Author's Response

Gaseous products and Secondary Organic Aerosol formation during long term oxidation of isoprene and methacrolein

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Point-by-point response to the reviews

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?

Response: *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?

Response: *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.*

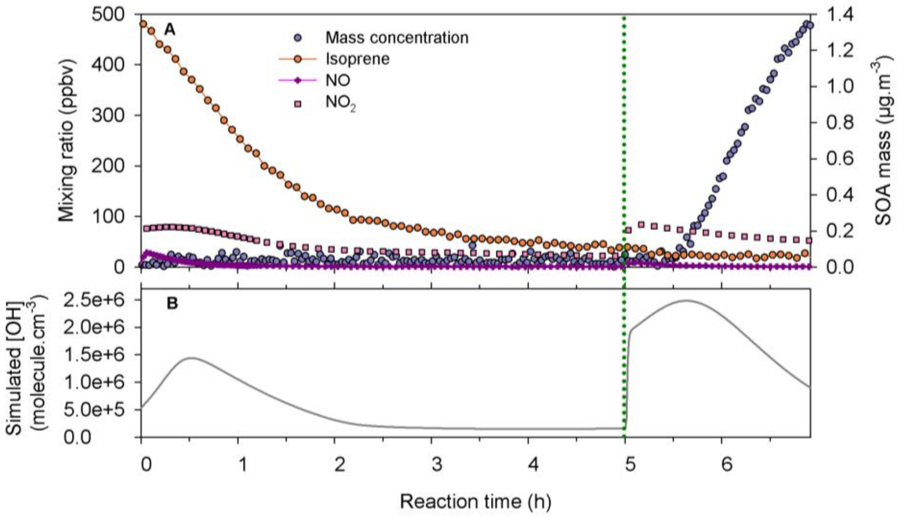

Figure R1 Time profiles of (A) isoprene, NO_x, SOA mass and (B) simulated OH concentrations (determined using MCM V3.1 (Jenkin et al., 1997; Saunders et al., 2003)) during an isoprene photooxidation experiment without NO continuous flow. The green dotted line indicates the time of the second NO_x injection.

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.

<u>Response:</u> *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.*

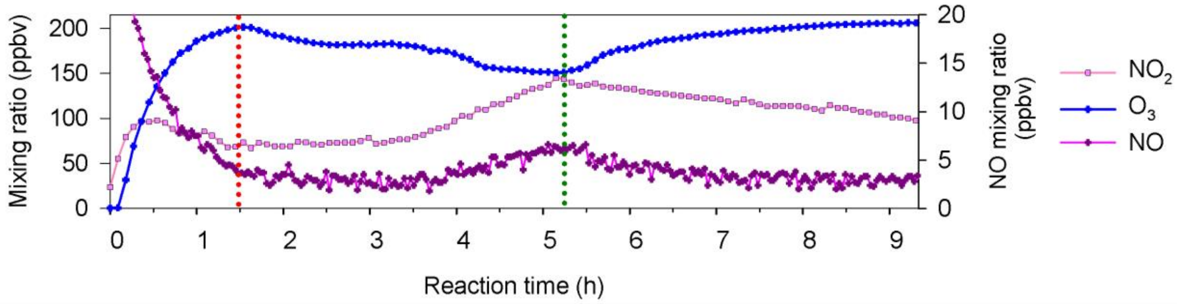

Figure R2 Time profiles of NO_x and O_3 during isoprene photooxidation (experiment I280113) performed with no seeds and with HONO as OH source. The red dotted line indicates the start of NO continuous flow and the green dotted line, its stop.

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.

Response: 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."

Response: Corrected

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

Response: 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.

Response: Corrected

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

Response: Corrected

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

Response: Corrected

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

Response: Corrected

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

Response: Corrected

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

Response: Corrected

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

Response: Corrected

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

Response: 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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Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation under high-NOx conditions, Geophysical Research Letters, 32, 2005.

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Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, Atmospheric Chemistry and Physics, 3, 161-180, 2003.

Zhang, H., Surratt, J. D., Lin, Y. H., Bapat, J., and Kamens, R. M.: Effect of relative humidity on SOA formation from isoprene/NO photooxidation: enhancement of 2-methylglyceric acid and its corresponding oligoesters under dry conditions, Atmospheric Chemistry and Physics, 11, 6411-6424, 2011.

Anonymous Referee #2

We would like to thank Referee #2 for the time spent evaluating this manuscript and for his/her helpful comments. We have conducted additional work and answered all the comments. They have helped us improving the manuscript.

1/ In the case of methacrolein oxidation they claim to observe the primary production of acetaldehyde by PTR-MS.

