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Reply on RC2

Shijie Liu et al.

Author comment on "Synergetic effects of NH₃ and NO_x on the production and optical absorption of secondary organic aerosol formation from toluene photooxidation " by Shijie Liu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-560-AC3>, 2021

Response to Reviewers

Ms. Ref. No.: acp-2021-560

Synergetic effect of NH₃ and NO_x on the production and optical absorption of secondary organic aerosol formation from toluene photooxidation

Dear Editor:

We greatly appreciate the time and effort that the editor and reviewer spent in reviewing our manuscript. After reading the comments from the reviewers, we have carefully revised our manuscript. All the changes we made are marked in red. Our responses to the comments are itemized below. The referee's comments are in black, authors' responses are in blue.

Anything for our paper, please feel free to contact me via ghwang@geo.ecnu.edu.cn.

All the best

Gehui Wang

Oct. 14, 2021

Reviewer #2

This manuscript describes a set of four environmental chamber experiments studying the formation of organic aerosol from the photooxidation of toluene. The authors show that the addition of NO_x during photooxidation suppresses SOA formation, while the addition of NH₃ enhances SOA formation, consistent with previous studies. They then show that photooxidation of toluene in the presence of both NO_x and NH₃ together results in an even greater enhancement of SOA formation than NH₃ alone. They ascribe this to a

"synergistic" effect whereby the more-volatile compounds produced by photooxidation with NO_x are able to form SOA efficiently when they can react with NH₃ (or NH₄⁺). AMS and optical observations are also reported and used to support the hypothesis that carbonyl + NH₃/NH₄⁺ reactions are responsible for the observed SOA enhancement.

Overall, the study reports an interesting effect that could be important in the atmosphere. The introduction also gives a great summary of all the reactants involved and their expected effects on SOA formation in the atmosphere. However, the methods leave a lot of unanswered questions that make it difficult to know how to interpret results. In particular, the lack of replicate experiments, lack of reported data on the amount of toluene oxidized or its rate of oxidation, and lack of consideration of vapor wall losses and potential variability of particle wall loss, all conspire to introduce a great deal of uncertainty into the results, which are largely reported without any estimates of error or uncertainty. More details on these methodology questions are provided below.

Furthermore, the conditions for the experiments performed here are far removed from the ambient atmosphere and make it difficult to say whether the observed effects would apply in the atmosphere. A number of statements in the paper suggesting that this synergistic chemistry is responsible for ambient observations are therefore not supported by the evidence, e.g. L 255-258, "This may explain why predictions of SOA concentrations in large-scale atmospheric models, which typically describe SOA formation from data derived from chamber experiments, are frequently lower than field observations" and also L 519-520, "In the actual atmosphere, NO_x and NH₃ co-exist. Therefore, the findings presented here clearly show that the synergetic effects of NO_x and NH₃ should not be neglected." Alternatively (even better!), more analysis or further experiments should be provided to characterize how the observations herein might be expected to differ when applied to the conditions of the ambient atmosphere, and greater discussion should be included on this point.

I'm generally very hesitant to say more experiments need to be done in the review stage, but unless there are others that have been done already but aren't clearly reported here (or more specific data from the ones that have been performed), I think this is a case where more is needed. There are too many confounding variables here that aren't easily explained away (reproducibility? Dependence on oxidation rate / OH? How much toluene was oxidized in each? Dependence on concentrations? Wall losses? Balance of NO and NO₂?). Hopefully the more specific questions below on the methods will provide more detailed guidance on how the manuscript can be improved to help mitigate these uncertainties.

Author reply:

We thank the reviewer for the comments above, which are very important and helpful for improving our paper quality and mitigating the related result uncertainties. We have carefully revised our work. Followings are the detailed answers.

General questions on methods:

- Were any replicate experiments performed at the separate reaction conditions, and if so, how reproducible were the results? The only uncertainty estimates I see are on temp/RH (how are those arrived at) and SOA formed which I assume is from SMPS measurements (how is uncertainty calculated from that?), but doesn't tell us anything about reproducibility of the results from experimental variability, e.g. of the reactant injections and wall losses. Without this, it's difficult to know what uncertainty to ascribe to the results.

Author reply:

We express our appreciation to the reviewers for the comments.

The repeated experiments were not carried out here. The error bars in Fig. 1 were calculated by the fluctuation of SOA concentration when the UV light was turned off at the end of each photooxidation experiment. In order to make this section clearer, the sentences of "The error bars were calculated by the fluctuation of measured SOA concentration after the UV light was turned off at the end of each experiment." was added in the caption of Fig.1.

