing the total loss rate and the wall loss rate allowed the determination of ELVOC condensation onto the particles, as well as the fraction of condensation F_p: $\left(F_P = \frac{Loss\ on\ particles}{Loss\ on\ particles + loss\ on\ walls}\right)$. The measured mass was then corrected accordingly, by dividing by F_P. We verified this correction procedure for experiments with α-pinene and β-pinene with particle surfaces varying over a wide range, including different amounts of ammonium sulfate seed aerosols. - Note that the numbers obtained for wall loss correction are only valid for the chamber used in this study."

- When controlling OH concentrations, the shortwave UV radiation is varied to change J(O1D). Is there any indication that changing the shortwave UV changes SOA? Many aldehydes can potentially photolyze in that range of wavelengths.

Response: This is correct; many aldehydes can photolyse in the near UV. However, at the wavelength of 254 nm where we photolyse ozone, the absorption cross sections of important aldehydes are 2 to 3 orders of magnitude lower than that of O_3. ($\sim 4 \cdot 10^{-21}$ cm^2 for formaldehyde, $\sim 2\ 10^{-20}$ cm^2 for acetaldehyde, IUPAC, Atkinson et al. 2004, $<5\ 10^{-20}$ cm^2 for pinonealdehyde, Capouet et al., 2004) compared to $\sim 10^{-17}$ cm^2 for O_3). As there is also not very much actinic flux from our lamp we assess aldehyde photolysis at 254 nm to be unimportant with respect to SOA formation.

We also varied OH in a different way than by $J(O^1D)$. Instead we varied water vapour concentrations at constant $J(O^1D)$ or we added carbon monoxide at constant $J(O^1D)$. Both procedures vary OH but cannot change the photolysis of the aldehydes present in the system. From these measurements, there is no indication that photolytic processes at 254 nm had significant impact on SOA formation in our chamber.

Please note that there were effects of UV radiation on SOA formation when changing the light of UVA lamps (12 lamps, Phillips, TL 60 W/10-R, 60W, λmax =365 nm). The actinic flux from these lamps was much higher than that from the 254 nm lamp and, consistent to the findings of Kroll et al. (2006), higher light intensity of the UVA lamps caused lower particle mass.
This was the reason why we kept the light intensity in the UVA range always constant and why we changed the $[NO]/[NO_2]$ ratio by changing $[O_3]$ and not by changing $J(NO_2)$. The observed effects of NOx therefore were clearly attributed to NOx and not to changes in aldehyde photolysis in the UVA range.

- Does NO3 play a role in the differences in SOA yields? In Section 2.1, JNO2 is computed. Similarly, JNO3 should be computed so as to ensure that NO3 plays a minor role, since changes in radiation or in O3 may result in differences in NO3, which can react with beta-pinene rapidly.

Response: We measured the NO_3 concentrations in our chamber at other instances. Under experimental conditions described here, NO_3 concentrations were negligibly low. This can be understood from the low production rate of NO_3 (the rate constant of NO_2 + O_3 reaction is only around 3.2×10^{-17} $cm^3\ s^{-1}$). Thus, not much NO_3 is produced within the residence time of the air in our chamber (45 min.). Furthermore, the measurements described here were made under illumination with HQI lamps that were used to simulate sunlight and strongly photolyse NO_3. In addition, the UVA lamps produced NO that scavenges NO_3; and last but not least, our measurements were made at a relative humidity of ~ 63 %, high enough to suppress N_2O_5.
From the conditions during the experiments described here, we are confident that NO_3 reactions play a minor role.

- pg. 9 lines 11-12: how are ammonium sulfate particles generated? Presumably using an atomizer? The apparatus should be mentioned.

Response: We added more information on the generation of seed particles in the revised manuscript (Page 10, Line 20 – Page 11, Line 3) as given below:

“The seed particles were generated using a constant output aerosol generator (TSI, Model 3076) by atomizing. $(NH_4)_2SO_4$ solutions (typical concentration ~ 40 mg/L) at a pressure of around 1.4 bar. The generated aerosol then passed through a silica gel diffusion drier before entering the reaction chamber. In the control experiments, distilled water was used for atomization to keep the experimental conditions constant.”