1A/ This m/z could also be a fragment from higher masses

Response: *As it was mentioned in the text (P22523, lines 12-14) "The presence of fragments of higher molecules contributing to this signal (like methylglyoxal; Müller et al. (2012)) cannot be excluded".*

1B/ or eventually even be released from the walls.

Response: *A release from the walls is unlikely since it was not observed in control experiments (i.e. irradiation of a N_2/O_2 mixture (80 % / 20 %)).*
The sentence "Furthermore, a release from the walls is unlikely since acetaldehyde was not observed in control experiments (i.e. irradiation of a N_2/O_2 mixture (80 % / 20 %))." was added in the text (P22523, line 16).

1C/ The authors provide a speculative mechanism as to how it could form. According to Figure 5 acetaldehyde is continuously increasing reaching about 15 ppb at the end of the experiment. It is not clear to me why it should not reach levels above the detection limit of FTIR (20ppb) in experiments with doubled precursor concentrations. If this was not the case, such an experiment should be performed.

Response: *As it was mentioned in the text (P22523, line 11), the observed yields for acetaldehyde were variable (2-6 %). Experiments starting from the highest methacrolein (MACR) initial concentration (927 ppb and 735 ppb) lead to a maximum acetaldehyde ($(C_2H_4O)H^+$ signal at m/z 45 measured by PTR-ToF-MS) concentration of around 20 ppb which corresponds to the FTIR detection limit and does not allow for a definitive conclusion on the actual acetaldehyde concentrations in the system.*
As a result, no definitive conclusion can be drawn concerning the presence of a primary production of acetaldehyde in our experiments. Because one cannot exclude the presence of fragments of other compounds contributing to this $(C_2H_4O)H^+$ signal at m/z 45 measured by PTR-ToF-MS (Müller et al. (2012), we propose to replace "acetaldehyde" by "$(C_2H_4O)H^+$" in Figure 5C.

2/ The authors also report SOA yields from both precursors. In general they find smaller yields compared to literature.

Response: *As it was mentioned in the text (P22508, lines 8-9), yields obtained in this study are not smaller than other yields from the literature but "consistent with the lowest values found in the literature" that is to say, in good agreement with the results by Dommen et al. (2006) and by Zhang et al. (2011) for isoprene experiments, and similar to yields obtained by Zhang et al. (2012) for methacrolein experiments.*

3/ They speculate, that this could be due to the light source (xenon lamps), which produces a light spectrum similar to sun light. Most studies are done using black lights, which lack the emission of longer wavelengths. This speculation may be true or not, but it cannot be drawn based on the analysis given.

<u>Response:</u> *We disagree with the referee interpretation of our statement. In fact this is more a "hypothesis" than a "speculation". We believe that the yield results from literature are excessively scattered considering the technology available nowadays and while none of the other authors commented this fact, we did, trying to find commonalities and differences. Light source is obviously one of them. Certainly more studies will be necessary in the future to assess the effect of light source but this paper, when published, can be also used by the community to support the need for such studies.*

4/ The authors calculate the SOA yield from the measured aerosol mass at maximum concentration.
4A/ They consider neither wall loss of particles, dilution flow

<u>Response:</u> *Dilution flow was of course taken into account for the yield calculations. In order to clarify this point, we propose to add in the text (P22518, line 20) "All values were dilution corrected". Concerning wall loss of particles, it was mentioned in the text (P22512, lines 2-5) that "Due to the very low level of charges on the walls (conductive and grounded), aerosols exhibit a long lifetime (between 10 h and 4 days, depending on the particle size distribution) in the chamber (McMurry and Rader, 1985; Wang et al., 2011)". Hence particles wall losses are not significant in our experiments as it can be seen with the following figure showing the stability of aerosol mass concentration in the chamber when dilution correction is applied:*

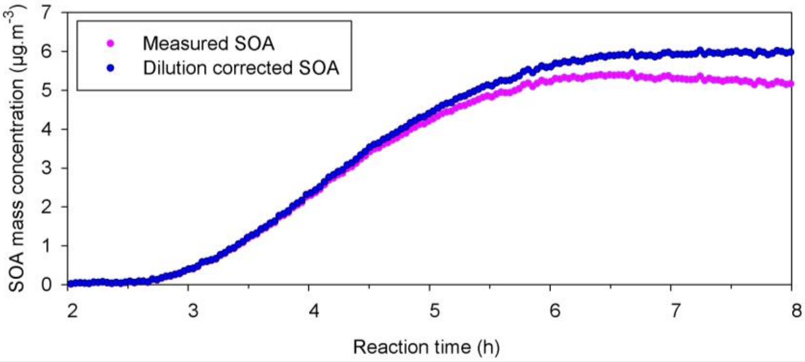

Figure R1: Time profile of SOA mass concentration during an isoprene experiment (I150211; table 1)

4B/ nor wall losses of gaseous condensable species. It has to be admitted, that the latter point is not considered in most yield determinations either, but it seems to be quite large in this chamber.