- Do you have any way of knowing how much toluene was oxidized in each experiment, and how quickly (i.e. how much OH there was)? This would be nice for converting from the SOA mass formed that you report to an SOA mass yield, which would be easier to compare to previous studies. It would also help to know whether differences in OH (and therefore the rate of oxidation and the peak RO₂ radical production) could explain some difference in the observed SOA formed and the SOA properties, as has been shown in the past.

Author reply:

We are very grateful to the reviewer for this comment. We measured the toluene concentration with PTR-MS on-line. The evolution of toluene concentration at different experiment conditions was shown below and added in the Supporting Information. The evolution of toluene concentrations was almost uniformly at different NO_x and NH₃ conditions.

Fig.S1 The evolution of toluene concentration for each experiment.

In the revised manuscript, we have added the sentences in line 163 as follows: "Toluene concentration was measured with a Proton Transfer Reaction-Mass Spectrometry (PTR-ToF-MS, Ionicon Analytik, Austria). The evolution of toluene concentration for different experiments was shown in Fig.S1."

we also added the sentences of "SOA yield (Y) is defined as $Y = \Delta M_0 / \Delta HC$, where ΔM_0 is the produced organic aerosol mass concentration ($\mu\text{g m}^{-3}$), and ΔHC is the mass concentration of reacted toluene ($\mu\text{g m}^{-3}$)." in line 235.

"The SOA mass concentrations at different conditions are shown in Fig. 1." in line 234 was changed as "The evolution of SOA mass concentrations and SOA yield at different conditions during the photooxidation process were shown in Fig.1"

Table 1 was also updated as below:

Table 1. Summary of experimental conditions in this study

No.	Tol ₀	ΔTol	NH ₃ ^a	NO ₂	RH	SOA mass conc. ^{b,c}	SOA yield ^b
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	(ppb)	(ppb)	(ppb)	(ppb)	(%)	($\mu\text{g m}^{-3}$)	(%)
Exp.1	664.1	551.2	-	-	-	25 ± 1	$637 \pm 14.628.1$
Exp.2	618.7	499.4	~ 200	-	-	23 ± 1	$867 \pm 12.734.7$
Exp.3	620.9	516.1	~ 200	62	62	26 ± 1	1020 ± 42.7 10.6
Exp.4	645.7	532.5	-	63	63	25 ± 1	$452 \pm 18.919.5$

^a The concentration of NH_3 is estimated by the amount of NH_3 added and the volume of the smog chamber. ^b SOA concentration and yield were calculated after taking into account the wall loss. ^c The reported SOA mass concentrations is the peak values after the wall loss correction.

In the revised manuscript, we have added the description of OH concentration calculation in line 163 as follows: "OH concentration in the chamber was calculated based on the first order decay of toluene concentration. There was no obvious difference of OH concentrations in the different NO_x and NH_3 levels (Fig. S2)."

The highest OH concentration of 1.02×10^8 molecule cm^{-3} was observed at the beginning of the reaction. The average OH concentration over the entire reaction period was 5.87×10^7 molecule cm^{-3} . The calculation of OH concentration was added in the Supporting Information as below:

"S1 OH Concentration Calculation Process

The OH concentration was calculated based on the decay ratio of toluene concentrations and the known rate constant with respect to OH. The change of toluene concentration over time can be expressed as:

(RS1)

Where, K_{OH} is the reaction rates constant of OH radicals with toluene ($K_{OH}=5.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Assuming that the concentration of hydroxide did not change during the experiment, then we can get:

$$(RS2)$$

Thus, plotting the variation curve of $\ln([\text{toluene}]_0/[\text{toluene}]_t)$ vs. time t showed as Fig.S1. The $\ln([\text{toluene}]_0/[\text{toluene}]_t)$ in Fig.1(b) was not a straight line. This is because the OH is consumed as the reaction goes on. The evolution of OH concentration at experiment conditions was shown in Fig.S2. The different experiment conditions in this study did not affect the OH concentration obviously. The highest OH concentration of $1.0 \times 10^8 \text{ molecule cm}^{-3}$ was observed at the beginning of the reaction. The average OH concentration over the entire reaction period is $5.9 \times 10^7 \text{ molecule cm}^{-3}$.

Fig.S2 The evolution of OH concentrations at different experiment conditions.