- pg. 10 line 8: "differed" should be "different"

Response: Corrected, thanks for pointing this out.

- I find this notation confusing: J(O1D) refers to the photolysis rate of O3 to form O1D (and not the photolysis rate of O1D), but J(NO2) refers to the photolysis rate of NO2.
This notation seems inconsistent.

Response: This is just a common terminology that we used.

Anonymous Referee #2:

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.

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 RO2 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 RO2 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.

Response: The sentence on Page 2 Line 15 indeed could be misunderstood. The word "It" at the beginning of the sentence was therefore exchanged by "Our results". To avoid confusion we furthermore changed the sentence on Page 2 Lines 19-21, by exchanging the word "overall" by the word "remaining".

Regarding the phrasing "direct" and "indirect" effects of NO_x, we ourselves might have raised confusion by using this terminology twice. However, there is no direct effect of NO_x on SOA formation because neither NO nor NO_2 efficiently condense on particles. There are only "indirect" NO_x effects. NO_x acts by steering chemical and physical processes, i.e. OH recycling, NPF, and the branching of RO_2 chemistry as the dominant ones. All these processes are indirect and separation into direct and indirect effects is not meaningful. We therefore refrain from using this terminology and we deleted the words "direct" and "indirect" when combined with NO_x effects.

To clarify the discussion we changed the title of Section 3.2 from "Role of NO/NO_2 ratio in SOA formation" to "Possible role of peroxy radical chemistry and [NO]/[NO_2] ratio in SOA formation" and mentioned impacts of NO_x on peroxy radical chemistry at the end of this section (see also our response on the respective comment no. 3 of reviewer #2).

Otherwise there is no need for further pointing out that there are different processes by which NO_x affects SOA yields.

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 RO2 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?

Response: In our opinion it is always helpful if a mechanism is better characterized and a process is better understood. This is also helpful for models. Also modelling has to consider basic mechanisms. Otherwise results from modelling may be wrong or correct just by chance because different errors cancel out. The better characterized the model the more confidence we have in extrapolating from laboratory conditions to the real atmosphere.

Nevertheless, we deleted the respective sentence (former page 4 lines 16 – 19) and added the following:

"… and to better characterize mechanisms leading to effects of NO_x on SOA yield."

3. Expand the discussion on the effect of NOx on RO2 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 RO2 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 RO2+HO2 and RO2 +NOx are quite different?

Response: We have added the following sentences with respect to the remaining impact of NO_x at the end of Section 3.2 in the revised manuscript:

"After separating the impacts of NO_x on OH and NPF, there was a remaining effect on SOA formation. According to the present knowledge (e.g. Hatakeyama et al., 1991; Pandis et al., 1991; Kroll et al., 2006) this effect is due to impacts of NO_x on RO_2 chemistry. The most obvious impact of NO_x is the change in product composition. Organic nitrates are formed as an alternative to hydroperoxides and formation of organic nitrates may have an effect on the average volatility of the product mixture. Also decomposition of alkoxy radicals may play a role here. Decomposition of alkoxy radicals can lead to products with higher volatility and thus to a mixture with an average higher volatility.
We found that diminishing of SOA is more effective at higher $[NO]/[NO_2]$. This points to NO as a major player and thus to a role of alkoxy radical decomposition. As alkoxy radicals are produced by only RO_2 + NO reactions, more effective suppression of SOA formation at higher $[NO]/[NO_2]$ would be consistent with alkoxy radical decomposition leading to decomposition products with on average high vapor pressures. However, from our results no clear conclusion can be given with this respect."

As all this is already discussed intensively in the existing literature we kept the new text as short as possible.

With respect to the moderateness of the remaining impact of NO_x we can only speculate at the moment. We refrain from too much speculation and just give the fundamental conclusion from our results (see text).

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 RO2 fate and oxidation products. Thus, the suppression of NPF should not be considered as a separate effect.

