



## Reviewer comment on acp-2021-560

Anonymous Referee #2

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Referee comment on "Synergetic effect of NH<sub>3</sub> and NO<sub>x</sub> 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-RC2>, 2021

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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<sub>x</sub> during photooxidation suppresses SOA formation, while the addition of NH<sub>3</sub> enhances SOA formation, consistent with previous studies. They then show that photooxidation of toluene in the presence of both NO<sub>x</sub> and NH<sub>3</sub> together results in an even greater enhancement of SOA formation than NH<sub>3</sub> alone. They ascribe this to a "synergistic" effect whereby the more-volatile compounds produced by photooxidation with NO<sub>x</sub> are able to form SOA efficiently when they can react with NH<sub>3</sub> (or NH<sub>4</sub><sup>+</sup>). AMS and optical observations are also reported and used to support the hypothesis that carbonyl + NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> 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<sub>x</sub> and NH<sub>3</sub> co-exist. Therefore, the findings presented here clearly show that the synergetic effects of NO<sub>x</sub> and NH<sub>3</sub> 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 NO<sub>2</sub>?). 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.

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.

- 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 RO<sub>2</sub> radical production) could explain some difference in the observed SOA formed and the SOA properties, as has been shown in the past.

- 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 NO<sub>x</sub> in the chamber? It seems this could explain a large portion of the "enhancement" in particle mass in the NH<sub>3</sub> + NO<sub>x</sub> 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 NO<sub>x</sub>-NH<sub>3</sub> synergy, I suppose, but seems less chemistry-dependent than the effects to which you ascribe the synergy).

- 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 NO<sub>2</sub> and NO in the high-NO<sub>x</sub> experiments. These two NO<sub>x</sub> 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 RO<sub>2</sub> reacts with NO, how much HNO<sub>3</sub> is formed, and whether PANs form from the reactions of acyl peroxy radicals with NO<sub>2</sub>, for example.

- Why were such high concentrations of toluene used, and how much could RO<sub>2</sub> + RO<sub>2</sub> chemistry participate, especially in the low-NO<sub>x</sub> experiment? How does this compare to the amount of toluene-RO<sub>2</sub> that are expected to react with toluene-RO<sub>2</sub> in ambient conditions in the atmosphere? It seems that excessive RO<sub>2</sub>-RO<sub>2</sub> chemistry could make these "low-NO<sub>x</sub>" results unrepresentative of "low-NO<sub>x</sub>" conditions in the atmosphere, making interpretation difficult.

- 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.

- 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.

- 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?

- 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?

- 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.

Additional (mostly minor) comments:

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

L 101-103: Needs more detail. Is this NO<sub>x</sub> 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<sub>x</sub> concentration? Finally, is it all due to the RO<sub>2</sub> chemistry as the following sentence suggests, or can some of the increase be ascribed to changing OH as NO<sub>x</sub> increases?

L 107: "participated" should be "precipitate"

L 111-112: The change in OH with NO<sub>x</sub> is not as simple as "suppression", and in many cases NO<sub>x</sub> may increase OH (see, e.g., Figure 8 in <https://acp.copernicus.org/preprints/acp-2021-605/>).

L 123: unclear; does this mean a reduction in NH<sub>3</sub> improves PM<sub>2.5</sub> pollution \*more than\* a reduction in SO<sub>2</sub>? Is that when reducing both by the same amount?

L 238: Are these previous studies on toluene or other precursors? How does the

magnitude of your SOA-enhancement due to NH<sub>3</sub> addition compare to these previous studies?

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<sub>x</sub> addition compare to the magnitudes observed in these previous studies?

L 248: "participate" should be "precipitate"

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<sub>x</sub> and with and without seed aerosol that usually contains ammonium. If the "synergistic" mechanism you propose (carbonyls+NH<sub>4</sub><sup>+</sup>) 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?

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?

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 photoproduced, and that they had a lower OSc?

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

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

L 390: Section should be numbered 3.3

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.

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 NH<sub>3</sub> in the gas phase?

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

L 511: "participation" should be "precipitation"

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.