<u>Response:</u> *We considered this possibility in the text (P22519, lines 9-11). Thanks to the works of Loza et al. (2010); Matsunaga and Ziemann (2010) and Zhang et al. (2014) who highlighted the effect of such losses on SOA yields, it is clear that all the chamber groups have now to work on the wall losses of semi-volatile intermediate species. This work has been initiated at our institute but one can already find some first order losses measured in the CESAM chamber in Wang et al. (2011) (table 5). These first values do not seem to exhibit tremendous differences with other chamber's losses (while most of the data from other studies are not published in peer reviewed journals). Furthermore, SOA formation from other chemical systems have been studied in the CESAM chamber (such as α-pinene ozonolysis in Wang et al. (2011)) and led to SOA yields in agreement with previous studies.*
We agree nevertheless that gaseous wall loss characterization will be clearly needed for a better use of simulation chamber data in the future. It will be a long term effort (that we have started) in both the setting of the appropriate formalism as well as the quantification of the relevant parameters. In between, we believe that it should not prevent publication (as it is the case for other groups).

We propose to add in the text (P22519, line 18) "Some pseudo-first order rates for loss processes of organic compounds in the CESAM chamber can also be found in Wang et al. (2011): although the dataset is limited, these values are of the same order of magnitude as those obtained with other *simulation chambers. Furthermore, a SOA yield study for a well-known system (α-pinene ozonolysis) is provided in this study without any significant difference with already published values.”.*

4C/ When the chamber was manually cleaned almost no SOA production occurred anymore.

Response: *For isoprene experiments only, we observed, for some experiments with manual cleaning the day before, a very low SOA production. It hence seems to highlight the existence of an impact of the state of the walls on the nucleation step in this system which needs a lot of oxidation steps to form SOA. It appears that we can’t control the parameter linked to this variability. This parameter could be linked to the state of the walls but not necessarily to wall loss of gaseous compounds. It can be linked to OH production (for instance via HONO production) and to the competition between OH and photolysis in isoprene products oxidation.*

4D/ The question is therefore, what contributed to SOA formation in an aged chamber and how much. No blank experiment with seed aerosol was performed determining the blank production of SOA in the chamber.

Response: *A control experiment (i.e. irradiation of a N_2/O_2 mixture (80 % / 20 %) and HONO) with ammonium sulfate seed particles was performed in the chamber and no SOA production was observed.*
One must also underline that even when an "aged" chamber was used, the yields were lower than the highest yields published so far. Did these chambers present more “aged” conditions than ours and contributed even more to the SOA formation? (And if so, would it be necessary to underline this in a peer reviewed paper?)
If, on the contrary, it is considered that "too clean" walls may be an enhanced sink for semi-volatile species then the only control experiment would be to compare the SOA formation of a very well-known system. As already said, this has been done with the best known system - α-pinene ozonolysis- with no significant differences between very clean walls (CESAM chamber) and clean walls (Teflon chambers)(Wang et al., 2011).

4E /Therefore, there exist enough possible processes to explain the lower yields. The analysis of the experiments needs to be done more carefully.

Response: *We easily recognize that there is some kind of irreproducibility in the absolute yields obtained. This may also be linked to the fact that the yields are so low and the experiments so long that it may be difficult to control all parameters: a change in the triggering of the SOA formation can be due to a change in the oxidant level, and/or in the nucleation process. In the case of weak aerosol producers, such as isoprene, a small change in the oxidant level, or in the nucleation process would affect the SOA yields at two successive orders: at the first order, it may directly affect the production of semi-volatile compounds, but at the second one, the same change is amplified by the fact that it affects the production of aerosol available for the further condensation of the semi-volatile compounds.*
We have tried to overcome this second order effect by providing a highly controlled quantity of aerosol for condensation by seeding the chamber with a monodisperse aerosol. Because of particle coagulation in the chamber, an initial narrow monodisperse seed aerosol should result in a controlled size distribution of the aerosol in the chamber, inducing a measurement of the total aerosol volume with low uncertainties. However, the problem is that it is so far almost impossible to fill a large simulation chamber with a narrow monodisperse seed aerosol in a reasonable amount of time. The consequence of using a polydisperse aerosol for seeding the chamber is that the uncertainties on the total aerosol volume concentration measurements increase due to the fact that each channel of the

SMPS provides a signal with its own uncertainty which is added to those of the other channels. In the case of such a weak SOA producer such as isoprene, the polydisperse seed volume concentration uncertainties are finally larger than the SOA volume concentration. Therefore, most of the experiments were done without seed particles.
Nevertheless, we believe that the yield behavior with the aerosol quantity available for condensation (Odum plot, Figure 3) showed a very good internal consistency, and this behavior is used for comparison with other works (which is also useful for models). This consistency carries some chemical information which are meaningful and deserve to be discussed.