Response: As shown by Wildt et al. (2014), the impacts of NO_x on NPF and mass formation are very different. With increasing NO_x, NPF can be suppressed by more than an order of magnitude whereas the SOA yield stays constant. This is a fundamental difference.

We furthermore showed that SOA mass formation is hindered if the surface of particulate matter is small due to the suppression of NPF by NO_x. This is an effect of particle surface and only indirectly connected to the fate of RO_2. This should be clear from the information given in the supplement. We therefore keep the effect of NO_x on NPF separate.

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.

Response: Indeed the effect of OH is not absolutely novel and we have rectified the neglection of these key references. We added a few sentences in order to give reference to Healy et al. (2009), Ng et al. (2007b), Song et al. (2007) and Eddingsaas et al. (2012a and 2012b) in Section 3.3.1 of the revised manuscript:

"Increasing yields with increasing OH concentrations have been previously observed. More efficient NPF and/or higher abundance of low volatile vapours at higher oxidant levels were suggested to be reason. The first should lead to larger particle surface, allowing more semi-volatile vapours to condense on (Ng et al., 2007b; Healy et al., 2009). As we corrected for wall losses of HOMs this effect should be of minor importance in our case. Therefore other reasons for this dependence have to be considered. Such other reasons might be the secondary reactions (Song et al., 2007; Eddingsaas et al., 2012a, 2012b)."

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.

Response: Yes, previous studies have found inconclusive effects of the OH concentration when studying the effects of NO_x on SOA yield. However, we here separated the different effects and show that the increases of [OH] cause the increases of yields with increasing NO_x for β-pinene. This is novel and to clearly demonstrate this we need section 3.3.1. Section 3.3.1 is therefore left intact.

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.

Response: In Xu et al. (2014) we cannot find a detailed discussion on an [OH]-dependence of SOA formation. There is one statement: "However, the effect of OH concentration alone is unlikely to explain our observations of the dependence of SOA properties on NO_x levels."
This statement is in accordance to our findings. We also found other effects of NO_x on SOA formation besides the effect of OH. We also agree with the statement that the effects of NO_x also depend on the VOC under consideration.

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.

Response: We here isolated the OH effect by adjusting OH concentrations to the same level. We showed this way that the increase of the yield with increasing NO_x as observed for β-pinene at low NO_x levels was caused by the increased OH concentrations. We therefore do not see the need to conduct other experiments.

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.

Response: There seems to be a misunderstanding here. Ehn et al. (2014) did not state that HOMs only account for a small mass fraction. On the contrary, Ehn et al. (2014) showed that HOMs contribute to about two thirds to the particle mass at particle mass densities of around 10 µg m^{-3}.

As described in Mentel et al. (2009) we measured wall losses of particles in our chamber. Wall loss rates of 100 nm particles were nearly two orders of magnitude lower than the wall loss rates we found for HOMs. As HOMs contribute significantly to the particle mass formed in our chamber, mass losses by wall effects of HOMs are even more important than wall losses of particles itself.

However, following reviewer #2 we added a short explicit estimation in the revised supplement:

"As mentioned by Ehn et al. (2014) HOMs contribute the majority of SOA mass at low mass loadings and low BVOC concentrations. Even at SOA mass densities around 10 µg m^{-3} they contribute about two thirds to the formed SOA mass. As we measured at mass loadings between 10 and 30 µg m^{-3}, the contribution of HOMs might be somewhat lower and, as a lower limit we here assume a contribution of one third. We now estimate the mass loss in our chamber by losses of HOMs, [HOM]·L(HOM), in relation to the mass losses of particles, [P]·L(P):

$$\frac{[HOM]\cdot L(HOM)}{[P]\cdot L(P)} \qquad \text{(ES7)}$$

Wall loss rates for particles with diameters around 100 nm were ~7.7 10^{-5} s^{-1}, loss rates for HOMs were ~0.0067 s^{-1}. With one third of the particles being produced from HOMs, Equation ES7 gives about 26 times faster mass loss in form of HOMs than mass losses in form of particles. At the particle sizes appearing during our measurements on SOA formation, losses of particle precursors were much more important than losses of particles themselves."