- Do you know, either from the AMS or a control experiment without toluene, how much inorganic aerosol was formed from the interaction of ammonium and NOx in the chamber? It seems this could explain a large portion of the "enhancement" in particle mass in the NH3 + NOx experiment. It could also affect gas-particle partitioning by acting as a "seed" aerosol on which more vapors can condense (which is a form of NOx-NH3 synergy, I suppose, but seems less chemistry-dependent than the effects to which you ascribe the synergy).

Author reply:

The concentration variations of NO_3^- and NH_4^+ during the experiments were measured by the AMS. The content of NO_3^- and NH_4^+ is very low in particulate matter. The content of NO_3^- and NH_4^+ for each experiment was list in the table below.

Table S1. The content of NO_3^- and NH_4^+ in the particle-phase for each experiment

	$[\text{NOx}]_0$	$[\text{NH}_3]_0$	$[\text{NO}_3^-]/[\text{Org}]$	$[\text{NH}_4^+]/[\text{Org}]$
	(ppb)	(ppb)	(%)	(%)
Exp.2	-	~200	-	1.9

Exp.3	62	~200	4.0	2.6
Exp.4	63	-	□0.2	-

As seen in Table S1, when only NO₂ was introduced into the chamber, the content of NO₃⁻ in particulate matter was less than 0.2%. Based on the consumption of NO₂, most of the NO₃⁻ was present in the gas phase in the form of nitric acid. When only NH₃ was introduced in the chamber, the content of NH₄⁺ was about 1.9%. When both NO₂ and NH₃ were simultaneously introduced into the chamber, the NO₃⁻ reacted with NH₄⁺ to form ammonium nitrate particles, which accounted for 6.6% of the total mass of particulate matter in the chamber. AMS cannot distinguish whether NO₃⁻ and NH₄⁺ come from organic or inorganic phase, but 6.6% is obviously the upper limit of inorganic components in particulate matter if we assume that both are entirely derived from inorganic phase. The particle mass increased about 59% in the NH₃ + NO_x experiment compared that with no NH₃ or NO_x, which cannot be explained by the formation of inorganic NH₄NO₃ but can only be ascribed to the synergetic effect of NH₃ and NO_x on the toluene SOA formation. The following sentences were added in line 253 of the manuscript to explain the possible influence of the smaller amount of the inorganic aerosol on the enhancement in particle mass in the NH₃ + NO_x experiment.

“Although inorganic aerosol was formed from the interaction of NH₃ and NO_x in the chamber, the upper limit of the inorganic matter only account for 6.6% of the total mass of particulate matter (Table S1) in the NH₃ + NO_x experiment. Therefore, it was not the main cause of the increase in particulate matter.”

- - Were gas-phase reactant concentrations measured during experiments? In addition to helping determine how much toluene was oxidized and how quickly during each experiment (see above), this would be really helpful for knowing the balance of NO₂ and NO in the high-NO_x experiments. These two NO_x compounds have very different effects on gas-phase chemistry, and even if they do interconvert with the lights on, it's important to understand their relative abundances to know how much RO₂ reacts with NO, how much HNO₃ is formed, and whether PANs form from the reactions of acyl peroxy radicals with NO₂, for example.

Author reply:

We express our gratitude to the reviewer for this comment. The gas-phase reactant concentrations were measured (see our reply to the reviewer comments #2 above). NO_x concentration is one order of magnitude lower than toluene concentration, and this may be the reason why NO_x has no obvious effect on OH concentration.

In the atmosphere, nitrogen oxides are emitted from natural and anthropogenic sources primarily as NO, which rapidly achieves steady state with NO₂. In the presence of VOCs, NO₂ can be lost by reaction with RO₂ to form peroxy nitrates (RO₂NO₂) (O'Brien et al., 1995). RO₂NO₂ species are thermally unstable at boundary layer temperatures and

decompose back to NO_2 and RO_2 on a timescale of minutes (Fisher et al., 2016). RONO_2 species formed from $\text{RO}_2 + \text{NO}$ can dominate NO_x loss (Zhao et al., 2018; Browne et al., 2014). Longer-lived peroxyacylnitrates (PANs) can also be formed through $\text{RO}_2 + \text{NO}_2$ reaction, but Mao et al. (2013) pointed PANs were less efficient for reactive N export than RONO_2 . All in all, although NO_2 is a major component of NO_x in the chamber, the reaction of RO_2 with NO is still the main process for RO_2 consumption.