The referee seems to only consider wall characteristics to explain the differences in yields. Doing so, the referee does not seem to consider the fact that similar yield behaviors were obtained with very different chambers (with differences in the wall's material, the history and the surface-to-volume ratio) (see for example Dommen et al. (2006); Zhang et al. (2011) and our study) and discards other differences in the experimental protocols.

5/

5A/ Somehow peculiar is the increase of O/C from AMS measurements in the beginning of the experiment (Figures 4 and 8), which is attributed to "oxidation processing during particle formation" (p22522, line1).

<u>Response:</u> The O/C increase in the beginning of the experiment is rather typical than peculiar. Similar O/C ratios time evolution have been previously observed during SOA precursors oxidation experiments, including isoprene experiments (see for example Chhabra et al. (2010)). Indeed as oxidation proceeds, O/C increases as more oxidized species are formed with increasing partitioning to the particle phase.

5B/ It is generally assumed that condensable gases need to be of low volatility. This implies highly oxygenated compounds. How can the authors explain the condensation of compounds with such low O/C?

<u>Response:</u> It is not really a question of complete condensation but rather a partitioning (even if the major part is in the gas phase, only a small fraction needs to be in the particulate phase). Furthermore, it was often observed (Healy et al., 2008) that we can find in particulate phase more species than their vapor pressure could suggest. In particular, carbonyl compounds bearing an O/C of 0.6 that are relevant to our study such as hydroxyacetone or methylglyoxal, have been previously observed to partition into the particle phase (Bao et al., 2012; Healy et al., 2008; Kawamura et al., 2013). It is also noteworthy to note that the O/C values obtained in this study are in agreement with the ones obtained in previous simulation chambers experiments using AMS measurements (Aiken et al., 2008; Chhabra et al., 2010) as shown in Table 3.

5C / Could this be due to impurities in the chamber (needs blank experiment)

<u>Response:</u> Control experiments, i.e. irradiation of a N_2/O_2 mixture (80 % / 20 %) did not show any gaseous release nor formation of SOA in the chamber.

5D/ or an issue of data analysis?

<u>Response:</u> *Issues in the data analysis can be reasonably excluded and data analysis for the AMS is quite well standardized. Furthermore, the values of the O/C ratios measured in our study are very reproducible (and in good agreement with previous studies as mentioned above) thus occasional instrumental artefacts can be excluded too.*

It must be recognized however that despite a careful data analysis, O/C ratios provided by AMS have been previously found to underestimate O/C values (Aiken et al., 2008). Uncertainties in AMS elemental analysis are discussed in details in Chhabra et al. (2010); (2011).

5E/ Such an effect has not been observed so far. More often a slight decrease of O/C is seen because of condensation of less volatile and thus less oxygenated species with increasing aerosol mass concentration.

<u>Response:</u> *In the study by Chhabra et al. (2010), it can be seen for isoprene experiments in the presence of NO_x that, like in our experiments, the O/C ratios increased at the beginning of the SOA formation and then reached a plateau which remained stable over the course of the experiment (with reproducible results). An increase of the O/C ratios with increasing SOA mass concentration can also be seen in other systems like in gasoline exhaust aging experiments by Platt et al. (2013) (a minor contribution from primary material was observed but with negligible importance respect to SOA after a few hours).*

6/ It is observed that the use of HONO as OH source leads to higher SOA yields. This is attributed to higher OH concentrations at the beginning of the experiments (page 22524, line 3). However, Figure S4 shows quite the opposite, lower OH for HONO experiments.