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.

Response: We assumed that Fp is the same for semi-volatiles as for HOMs. Otherwise the measured behavior as shown in Figure S4 would not be explainable (see also our response to the next comment). Please note that this is a result from an experiment.

We are aware that previous studies have investigated vapour wall losses. However, wall losses are not at all in the focus of our manuscript and their determination is just a prerequisite for developing a method for correcting yields. Focus of our manuscript is on the impact of NOx on SOA formation. Therefore the whole text on wall losses and correction procedure was given in the supplement.

It is self-evident that wall losses of vapours depend on the vapour under consideration, on the respective chamber, and on its material as well as on the mixing of air in the chamber. A discussion of wall losses measured in different chambers will just lead to two basic statements. One of them would be that wall losses of vapours are different in different chambers. The other one would be that “numerical data obtained for wall loss correction are only valid for the chamber used in” the respective study. The second of these basic statements is given in the manuscript (see above).

With respect to wall losses we cite our study Ehn et al. (2014). Not only that this was the first publication on wall losses of HOMs/ELVOCs, but also these data are directly comparable as they were made in the same chamber.

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.

Response: This is described in the revised manuscript (Page 8, Lines 5-11) as of the following:

“Particle formation was induced by switching on ozone photolysis and thus producing OH radicals. From such a measurement the formed particle mass as well as the amount of consumed BVOC was obtained. Repeating such experiments using different amounts of BVOC gave a set of data on SOA mass and consumed BVOC. Plotting the SOA masses in dependence of consumed BVOC gave nearly linear relationships. The slopes of such plots were used as the incremental yields.”

(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?

Response: We have expanded the text on the correction procedure in the revised manuscript. See the similar comment of reviewer #1 where the new text is given. However, we want to stay as short as possible since this is described in detail in the supplement.

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).

Response: We would like to clarify, that JPAC is a stirred reactor which is turbulently mixed. As a consequence all wall losses are eventually limited by diffusion through the surface layer. Since our particle volume size distributions peak well below one micrometer, gravitational settling can be neglected. Thus it is clear that particle losses are sized dependent, as diffusion of particles is size dependent.
Please note that the wall loss rates for particles given here were obtained from measurements, i.e. the numbers were derived for typical particle size distributions in our chamber. Please also note that wall loss rates of particles were of minor importance compared to wall losses of HOMs.

(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),

Response: There seems to be a misunderstanding here. Figure S3 shows the losses of HOMs on particles. Losses on particles (termed as L_p) are different from the fraction of HOMs that contribute to particle formation (termed as Fp).

Our motivation to use one function for Fp to correct for losses of HOMs on the chamber walls is based on kinetic gas theory: The boundary layer near to the walls of our chamber can be penetrated by molecular diffusion only. Molecular diffusion is described by diffusion coefficients that also contain the mean velocity, $\bar{\upsilon}$, of the respective molecule. $\bar{\upsilon}$ is also used when calculating effective uptake coefficients and eventually cancels out.
This all is described in detail in the supplement (Page 7, Lines 3-22). Please note that experimental results and basic gas kinetic theories agree quite well (see Figure S4).

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

Response: Thanks for the hint. As written this sentence was not understandable. The sentence is corrected in the revised manuscript as:

"Note that the numbers obtained for wall loss correction are 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?

Response: Thanks for pointing this out. The phrase "above mentioned" was incorrect. We changed the phrase by "the procedure described in the supplement".

For the wall loss corrections, HOMs were produced under low and high NO_x conditions. With respect to F_P no substantial differences were found. We now note this in the figure legend of figure S4 in the revised supplement:

"While the measurements with α-pinene were performed at low NO_x conditions ([α-pinene]/[NO_x] ~ 33 ppbC·ppb^{-1}) the measurements with β-pinene were performed at high NO_x conditions ([β-pinene]/[NO_x] ~ 1.8 ppbC·ppb^{-1})."