- - Why were such high concentrations of toluene used, and how much could $\text{RO}_2 + \text{RO}_2$ chemistry participate, especially in the low- NO_x experiment? How does this compare to the amount of toluene- RO_2 that are expected to react with toluene- RO_2 in ambient conditions in the atmosphere? It seems that excessive RO_2 - RO_2 chemistry could make these "low- NO_x " results unrepresentative of "low- NO_x " conditions in the atmosphere, making interpretation difficult.

Author reply:

We fully agree with the reviewer on this opinion. Considering the performance of this chamber, as well as to obtain more accurate analysis of chemical composition, a higher concentration of toluene was used in this study. The atmosphere is very complicated, and the experimental conditions in the chamber cannot be the same as the real environment. In our work, the proportion of the key components is comparable to the ambient level. The mean concentration of aromatics VOCs and OH was about 11 ppb (Zou et al., 2015) and 1×10^6 molecule cm^{-3} (Prinn et al., 1995), respectively, which was consistent with the VOCs/OH ratio (~ 700 ppb/ 5.9×10^7 molecule cm^{-3}) in our study.

We thank the Referee for this insightful comment. We also think the quantitative of $\text{RO}_2 + \text{RO}_2$ chemistry is very important. Unfortunately, we do not know how much could $\text{RO}_2 + \text{RO}_2$ chemistry participate at different NO_x conditions. As suggested by the reviewer, $\text{RO}_2 + \text{RO}_2$ chemistry is excessive when NO_x was not added into the chamber. But the original objective of our study was not to determine the property of $\text{RO}_2 + \text{RO}_2$ and $\text{RO}_2 + \text{NO}$ on toluene SOA formation. The different "low- NO_x " conditions between chamber and real atmosphere does not affect the purpose of chamber experiment to obtain the effect of NO_x on the photooxidation mechanism.

To provide a better illustration of the experiment condition, the following sentences have been added in the revised manuscript in line 170:

"In our work, the OH and toluene concentrations were higher than those of urban conditions. The purpose of the high OH and toluene concentrations is to obtain enough particle production samples for off-line collections and accurate measurements. The toluene concentrations remained stable under the different experimental conditions, the variation of toluene-derived SOA mass concentration and yield was only affected by the different NO_2 and/or NH_3 concentrations in this study. Toluene was studied here as the representative of total aromatic VOCs in the urban atmosphere. The concentration ratio of toluene to OH in this study is similar to that under the real atmospheric conditions (Zou et al., 2015; Prinn et al., 1995)."

The following sentences were also added in line 523 of the revised manuscript: "It has to be noted that the concentration of reactants used for the experiments is much higher than that observed in polluted areas, the effect of NH_3 and NO_x on the photooxidation of toluene with lower concentrations would be checked in the further study."

- - Particle wall losses are known to be affected by both particle size and composition, both of which evolve between and over the course of your experiments (as might the surface-area-to-volume ratio of the chamber). It seems the use of a single particle wall loss rate across all sizes and across experiments could introduce substantial error or at least uncertainty to the calculations of particle mass formed. Even if it proves too difficult to quantify size- and composition-dependent wall loss rates, more discussion is needed regarding the limitation of this method.

Author reply:

The presence of NH₃ could lead to an increase in particle wall loss ratio. All the particle mass concentration was corrected with the same way of Jiang et al. (2020) and Pathak et al. (2007) to constrained the influence of wall losses of different SOA formed with different experiment conditions. For each experiment, we continued to monitor the particle concentration in the dark condition for 1 hour, and recalculated the particle wall loss constant according to the variation of particle concentration.

The following was added at line 168 for clarification.

“However, the particle wall loss rates were detected at the end of the chamber experiment after the UV-lamps were turned off, and the mass concentration was corrected with the same way of Jiang et al. (2020) and Pathak et al. (2007)”

- - Similarly, vapor wall losses are likely to play a major role in these experiments, especially in a relatively small chamber, and it's been shown they can bias measured SOA yields from toluene when no seed aerosol is used (see <https://acp.copernicus.org/articles/15/4197/2015/> and <https://www.pnas.org/content/111/16/5802>). They will also vary over the course of the experiment, and could differ between experiments if (a) the reactive intermediates formed have different volatilities, and (b) the particles are formed at different rates and therefore the semivolatile vapors experience different wall-vs-particle competition for partitioning. How might this affect the results? Seeded experiments would be particularly useful here to understand these effects.

