# Anonymous Referee #1

*We would like to thank Referee #1 for the time spent evaluating this manuscript and for his/her helpful comments. We have answered all comments. They have helped us improving the manuscript.*

## General Comments

This paper describes results from a series of simulation chamber experiments to study the formation of gaseous products and secondary organic aerosol (SOA) resulting from photo-oxidation of isoprene and its major oxidation product, methacrolein. A range of on-line techniques have been used to probe the gaseous species and characteristics of the SOA.

The key feature of this work is the relatively long timescale (7-8 hours) over which the species are monitored which enables investigation of the chemical evolution of the various products and also the aerosol. The concentration-time profiles for the gaseous species are dynamic and nicely reflect the primary and secondary chemistry in detail.

In contrast, the composition of the SOA appears to change only for the first 2 hours or so.

The article is, in general, well written and the results are presented in a clear and logical manner. The experimental data are of high quality and the interpretation and discussion of the results is generally appropriate. There are a few minor issues that should be discussed, but overall this is a good piece of work that is of interest to the atmospheric chemistry community. I recommend publication following revision of the manuscript in line with the following comments.

## Major Comments

1. One of the key results of this work is that the yields of SOA for both isoprene and methacrolein photo-oxidation are smaller than those observed in most previous studies. The authors attribute this to different light sources used in the various studies. However, there are of course many other factors (discussed in the manuscript) which influence SOA yield. A key factor is the level of NOx in the chamber and in this work, as well as the initial introduction of NOx or HONO, NO is continuously added throughout the experiments. As pointed out by the authors themselves (p 22510, lines 3-10), this is expected to produce less SOA because under these conditions the $RO_2$ + $HO_2$ reactions are less favourable than $RO_2$ + NO reactions.

a) Could this also be a contributory factor to the observed lower yields found in this study?

*<u>Response:</u> Concerning $RO_2$ chemistry, it can be seen in Figure 3 that the lowest yields found in the literature were measured for experiments under high $NO_x$ conditions (Edney et al., 2005; Kleindienst et al., 2006), in which $RO_2$+NO reactions dominate. For systems in which $RO_2$ radical can react with some combination of NO, $HO_2$, and $RO_2$ radicals like ours (middle $NO_x$ conditions), yields from the literature differ from one study to another. Our yields were lower than the yields obtained by Kroll et al. (2005), but they were also similar to those obtained by Dommen et al. (2006) and Zhang et al. (2011) while all these experiments were carried out under similar $NO_x$ conditions. It can also be noted that, as it was mentioned in the text (P22518, line 27), no influence of $NO_x$ levels on SOA yields was observed in our experiments. As a result, we consider that $NO_x$ levels didn't appear to be a contributory factor to the observed difference between our yields and the higher yields found in the literature.*

b) Did the authors perform any experiments without the continuous addition of NO to see if the yields increased?

*<u>Response:</u> In our experiments, the aim of the continuous flow of NO was to maintain an OH level in the chamber of the same order of magnitude as the one in the atmosphere during the entire experiment length. That is to say to keep sufficient $RO_2$ + NO and $HO_2$ + NO propagating steps while*

*minimizing $RO_2 + HO_2$, $OH + NO_2$ and $RO + NO_2$ terminating reactions. Experiments performed without this continuous NO flow showed a fast decrease of OH concentrations due to a fast consumption of NO in the first hours of the experiment. The oxidation level thus became insufficient to lead to SOA formation. Another $NO_x$ injection in the system allowing the increase of OH concentration level was thus necessary to observe SOA formation in the chamber as it can be seen in Figure R1.*

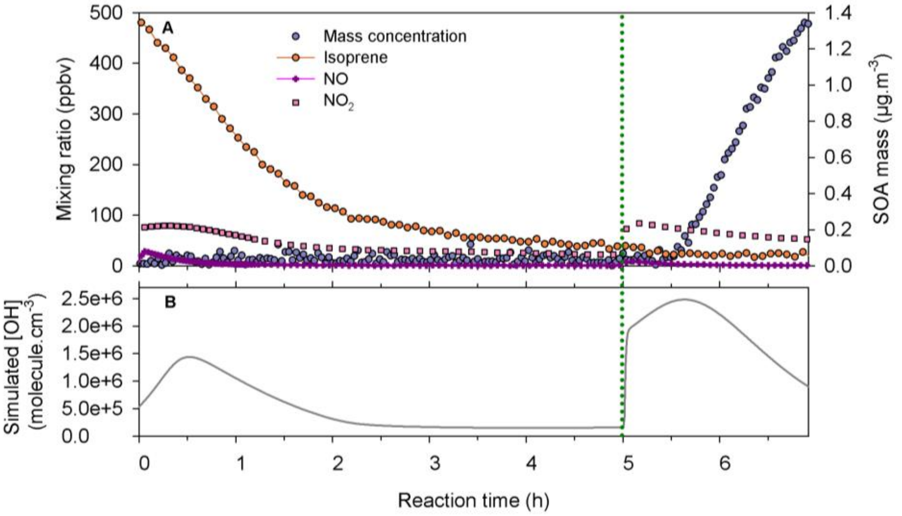

**Figure R1** Time profiles of (A) isoprene, $NO_x$, SOA mass and (B) simulated OH concentrations (determined using MCM V3.1 (Jenkin et al., 1997; Saunders et al., 2003)) during an isoprene photooxidation experiment without NO continuous flow. The green dotted line indicates the time of the second $NO_x$ injection.