<u>Response:</u> *There was an inversion in the legend, this error has been corrected and it now reads:*

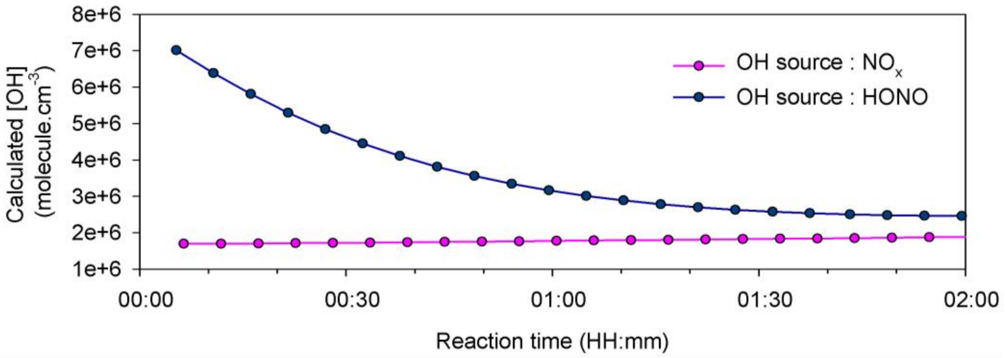

Figure S4 Time profiles of calculated OH concentrations during MACR photooxidation experiments performed with HONO (blue curve; M230113) and NO_x (pink curve; M240512) as OH source.

7/ This paper has some serious deficits and this reviewer cannot recommend publication of this paper.

<u>Response:</u> *Investigating such a weak SOA precursor as isoprene is not without any difficulties, especially if one wants to have a realistic oxidation rate that requires performing photolysis experiments during a long time (up to 9 hours).*

While SOA yields determination was not without any issue, we believe that our gas phase reaction products analysis, which provides a good agreement with previous studies for the well-known first generation products, brings valuable new information for the higher generation species.

Concerning the SOA formation, we consider that our Odum plots (Figures 3 and 7) show a consistent picture which is chemically meaningful. These results are in agreement with a part of previous publications and in disagreement with the highest yields published. We believe this deserves to be publically discussed through a peer review paper, especially because the highest values are often used by models to estimate the large scale impact of isoprene on SOA levels but also because they are used for the justification of a tremendous number of research proposals.

The community needs to have access to results and datasets which have been collected with different instruments (not only Teflon film chambers and fluorescent lamps) and different protocols to finally extract the usable chemical reactivity.

We do not claim that we bring the final answer but we bring our contribution to a global picture that still requires some work and we try to highlight some possible research perspectives. Light source is clearly one of them (even though many chambers are using black lights). Both positive (bringing impurities from dirty wall to form SOA) and negative (trapping semi-volatile gases to the wall) wall effects are also clear for which the whole community will soon have to provide datasets thanks to the pioneer works of Loza et al. (2010); Matsunaga and Ziemann (2010) and Zhang et al. (2014).

To do so, one has to let be published publically the work that pushes towards these directions.

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List of all relevant changes made in the manuscript

Relevant changes made in the manuscript:

- In order to improve the English content of the manuscript, it has been read by two native English speakers. The abstract and the conclusion have been corrected.
- Ions measured by PTR-ToF-MS were added in the legend of Figure 1 and Figure 5.
- Explanations about the continuous flow of NO were added to the Supplementary Material.
- The sentence “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.” was added in the text (P22513, line 9).
- The sentence ”All values were dilution corrected” was added in the text (P22518, line 20)
- The sentence “These observations exhibit a clear secondary products type growth (Ng et al., 2006)” was replaced by “These observations are typical of a SOA formation induced from the oxidation of secondary products as observed by Ng et al. (2006)” in the text (Page 22518, lines 13-14).
- The sentences “Some pseudo-first order rates for loss processes of organic compounds in the CESAM chamber can also be found in Wang et al. (2011): although the dataset is limited, these values are of the same order of magnitude as those obtained with other simulation chambers. Furthermore, a SOA yield study for a well-known system (α-pinene is provided in this study without any significant difference with already published values.” were added in the text (P22519, line 18).
- The sentence “Furthermore, a release from the walls is unlikely since acetaldehyde was not observed in control experiments (i.e. irradiation of a N_2/O_2 mixture (80 % / 20 %)).” was added in the text (P22523, line 16).
- “…with the two OH sources, two yield curves…” was replaced by “…with the two OH sources (which lead to similar initial NO2/NO ratio), two yield curves…” in the text (P22524, line 21).

Marked-up manuscript version

Gaseous products and Secondary Organic Aerosol formation during long term oxidation of isoprene and methacrolein