Author reply:

We agree with the Referee that the wall loss rates are also different dependent on vapor wall losses. The walls serve as a large reservoir of equivalent OA mass that compete with the particulate SOA. But the wall loss effect of gas-phase products on SOA formation have not yet been quantitatively established. After the wall loss correction, the particle mass concentration was almost constant (New Fig.1), we believe that our results are reliable and credible.

To clarify the statement, we modified the sentences in the revised manuscript. The new one reads as follows:

“Recent experiments shown that the wall loss of organic vapors to the Teflon walls should not be ignored (Zhang et al., 2014;Zhang et al., 2015), and represented a major challenge in investigating SOA formation with environmental chambers (Zhang et al., 2014;Krechmer et al., 2020). The formation of SOA in laboratory chambers may be substantially suppressed due to losses of SOA-forming vapors to chamber walls, but this effects on SOA formation have not yet been quantitatively established. However, the particle wall loss rates were detected at the end of the chamber experiment after the UV-lamps were turned off, and the mass concentration was corrected with the same way of

Jiang et al. (2020) and Pathak et al. (2007). After the wall loss correction, the particle mass concentration was almost constant, the different wall loss effect caused by gaseous oxidation products formed in the different experiment conditions was considered remedied.”

We also discussed the wall loss in the section 3.1 and added the following sentence at line 235.

“Interestingly, wall loss is increased 66% and 205% in Exp.2 (in the presence of NH₃) and Exp.3 (in the mixed condition of NH₃ and NO_x), respectively, when compared with the experiments with no NH₃ (Exp.1 and 4). The larger particle wall loss in the presence of NH₃ could be explained by increasing condensation process of oxidized organic vapors onto the Teflon chamber wall via oligomerization (for dicarbonyls) and ionic dissociation/acid-base reaction (for organic acids).”

As pointed by the Referee the seed particles in the chamber provided adequate seed surface area at the beginning of the reaction, which constrained the influence of vapor wall losses of the semi-volatile vapor. Because of the high concentrations of toluene and H₂O₂ in this study, the maximum number concentration and maximum particle surface area is $4.6-5.7 \times 10^5 \text{ cm}^{-3}$ and $1.3-1.8 \times 10^4 \mu\text{m}^2 \text{ cm}^{-3}$, respectively. The resulting total AS seed surface area in the study of the Zhang et al. (2014) ranged from $\sim 1 \times 10^3 \mu\text{m}^2 \text{ cm}^{-3}$ up to $\sim 1 \times 10^4 \mu\text{m}^2 \text{ cm}^{-3}$. The loss of condensable vapors to the chamber walls leads to a low bias in the observed SOA formed even for the experiments with the highest seed SA. In their study, the vapor wall loss bias (R_{wall}) did not change much when the seed surface area is greater than $5.5 \times 10^3 \mu\text{m}^2 \text{ cm}^{-3}$. Meanwhile, the calculated R_{wall} varies with oxidant and precursor concentration (actually, VOC loss rate), smaller R_{wall} is obtained when oxidation is faster and precursor VOC concentration is larger. We believe that the addition of seed particles would not impact on SOA formation significantly in this study.

We also need to emphasize that, in future studies, especially when the SOA formation is studied with low VOCs and OH concentrations, seeded experiments would be very useful for us to understand vapor wall losses at different experiment conditions, and improve the accuracy of SOA formation in the chamber study.

- - Is the chamber operated in batch mode, or with a continuous dilution flow during experiments? If there's no flow, how might the changing bag volume and shape affect particle or vapor wall losses? If there is a dilution flow, how was this accounted for in calculations of particle mass concentration, and in terms of the dilution affecting gas-particle partitioning of semivolatile vapors?

Author reply:

This chamber was operated in batch mode, and no dilution flow was used here, because the Teflon bag is flexible and thus the volume is variable. The total sampled volume for the online measurement was only 3 L min^{-1} . The illumination time of UV light was 120 min. The total sample volume was lower than 8% of the total volume. The change rate of chamber volume is even lower than the systematic error of SMPS (10%) (Liu et al., 2017). Therefore, the change of chamber volume does not significantly affect particle or vapor wall loss during the whole photooxidation process of each experiment. The volume and the change rate of chamber volume were consistent in each experiment. Therefore, particle or vapor wall losses affect by the changing volume of the chamber will not introduce much uncertainties in one experiment or between all the experiments in the present study.