*These explanations and figure R1 were added to the Supplementary Material of the new version of the manuscript.*

2. The $NO_2$ and $O_3$ concentration-time profiles shown in Figure 1b are a little unusual. After about 4 hours the $NO_2$ mixing ratio starts to increase. Why is this? Interestingly this occurs during the period where particle formation begins. Are these observations connected? The $NO_2$ signal continues to increase for a further hour or so and then falls. Meanwhile, the ozone signal also shows a corresponding increase. This interesting behaviour should be discussed and explained if possible.

*Response: These unusual time profiles of $NO_2$ and $O_3$ are due to NO continuous injection. In order to keep NO level at around 2-5 ppb during the entire experiment and to avoid an accumulation of NO in the system, it was necessary to modulate the flow of NO. Hence, the NO flow was started only when NO concentration in the system reached a mixing ratio below 5 ppb and this flow was stopped if an accumulation of NO was observed in the system as it can be seen in Figure R2.*

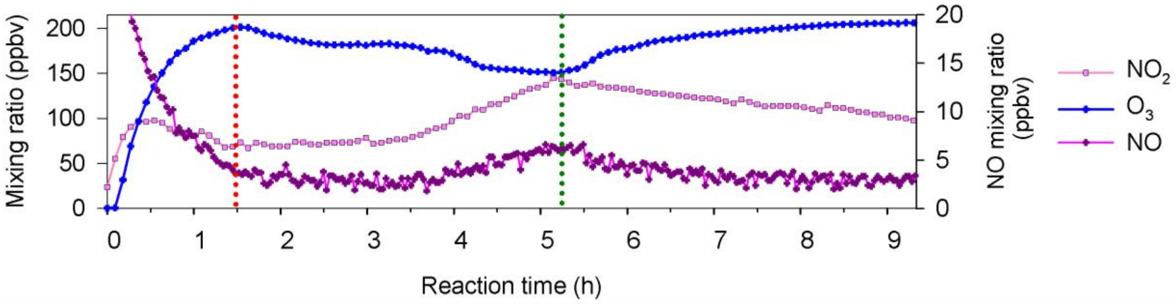

**Figure R2** Time profiles of $NO_x$ and $O_3$ during isoprene photooxidation (experiment I280113) performed with no seeds and with HONO as OH source. The red dotted line indicates the start of NO continuous flow and the green dotted line, its stop.

*This figure shows that NO accumulation in the system leads to $O_3$ consumption and $NO_2$ production (due to the reaction: $NO + O_3 \rightarrow NO_2 + O_2$). When the flow of NO is stopped, NO concentrations become limited, minimizing $NO_2$ production and $O_3$ consumption, leading to an increase of $O_3$ mixing ratios, and a decrease of $NO_2$ mixing ratios. This unusual $NO_2$ increase is thus not connected to the beginning of SOA formation but is only a consequence of NO continuous injection.*

*We propose to add in the text (P22513, line 9) "The NO flow was started only when NO mixing ratio in the system reached a concentration below 5 ppb and was manually adjusted to avoid an accumulation of NO in the system in order to maintain a NO mixing ratio between 2 and 5 ppb during the entire experiment."*

**<u>Minor Comments</u>**

1. Page 22508, Abstract: The abstract is not very well written. The English could be improved, e.g., rephrase "general dispersion" and "the solar one". There is no need to use numbers to list the two main findings.

<u>*Response:*</u> *In order to improve the English content of the abstract, the manuscript has been read by two native English speakers and the abstract has been corrected.*

2. Page 22511, line 3: Rephrase "...could also contribute to the observed variability in SOA yields, including...."

<u>*Response:*</u> *Corrected*

3. Page 22515, line 6: Should be "BFSP"?

<u>*Response:*</u> *Corrected*

4. Page 22515, line 14: Rephrase "In all our experiments....."

<u>*Response:*</u> *Corrected*

5. Page 22515, line 23: "photolyzes"

<u>*Response:*</u> *Corrected*

6. Page 22515, line 24: delete "an"

<u>*Response:*</u> *Corrected*

7. Page 22515, line 25 and throughout the rest of manuscript: "ppbv" with the "v" not as subscript.

<u>*Response:*</u> *Corrected*

8. Page 22516, 16: Rephrase "....due to sampling and was found to be around ..."

<u>*Response:*</u> *Corrected*

9. Page 22517, lines 6-7: Referring to Table 2, the authors state that their measured yields are in good agreement with those in the literature. They certainly do agree within experimental error, but it should also be noted in the text that they have the highest yields for formaldehyde and

methacrolein, as well as the lowest yields for methyl vinyl ketone and 3-methylfuran. In addition, all other studies report higher yields for methyl vinyl ketone than methacrolein, whereas the opposite is true in this study. Is there an explanation for this? Maybe some further comment is required here.