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Abstract

First- and higher order -generation products formed from the oxidation of isoprene and methacrolein with OH radicals in the presence of NO_x have been studied in a simulation chamber.~~: (1)~~ Significant oxidation rates have been maintained for up to 7 hours allowing the study of highly oxidized products.~~; (2)~~ Gas-phase product~~products~~ distribution and yields were obtained~~are provided~~, and show good agreement with previous studies. Secondary organic aerosol (SOA) formation ~~resulting from these experiments~~ has also been investigated. ~~Among the general dispersion exhibited by~~ SOA mass yields from previous studies show large discrepancies. The~~, the~~ mass yields obtained here were consistent with the lowest values found in the literature, and more specifically in agreement with studies carried out with natural light or artificial lamps with emission ~~spectrum~~ similar to the solar spectrum. Differences in ~~one. An effect of~~ light source are therefore~~is hence~~ proposed to explain partially~~, at least in part,~~ the discrepancies observed between different studies in the literature

for both isoprene- and methacrolein-SOA mass yields. There is a~~A~~ high degree of similarity between~~is shown in~~ the~~ comparison of~~ SOA mass spectra from isoprene and methacrolein photooxidation, thus strengthening the importance of the role of methacrolein in SOA formation from isoprene photooxidation under our experimental conditions (i.e. presence of NO_x and long term oxidation). According to our~~Overall, if these~~ results~~ are further confirmed~~, SOA mass yields from both isoprene and methacrolein in the atmosphere could be lower than suggested by most of the current chamber studies.

1 Introduction

Isoprene (2-methyl-1,3-butadiene) is a biogenic Volatile Organic Compound (VOC) emitted by vegetation. It is one of the most abundant non-methane hydrocarbons emitted into the troposphere with annual global emissions of 440 to 660 TgC (Guenther et al., 2006). As a diene, isoprene is highly reactive in the atmosphere, resulting in low atmospheric lifetimes due to its reaction with atmospheric oxidants, especially the hydroxyl radical (OH), with a lifetime of 1.7 hour (Karl et al., 2006). Because of its large emission rates and high reactivity, isoprene can have a strong influence on tropospheric photochemistry on the local, regional and global scales. The OH-initiated oxidation of isoprene leads to the production of first-generation oxidation compounds, i.e. first stable products which result from the initial OH attack on isoprene and do not involve additional attack by atmospheric oxidants (OH, O_3 or NO_3). The major primary products, in the presence of nitrogen oxides (NO_x=NO+NO_2), are methyl vinyl ketone (MVK), methacrolein (MACR), and formaldehyde (HCHO) (Miyoshi et al., 1994; Paulson and Seinfeld, 1992; Sprengnether et al., 2002; Tuazon and Atkinson, 1990a). Isoprene photooxidation in the presence of sufficient NO_x is also known to result in the production of significant quantities of ozone on regional scales, in rural as well as in urban areas during summer (Biesenthal et al., 1997; Starn et al., 1998; Wiedinmyer et al., 2001).

For years, it was considered that, because of the high volatility of first-generation products, secondary organic aerosol (SOA) formation from isoprene photooxidation in the presence of NO_x was insignificant in the troposphere (Pandis et al., 1991). However, in the early 2000s, detailed analysis of natural aerosols from the Amazonian rain forest (Claeys et al., 2004) showed significant amounts of two diastereoisomeric 2-methyltetrols (2-methylerythritol and 2-methylthreitol). These compounds bear the isoprene skeleton and their biogenic sources are not primary. Following this discovery, SOA formation from isoprene has been reconsidered:

field observations (Edney et al., 2005; Ion et al., 2005; Kourtchev et al., 2005) and laboratory chamber studies (Boge et al., 2006; Edney et al., 2005; Kroll et al., 2005) confirmed the ability of isoprene (or its oxidation products) to contribute significantly to atmospheric SOA. In fact, even if isoprene leads to small SOA yields (few percent or less), the global contribution of isoprene to the total particulate organic matter could be important considering its large emissions on the global scale. Because organic matter (mostly with secondary origin) accounts for a large, and often dominant, fraction (between 20 % and 90 %) of fine particulate mass in the atmosphere (Kanakidou et al., 2005; Zhang et al., 2007), it is important to fully understand the SOA formation processes from isoprene oxidation, and especially the impact of the experimental conditions on SOA yields.

Laboratory chamber studies investigated the dependence of isoprene-SOA yields on NO_x levels (Kroll et al., 2006; Surratt et al., 2006). They showed that SOA yields are higher in the absence of NO_x, thus suggesting an important role of peroxy radical chemistry (RO_2). When RO_2 chemistry is dominated by the RO_2 + NO reaction, small alkoxy radicals (RO, which tend to fragment), and organic nitrates are formed and are likely sufficiently volatile to remain in the gas phase. On the contrary, in the absence of NO_x (< 1 ppb), RO_2 radicals react preferentially with HO_2 radicals to form hydroxy hydroperoxides and peroxy acids with lower volatility, leading to higher SOA yields. Experiments performed in the presence of NO_x also showed that SOA yields are higher for high NO_2/NO ratios (3 to 8) (Chan et al., 2010). This result is due to the dominating RO_2 + NO_2 reaction which leads to PAN-like compounds. In particular, MPAN (peroxy methacryloyl nitrate) was identified as an important intermediate to SOA formation from isoprene and MACR in the presence of NO_x (Surratt et al., 2010). MPAN formation is thus suppressed or delayed in the presence of high initial concentrations of NO, leading to lower SOA yields at low (< 1) initial VOC/NO ratios (Zhang et al., 2012).