- - 254 nm lights are fairly high-energy / low-wavelength -- does this mean the experiments had extremely high OH? Does it potentially cause rapid photolysis of highly photolabile compounds (like hydroperoxides and dicarbonyls), and how could that cause differences between chamber conditions and ambient environmental conditions?

Author reply:

The photolysis of gas-phase H₂O₂ through the 254 nm was widely used for the OH radical production (Ng et al., 2007; Liu et al., 2021; Jiang et al., 2020). As mentioned before, the average OH concentration in the chamber over the entire reaction period is 5.87×10^7 molecule cm⁻³. The high OH concentration was due to the high concentration of H₂O₂ (about 2 ppm) in the chamber. The UV-light intensity was not very strong. The direct photolysis can be neglected relative to the OH oxidation.

In the troposphere, main oxidation reaction of toluene was initiated by OH (Atkinson and Arey, 2003). The OH oxidation in this study was consistent with the atmospheric oxidation process of toluene in the real atmosphere.

- - Finally, are the reported SOA mass concentrations peak values or at the end of each experiment? It would be good to see their evolution vs. time, to understand how that differs between experiments and whether that could influence results.

Author reply:

The reported SOA mass concentrations was the peak values after the wall loss correction. Meanwhile, as shown in the Fig.1, SOA mass concentration is almost unchanged until the end of the reaction. The maximum concentration of SOA is the same as the concentration at the end of the reaction. We also added the sentences after Table 1: "The reported SOA mass concentrations was the peak values after the wall loss correction."

The sentence of "The SOA mass concentrations at different conditions are shown in Fig. 1." in line 234 was changed as "SOA yield (Y) is defined as $Y = \Delta M_0 / \Delta HC$, where ΔM_0 is the produced organic aerosol mass concentration ($\mu\text{g m}^{-3}$), and ΔHC is the mass concentration of reacted toluene ($\mu\text{g m}^{-3}$). The evolution of SOA mass concentrations and SOA yield at different conditions during the photooxidation process were shown in Fig.1."

The SOA mass concentration evolution vs. time was added in Fig.1.

Fig. 1. The evolution of mass concentration (a) and yield (b) of toluene-derived SOA in different experiments. All the mass concentrations were wall-loss corrected. The error bars of SOA yield were calculated by the volatility of measured SOA concentration after the UV light was turn off at the end of each experiment.

Additional (mostly minor) comments:

L 65: comma should be a period & start a new sentence

Author reply:

Corrected.

L 101-103: Needs more detail. Is this NO_x dependence for toluene SOA specifically, or from other precursors? And does "initially" mean early (temporally) in an experiment, or does it refer to slight increases in NO_x concentration? Finally, is it all due to the RO₂ chemistry as the following sentence suggests, or can some of the increase be ascribed to changing OH as NO_x increases?

Author reply:

For clarification, the sentence "Laboratory experiments have found that SOA formation was initially enhanced, but then suppressed with increasing NO_x concentrations (Sarrafzadeh et al., 2016; Yang et al., 2020)." in line 101-103 is changed to "A clear increase at first and then a decrease in the SOA yield was found with increasing NO_x concentration from the laboratory experiments with both artificial (trimethylbenzene) and biological (β-pinene) VOCs (Sarrafzadeh et al., 2016; Yang et al., 2020)."

we also changed the sentences in line 111-113 as follows: "In addition, the increase of OH concentration formed through NO + HO₂ ⇌ NO₂ + OH reaction at low-NO_x conditions, and a suppressing effect of NO_x on OH formation under high-NO_x conditions was partly responsible for the first increasing and then decreasing trend of SOA yield with NO_x concentration (Bates et al., 2021; Sarrafzadeh et al., 2016)."

L 107: "participated" should be "precipitate"

Author reply:

Suggestion taken.

L 111-112: The change in OH with NO_x is not as simple as "suppression", and in many cases NO_x may increase OH (see, e.g., Figure 8 in <https://acp.copernicus.org/preprints/acp-2021-605/>).

Author reply:

We thank the Referee for this insightful comment. As mentioned before, we have changed the sentences in line 111-113 as follows: "In addition, the increase of OH concentration formed through NO + HO₂ ⇌ NO₂ + OH reaction at low-NO_x conditions, and a suppressing effect of NO_x on OH formation under high-NO_x conditions was partly responsible for the first increasing and then decreasing trend of SOA yield with NO_x concentration (Bates et al., 2021; Sarrafzadeh et al., 2016)"

L 123: unclear; does this mean a reduction in NH₃ improves PM_{2.5} pollution *more than* a reduction in SO₂? Is that when reducing both by the same amount?