*<u>Response:</u> We disagree with the referee on this point because, due to the indicated uncertainties, there are no significant differences between our results and those of the cited studies.*

10. Page 22517, line 16: "...can be made."

*<u>Response:</u> Corrected*

11. Page 22518, lines 13-14: This sentence is unclear – rephrase.

*<u>Response:</u> We propose to replace "These observations exhibit a clear secondary products type growth (Ng et al., 2006)" by: "These observations are typical of a SOA formation induced from the oxidation of secondary products as observed by Ng et al. (2006)"*

12. Page 22518, line 22: a closing bracket is missing.

*<u>Response:</u> Corrected*

13. Page 22519, line 13: "....semi-volatile species...."

*<u>Response:</u> Corrected*

14. Page 22520, line 10: Rephrase "....exhibit some variation, our yields..."

*<u>Response:</u> Corrected*

15. Page 22520, line 23: Rephrase "....induces an increase in SOA yields..."

*<u>Response:</u> Corrected*

16. Page 22521, line 18: Rephrase "....different from that of alkenes..."

*<u>Response:</u> Corrected*

17. Page 22523, line 25 and several other places in the manuscript: units for density should be g cm-3.

*<u>Response:</u> Corrected*

18. Page 22524, line 8: Rephrase "…used: the extent of semi-volatile wall losses could be...."

*<u>Response:</u> Corrected*

19. Page 22524, line 18: Rephrase "…exhibit a fairly large variation."

*<u>Response:</u> Corrected*

20. Page 22524, lines 18-22: In this work the use of HONO produced higher SOA yields, whereas the opposite was observed in the study of Chan et al. (2010). Is there an explanation for this?

*Response:* *In our experiments, the use of HONO as OH precursor led to higher SOA yields than in experiments using* $NO_x$ *as OH source because higher OH concentrations were obtained at the beginning of the experiment when HONO was used (Fig. S4). These two precursors allow having the same* $NO_2$*/NO ratio. In the study of Chan et al. (2010), one of the OH source used is HONO but the other is* $CH_3ONO$*. We hypothesize that these two precursors lead to similar OH concentrations at the beginning of their experiments, but the use of* $CH_3ONO$ *as OH source allows achieving high* $NO_2$*/NO ratios, leading to higher SOA yields according to Chan et al. (2010).*

*We propose to replace in the text (P22524, line 21) "…with the two OH sources, two yield curves…" by "…with the two OH sources* ***(which lead to similar initial*** $NO_2$***/NO ratio)****, two yield curves…".*

21. Page 22525, line 11: Rephrase "....were very close..."

*Response:* *Corrected*

22. Page 22525, line 16: Delete "very"....in line with comment 9 above.

*Response:* *Corrected*

23. Page 22525 and 22526, Section 4: Parts of this Conclusions section are not very well written. The English could be improved.

*Response:* *In order to improve the English content of the conclusion, the manuscript has been read by two native English speakers and the conclusion has been corrected.*

24. Page 22535, Table 2: rephrase caption "Yields of first-generation....."

*Response:* *Corrected*

25. Page 22535, Table 4: rephrase caption "Yields of first-generation....."

*Response:* *Corrected*

26. Page 22535, Table 4: The yields are reported as a range of values and also without errors. Is there a reason for this? Why not list them in the same way as in Table 2?

*Response:* *As it was mentioned in the text (P22523, lines 4-5) these primary yields were impacted by the variability in initial* $NO_x$ *levels, contrary to the primary yields obtained in isoprene experiments. Considering this large variability, we chose to report them as a range of values. This choice was also made in other studies such as Orlando et al. (1999) for formaldehyde, carbon monoxide and MPAN.*

27. Page 22539, Figure 2: Typo "particle". Units of density should be changed.

*Response:* *Corrected*

28. Page 22543, Figure 6: Typo "particle". Units of density should be changed.

*Response:* *Corrected*

## References

Chan, A. W. H., Chan, M. N., Surratt, J. D., Chhabra, P. S., Loza, C. L., Crounse, J. D., Yee, L. D., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Role of aldehyde chemistry and NOx concentrations in secondary organic aerosol formation, Atmospheric Chemistry and Physics, 10, 7169-7188, 2010.

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Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, Atmospheric Environment, 31, 81-104, 1997.

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