Due to the identified link between MPAN and SOA formation from MACR, and the high degree of similarity of SOA mass spectra from isoprene and MACR photooxidation, MACR was recognized as the major contributor to SOA formation from isoprene in the presence of NO_x (Kroll et al., 2006; Surratt et al., 2006). Its gas-phase primary oxidation products in the presence of NO_x are CO, CO_2, HCHO, hydroxyacetone, methylglyoxal and MPAN (Galloway et al., 2011; Orlando et al., 1999; Tuazon and Atkinson, 1990b). SOA yields from MACR are globally higher than SOA yields from isoprene and are also influenced by NO_2/NO ratios (Chan et al., 2010).

Although the influence of NO_x levels on SOA yields from isoprene and MACR photooxidation is recognized, it cannot fully explain the high degree of variability observed among studies from the literature. As pointed out by Carlton et al. (2009), this variability can be explained by differences in OH concentrations (that are related to the employed radical precursor) which have an important impact on the extent of the reactions and the rate of formation of semi-volatile compounds. Other experimental parameters, far less studied, could also contribute to ~~explain~~ the observed~~SOA yields~~ variability in SOA yields, including the effects of different light sources as well as the role of the chamber walls. It was demonstrated by Zhang et al. (2014) that wall losses of semi-VOCs during photooxidation experiments can lead to lower SOA yields. Furthermore, Warren et al. (2008) used black lights and an argon arc lamp (which exhibits an emission spectrum more similar to the solar spectrum) on the *m*-xylene/NO_x photooxidation system and they observed an effect of the irradiation wavelength spectrum on the SOA yields. It was suggested that black lights may be missing photolysis reactions which are important in SOA formation, leading to an increase in SOA yields when the argon arc lamp was used.

In this work, we investigate the formation of gas-phase first- and higher-generation products and SOA during isoprene and MACR + OH reactions in the presence of NO_x. The experiments have been carried out in a stainless steel chamber with a very realistic irradiation to study the possible effect of the light source used and the state of cleanliness of the walls on SOA yields.

2 Experimental section

Experiments were performed in the CESAM chamber (French acronym for Experimental Multiphasic Atmospheric Simulation Chamber), described in detail elsewhere (Wang et al., 2011). This 4.2 m^3 cylindrical stainless steel chamber is equipped with three high-pressure xenon arc lamps and Pyrex® filters of 6.5 mm thickness that provide, inside the chamber, an irradiation with a spectrum that is very close to the solar spectrum at the ground level (Figure S1). For these experiments, NO_2 photolysis frequency was 2.8×10^{-3} s^{-1}. In order to avoid an increase of temperature during experiments due to irradiation, a cooling system was used. The system is based on the circulation of a liquid coolant (70 % water and 30 % ethylene glycol) in the chamber double wall. The liquid's circulation and temperature were controlled by a thermostat (LAUDA, Integral T10000 W). Temperature and relative humidity (RH) inside the chamber were continuously monitored by a Vaisala HUMICAP HMP234 probe. Due to the very low level of charges on the walls (conductive and grounded), aerosols exhibit a long lifetime (between 10 hours and 4 days, depending on the particle size distribution) in the chamber (McMurry and Rader, 1985; Wang et al., 2011).

2.1 Chamber conditioning

Prior to each experiment, the chamber was cleaned by overnight pumping at a secondary vacuum in the range of 6×10^{-4} mbar. This procedure has shown very satisfactory results for most chemical systems (Wang et al., 2011). In the case of isoprene photooxidation, due to the expected low aerosol yield, several experiments were preceded by an additional manual cleaning (Table 1). This manual cleaning was performed using ultrapure water (18.2MΩ, ELGA Maxima) and lint free wipes (Spec-Wipe® 3), then the chamber walls were heated at 40 °C prior to overnight pumping. This procedure leads to experiments with very high initial level of cleanliness of the chamber walls, leading to low OH formation due to low nitrous acid (HONO) formation from NO_x wall reaction at the beginning of the experiment ($< 5 \times 10^5$ molec.cm^{-3}, see Figure S2), thus requiring additional HONO introduction (Table 1).