Author reply:

For clarification, the sentence "Indeed, one study observed that a reduction of NH₃ emissions improved PM_{2.5} pollution compared to SO₂ in winter (Erisman and Schaap, 2004)." in line 101-103 is changed to "Indeed, field observation and model simulation have pointed out that the reduction of NH₃ emissions contribute much to the improvement of PM_{2.5} pollution compared to SO₂ in winter (Erisman and Schaap, 2004)."

L 238: Are these previous studies on toluene or other precursors? How does the magnitude of your SOA-enhancement due to NH₃ addition compare to these previous studies?

Author reply:

In the study of Qi et al., toluene was used as the SOA precursor. But α -pinene was used in the study of Na et al. We wanted to describe the promotion of NH₃ was observed in both anthropogenic and biological SOA.

In the study of Qi et al., the presence of NH₃ resulted in a 72% increase in SOA mass concentration. However, 200 ppb of NH₃ was injected into the chamber approximately 1.5 h after the UV lights were turned on when the SOA formation reached the maximum value. Because of the different experimental conditions and methods, we don't think the quantitative comparison of previous study to ours is necessary here.

For clarification, we delete the reference of Na et al. (2007) and add the reference of Chu et al. (2016). The sentence of "consistent with previous studies (Na et al., 2007; Qi et al., 2020)." in line 238 was deleted, and "which was consistent with previous studies (Qi et al., 2020; Chu et al., 2016)." was added after the sentence of "There was a noticeable increase in the SOA mass concentration in the presence of NH₃." in line 236

L 244-247: Same comment -- are these previous studies on toluene as well? How does the magnitude of your observed SOA-suppression due to NO_x addition compare to the magnitudes observed in these previous studies?

Author reply:

BVOC was used in the studies of Zhao et al. (α -pinene and limonene) and Liu et al. (cyclohexene), benzene was used in the study of Xu et al.

The branching of RO₂ loss among different pathways has an important influence on the product distribution and thus on SOA composition, physicochemical properties, and yields. The reaction of RO₂ + NO to form the RO intermediate is ubiquitous and not affected by the type of SOA precursors. The fate of RO₂ mainly depends on the concentrations of NO_x. High NO_x can make the RO₂ radical fate dominated by one single pathway (i.e., RO₂+ NO or RO₂+ NO₂). As mentioned before, the different experimental conditions and methods were used between previous studies and ours. Therefore, we did not compare the quantitative impact of NO_x on SOA in different studies.

The following sentences were added in line 253 of the manuscript "The branching of RO₂ loss among different pathways has an important influence on the products distribution and SOA formation. The fate of RO₂ mainly depends on the concentrations of NO_x (Zhao et al., 2018; Liu et al., 2019; Xu et al., 2020)."

L 248: "participate" should be "precipitate"

Author reply:

Suggestion taken.

L 258-260: It's not entirely accurate to say this combination hasn't been done before, because SOA-formation experiments have been performed with and without NO_x and with and without seed aerosol that usually contains ammonium. If the "synergistic" mechanism you propose (carbonyls+NH₄(+) in the aerosol phase) is occurring, that may have been seen before in studies investigating toluene SOA formation with ammonium sulfate seed aerosol. Are there any such studies you can reference and compare to?

Author reply:

Ammonium sulfate particle is acidic. It is well known that acid-catalyzed reactions have an important influence on SOA formation (Jang et al., 2002). Joint impact of NO_x and NH₃ on SOA formation has been studied before (Li et al., 2018; Qi et al., 2020). The following sentences were added in line 255 of the manuscript "Qi et al. (2020) observed the promotion of NH₃ on toluene SOA formation was more obviously under high NO_x concentration, SOA yield increased 3.7% and 4.6% for 70 ppb and 160 ppb initial NO_x concentration, respectively, when 200 ppb NH₃ was added into the chamber. Li et al. (2018) shown that the presence NH₃ can promote the particle size growth of SOA; at the same time, this particle growth rate was higher under low VOC/NO_x (or high NO_x) conditions. All in all, the joint effect of multiple environmental factors on SOA formation is not the simple summation of the influences of various factors on SOA formation."

Here, we used "not well-characterized" in the manuscript. For clarify, the sentence of "The effects of multiple factors are not well-characterized by chamber experiments, which was partly responsible for the gap between the simulations and field observations." was deleted.