6. Section 3.2 needs better organization and clarification.
Firstly, in this study, the role of NO/NO2 ratio in SOA formation is just a reflection of the effect of OH concentration. This needs to be clearly stated, because NO/NO2 ratio can affect SOA formation through other mechanisms. For example, the NO/NO2 ratio can affect RO2 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.

Response: We are not sure if we understand the reviewer #2 correctly. Our results on different [NO]/[NO_2] ratios are not at all just a reflection of different [OH]. Possibly the wrong impression arose because of a single paragraph (former page 14 line 19 to page 15, line 5). In this paragraph we showed that the lower increase at lower [NO]/[NO_2] was consistent to our statement of OH being responsible for the increase in yields. Since this paragraph might have created confusion, it was completely deleted.

As mentioned before (points 1 and 3 of reviewer #2), the title of Section 3.2 is changed now and we added some words on the role of NOx in peroxy radical chemistry. We believe that it is clearer now that the results obtained for different [NO]/[NO_2] also hint to a role of peroxy radical chemistry.

Secondly, in section 3.2, the role of NO/NO2 is probed by comparing high O3 and low O3 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?

Response: This is a good point. On Page 16, line 7 we added: "(compare Fig. 6 to Fig. 4)".
With respect to Figs. 5 and 7, it was already written as (former Page 15. Lines 10-15): "Comparing the yield profiles obtained from the low-O_3 and the high-O_3 experiments respectively (blue circles in Fig. 5 and Fig. 7), it can be seen ….". Therefore, this should be clear enough.

Figures 4 to 7 all contain a second trace giving information on the results obtained for constant [OH] which we want to show to the reader. Merging the figures would require to remove these traces or - if the traces for the same [OH] would be left in the figures - complicate the figures too much. In order to keep the figures as simple as possible we avoid merging the figures.

Thirdly, under the same O3 concentration (i.e., figure 5), does the NO/NO2 ratio change with NOx level? Is it possible that the moderate direction effect of NOx on SOA yield is confounded by the varying NO/NO2 ratio at different NOx level? Can the authors add the NO/NO2 ratio as a third x-axis in the figures? The authors can potentially probe the effect of NO/NO2 ratio on SOA yield through affecting the RO2 fate.

Response: The NO/NO_2 ratio did not vary substantially with NO_x level. We therefore did not add a third x-axis to the figures (see also next point).

Fourthly, in order to justify that the NO/NO2 ratio changes with adjusting O3, the author could Simply show the NO/NO2 ratio for high low O3 and high O3 experiments. If the authors want to theoretically prove the argument, the authors need to justify how the reaction of NO with RO2 can be neglected (Page 14 Line 3).

Response: The [NO]/[NO_2] ratio is added in Page 16, Lines 2-4 of the revised manuscript (see point before) as shown below:

"...NO_x experiments were performed with approximately 50 % higher O_3 concentration (74 ± 7 ppb, [NO]/[NO_2] = 0.018 ± 0.004 ppb · ppb^{-1}) than that of previous NO_x experiments where the [NO]/[NO_2] ratio was 0.035 ± 0.005 ppb · ppb^{-1}."

Here our argument on a "theoretical proof" of our statement that the [NO]/[NO_2] ratio is changed by changing [O_3] and the impacts of RO_2 can be neglected:

Using similar β-pinene and OH concentrations leads to similar RO_2 concentrations in the systems. Hence, deviations from PSS will be similar at high O_3 and low O_3. Therefore the $[NO]/[NO_2]$ ratio is predominantly changed by the changes in $[O_3]$.

This argumentation line is certainly not complicated. We nevertheless do not mention this in the text since this effect should be clear from the numbers given now. To avoid confusion we exchanged the phrase "Neglecting reactions of NO with peroxy radicals" by the phrase "Hence, to a good approximation".

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.

Response: On Page 18 Lines 5-9 it was written:

"The difference between yields determined with and without addition of seed particles indicates that at very small particle surface, our correction procedure underestimates wall losses of precursors. This might be due to either possible differences in uptake of the ELVOC by particles (mainly organic particles versus ammonium sulfate particles), or the differences in the size of particles. However, the real reason for this underestimation is not known yet."

We think that we provided enough discussion as the real reason for this difference is not known and this is clearly stated in the text.

We refrain from further commenting the differences in the impacts of seed at different levels of NO_x. Indeed, this might indicate an underestimation of precursor losses by our correction method at low particle surface and the suppression of NPF by NO_x is highest at highest NO_x. Therefore the extrapolations from our correction method have to be extreme at high NO_x and at high numbers for extrapolations there may be a substantial error. For the interested reader a detailed description of our error estimations for the correction method is given in the supplement, Section S4, Pages 13-15.

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)

Response: We measured at β-pinene concentrations between 4 and 25 ppb. In this range we found no substantial deviation from a linear relationship. However, we also cannot exclude a substantial nonlinearity at higher mass loading: Looking at Figure 3 and comparing the data points to the regression line is seems that there is a slight curvature in the data points hinting to this well-known phenomenon. Extrapolating this trend leads to the assumption that we can find a dependence of mass yields on ΔM_o. However, this would require much higher VOC concentrations as used here. Our data are therefore not in contrast to those given in literature; our data were just obtained in a concentration range where the expected dependence of yields on ΔM_o is much lower than the uncertainty limits of such measurements.

We are interested in studying SOA mass formation at concentrations relevant to the atmosphere (please note that the BVOC concentrations used here are still more than an order of magnitude higher than those in the real environment). We therefore accept minor deviations from a linear behavior. Within the error limits a linear approach as suggested by Mentel et al. (2009) is good enough.

A more detailed justification on "why" the dependence of yields on ΔM_o is low can be found in Ehn et al. (2014). Briefly, the main contribution to SOA mass formation at mass loads around 10 µg m^{-3} is from ELVOCs/HOMs. As ELVOC/HOM have low vapour pressures, re-evaporation and thus partitioning is not that important. A significant dependence of yields on ΔM_o is only anticipated if a large fraction of the condensing vapours consists of molecules that are semi-volatile. Compared to many other studies we use the quite low BVOC concentrations. Hence, low contributions of semi-volatiles and thus low dependence of yields on ΔM_o is to be expected.

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

Changed, thanks for pointing this out.

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

Fixed, thanks for pointing this out.

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

Response: We refrain from discussions in the abstract of our manuscript. Instead we added some words in Section 3. The new text reads:

"Different impacts of NO_x superimpose each other and the net effect of NOx is determined by the strongest impact in the individual chemical system. For SOA formation from α-pinene the suppressing effect via impacts on peroxy radical chemistry was obviously stronger than the increases in SOA yield by NO_x induced increases of [OH]."

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).

Response: We added a sentence with respect to the NO_x dependence of SOA formation from sesquiterpene photooxidation to the introduction:

"For sesquiterpenes such as longifolene and aromadendrene yields increase with increasing NO_x (Ng et al 2007a). However, results of the majority …"

The reference Kroll and Seinfeld (2008) is a review wherein the results of Ng et al. (2007a) are cited. We here refer to the original data.

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.

Response: the sentence was a citation of statements given in the peer reviewed literature:

e.g. Presto et al., 2005: "indicates that aerosol nitrate-containing species evaporated to the gas phase more readily - and were therefore more volatile - than species that contain only the carbonyl moiety" e.g. Kroll et al., 2006: “and organic nitrates may be relatively volatile”

We nevertheless deleted this half sentence in the revised manuscript as it was anyhow unnecessary. Instead we added some words on this in section 3.2 where the impacts of NO_x composition are discussed (see our response regarding the request to add some discussion on the remaining NO_x effect).

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.

Response: Please see our response to the comment of reviewer #1. We have no indication that photolysis of other species at 254 nm have any impacts on SOA formation.