L 295: "even there" -- missing a word, maybe? Does this mean "even if there" or "even when there" (i.e. is it hypothetical, or do you know at some point the OH in the chamber was zero?

Author reply:

The OH was zero is hypothetical. The real OH concentration was shown in comment #2. The expression here is not accurate. We express our gratitude for this suggestion.

"even there" was fixed as "even if there".

L 297-300: Unclear if these sentences refer to observations from the current study, or to hypotheticals, or to the cited study by Malecha and Nizkorodov -- was mass loss observed in these experiments, and do you know that OVOCs were photoproducted, and that they had a lower OSc?

Author reply:

These sentences refer to the cited study by Malecha and Nizkorodov. In their study, the calculation of SOA particles loss was about \square 1% based on the measured OVOC emission rates during summertime conditions in Los Angeles, California. The loss of SOA was very small.

The sentences in line 295-300 of the manuscript were fixed as: "Finally, as pointed by Malecha and Nizkorodov (2016), even if there was no OH in the chamber, the photodegradation of SOA can produce small oxygenated volatile organic compounds (e.g. acetaldehyde $OS_C=-1$, and acetone $OS_C\approx-1.3$) under UV light irradiation. The photoproduction of OVOCs from SOA had a lower OS_C value than that of SOA. Although the loss of SOA through photodegradation is small, the OS_C value of SOA still had increased to a certain extent (Malecha and Nizkorodov, 2016)."

L 318-320: Which experiment does this sentence refer to?

Author reply:

For clarification, the sentence in line 318-320 is changed to "After 60 min of UV light irradiation, there was no more SOA formation; however, the OS_C did decrease slightly in Exp.2 and 3, illustrating that the NH_3 could continue to react with SOA through heterogeneous processes."

L 338: both instances of "volatile" should be "volatility"

Author reply:

Corrected.

L 390: Section should be numbered 3.3

Author reply:

Yes, we corrected.

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L 398: why tentative? More detail is needed here (as opposed to the SI) about how the PMF analysis was performed (was it performed on the whole dataset from all experiments, or separately on each experiment?) and what the PMF analysis identified -- it seems from the later discussion that it identified two OA factors with differing N/C values, but that should be clearly stated here.

Author reply:

We change the sentences in line of 396-400 as below: "For the toluene OH-photooxidation experiments with NH_3 and/or NO_x presence, two factors were identified from the PMF analysis in the same way of Chen et al. (2019). The H/C, O/C, and N/C values of these two factors are shown in Fig. 5. The factor with higher N/C values was defined as high-

nitrogen OA (Hi-NOA). In contrast, the factor with lower N/C values was defined as low-nitrogen OA (Lo-NOA)."

L 414-416: Why is this likely? Because it did not start forming right away? Couldn't that just be because it was a later-generation gas-phase product that reacted with NH₃ in the gas phase?

Author reply:

As we discussed below, if the Hi-NOA formed from the later-generation gas-phase product, the time-dependent concentrations of Lo-NOA (earlier generational products) should continue to increase. But they exhibited a decline of Lo-NOA at longer reaction times, reflecting the conversion from Lo-NOA to Hi-NOA.

We deleted the sentence of "It was likely that the formation pathway of Hi-NOA did not involve the reaction of NH₃ with organic matter in the homogeneous gas phase."

This part has been revised on line 416-422.

"The Lo-NOA reached the maximum mass concentration after 30 min of the photooxidation, and then decreased. Such a decline trend of Lo-NOA at longer reaction times reflected the conversion of Lo-NOA into something else in the particle-phase. As the Lo-NOA decreased, the mass concentration of Hi-NOA gradually increased. Thus, the Hi-NOA should be derived from the heterogeneous reaction of Lo-NOA with NH₃/NH₄⁺. At the same time, it was proved that the formation pathway of Hi-NOA was not through reaction of NH₃ with later-generation gas-phase products in the homogeneous gas phase."

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L 509: "high volatile" should be either "highly volatile" or "high volatility"

Author reply:

Suggestion taken. "high volatile" was fixed as "highly volatile".

L 511: "participation" should be "precipitation"

Author reply:

Suggestion taken .

L 526: Data should be put somewhere publicly accessible like an online repository, or, per the ACP guidelines, "If the data are not publicly accessible, a detailed explanation of why this is the case is required." Particularly for these unique experiments I imagine researchers may want to be able to access the data

Author reply:

We express our appreciation for this suggestion. Our data will be put online soon.

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