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

Response: It doesn’t matter which procedure is used. Both procedures are identical if OH concentrations are determined from the decay of the precursor of SOA formation (see text in the manuscript p. 8, lines 4 – 7 of the old manuscript and the detailed description in the supplement, section S3)

9. Page 8 Line 14. Why is the low-NOx condition defined as [NOx]0 <30ppb and [BVOC]0 /[NOx]0 > 10?

Response: This was defined this way because near to this $[BVOC]/[NO_x]$ ratio the gross effect of NO_x on the yield switches from an increase with increasing NO_x to a decrease with increasing NO_x.

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

Response: Thanks for the suggestion, Xu et al. (2014) is included in the list of citations where the different trends of NO_x dependencies are described (Page 11 Line 16)

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

Added.

12. Page 10 Line 17. It is true that the RO2 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?

Response: We are not sure if we understand reviewer #2 correctly. We nevertheless give a short answer: Worldwide there is no chamber with the ability to exactly represent the atmosphere with its turbulent mixing of different air masses, with its large volume and the heterogeneous and often quite active surface. Different chambers can provide different insights into the basic mechanisms which is necessary for a full understating.

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

Response: We now added the rate constants for the respective reactions in the revised manuscript to show that nopinone reacts about 5 times slower than β-pinene.

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).

Response: There seems to be a misunderstanding here. Ehn et al. (2014) mainly studied ozonolysis. Indeed, as there is only one C=C double bond in α-pinene, there is only one ozonolysis reaction. However, we made experiments on photooxidation and so far there are no data in the peer reviewed literature that show that only one reaction with OH is required to form the HOMs / ELVOCs. We therefore leave the sentence as it is.

15. Page 15 Line 10-12. Does it mean the direct effect of NOx on SOA yield is related to OH concentration? If the O3 concentration is even higher, will the decrease in SOA yield become smaller? Why?

Response: No, this does not necessarily mean that the “direct” effect of NO_x on SOA yield is related to [OH]. As written in the sentence following the sentence on p. 15 line 10-12 this also implies that the effect of NO_x on SOA yield also depends on the composition of NO_x, i.e. on the relative abundance of NO and NO_2, respectively.
As we deleted the paragraph showing that the results of different [NO]/[NO_2] ratios were consistent with the results of the OH dependence (Page 14, Lines 19-20, Page 15, Lines 1-5 of the original manuscript) and furthermore, since the whole chapter is entitled “Possible role of peroxy radical chemistry and [NO]/[NO_2] ratio in SOA formation” this should be clear for a reader.

With respect to extrapolations to even higher [O_3]: we do not know the answer as we did not perform measurements at higher [O_3].

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?

Response: We have not concluded this statement; this was the description of the result obtained for α-pinene (see Figure 8). Please note the word “above” in the sentence.

With respect to the second question: Results obtained for the impact of NO_x do not only depend on [NO_x] but also on the concentration of the BVOC. That is the reason why often the notation $[BVOC]_0/[NO_x]_0$ is used in the scientific literature. Results obtained at the same [NO_x] are only equivalent to the results obtained with another BVOC if the BVOC concentrations or even better the reactivity of the respective BVOCs is the same in both experiments. We pointed this out by writing: “In sense of BVOC/NO_x ratios, the NO_x range scanned here is ~3 times higher” in the figure caption of figure 8. However, to avoid confusion possibly arising because of using the word “comparable” we exchanged the words “directly comparable” with the word “equivalent”.

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?

Response: The sentences on Page 16, line 15-17 of the manuscript say:

"The NO_x dependence of SOA formation therefore is different in different chemical systems. As the SOA yield was dependent on the actual OH concentrations, differences in OH recycling may be involved here as well."

This sentence means that differences in OH recycling may be involved in the differences observed between the NO_x dependencies of SOA formation from α-pinene and β-pinene, respectively. This sentence does not imply that there will be similar trends between α-pinene and β-pinene systems if 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."

Response: The sentence written on page 19 line 9 refers to the OH effect in general and is not related to NO_x. Furthermore, we proved the reason for the increasing yield with increasing NO_x only for β-pinene and, as the impact of NO_x on SOA formation also depends on the (B)VOC under consideration, we refrain from generalizing our finding at the moment.

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