After overnight pumping, the chamber was filled with synthetic air produced by mixing approximately 800 mbar of N_2 produced from the evaporation of a pressurized liquid nitrogen tank, and around 200 mbar of O_2 (Linde, 5.0). A known pressure of isoprene (Sigma Aldrich, 99 %), or methacrolein (Sigma Aldrich, 95 %), prepared in a known volume glass bulb was then introduced into the chamber by flushing with a low flow of O_2. Two different OH precursors were used: NO_x wall reaction (Wang et al., 2011) and HONO. NO_2 injection (Air Liquide, Alphagaz 99.9 % purity) in the chamber was made using a gas syringe and a septum valve. NO was injected from a gas cylinder (Air Liquide, 8 ppm in N_2) using a mass flow controller. HONO was prepared by dropwise addition of sulfuric acid (10^{-2} M) into a solution of $NaNO_2$ (0.1 M) and carried into the chamber with a flow of pure N_2. During this synthesis, NO_x were also formed and introduced in the chamber. For some experiments, inorganic seed particles were generated from a 0.0012 M aqueous ammonium sulfate solution using a constant output atomizer (TSI, model 3075) and were injected into the chamber through a diffusion dryer (TSI, model 3062). The irradiation started after these injections and lasted for 6 to 9 hours. Unless specified, time 0 denotes the irradiation start.

In order to avoid a decrease in the OH production efficiency due to a fast consumption of NO in the first hours of the experiment (see Figure S3),~~,~~ a low (0.3 L.min^{-1}) flow of NO (Air

Liquide, 8ppm in N_2) was continuously introduced into the chamber. 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. The pressure inside the chamber was maintained at a pressure slightly higher than the ambient by applying a flow of air (80 % N_2 and 20 % O_2) to offset the pressure loss due to the continuous sampling. The experimental initial conditions are summarized in Table 1.

2.2 Measurements

The gas-phase concentrations of isoprene, MACR, MVK, HCHO, PAN, methylglyoxal, MPAN, formic acid, carbon monoxide (CO) and NO_2 were monitored by Fourier Transform Infra-Red spectrometry (FTIR, Bruker®, TENSOR 37) interfaced with an in situ multiple reflection cell. To determine the contribution of the pure reference spectra to the mixture spectra, an automatic procedure based on matrix algebra was used and results were cross-checked by manual subtraction performed over selected spectra. Complementarily to FTIR measurements, a proton-transfer time of flight mass spectrometer (PTR-ToF-MS 8000, Ionicon Analytik®) was used for online gas-phase measurements in the m/z range 10-200 including isoprene, the sum of {methacrolein + methyl vinyl ketone}, formaldehyde, methylglyoxal, formic acid, 3-methylfuran (3-MF), acetaldehyde, the sum of {acetic acid + glycolaldehyde}, acetone, acrolein (using the $(C_3H_4O)H^+$ ion signal, contribution from fragmentation of higher-molecular weight products could not be excluded), hydroxyacetone, and a few other oxygenated VOCs. Pure standards tests were previously carried out to identify fragmentation patterns and sensitivities of the main oxidation products. The signal of the PTR-ToF-MS was calibrated using a certified gas standard mixture (EU Version TO-14A Aromatics 110L, 100 ppbv~~ppbV~~ each) before the set of experiments. Parameters of the PTR-ToF-MS during the series of measurements were as follows: drift tube voltage: 500 V, drift tube pressure ≈ 2.15 mbar, drift tube temperature: 353 K, resulting in a E/N of 120-125 Td (E being the electric field strength applied to the drift tube and N the density of the gas in the drift tube) (1 Td = 10^{-17} V cm^2). Data analysis of the PTR-ToF-MS measurements was carried out using the ToFViewer® software. ToF-to-mass assignment was performed using hydronium ion isotope ($H_3{}^{18}O^+$ m/z = 21.023) and protonated acetone ($C_3H_7O^+$ m/z =59.049). The mass resolution m/Δm of 4000 (at full width at half maximum) was achieved with the PTR-ToF-MS during the series of experiments. This enabled separation and formula assignment for most of the ions comprising the mass spectra. Some VOCs were measured using both FTIR and PTR-ToF-MS (isoprene, formaldehyde, methyl vinyl ketone, methacrolein…), thus providing intercalibration of their PTR-ToF-MS signal with the FTIR derived concentrations. Ozone was measured by a commercial UV absorption monitor (Horiba®, APOA-370). A commercial chemiluminescence NO_x analyzer (Horiba®, APNA-370) was used to monitor NO. Interferences on the NO_2 signal from the NO_x monitor could occur due to the presence of NO_y during the experiments (Dunlea et al., 2007), NO_2 mixing ratio was therefore determined using FTIR data.

HONO was measured using an~~a homemade~~ instrument constructed in-house (NitroMAC) based on a wet chemical derivatization technique and HPLC-VIS detection (Zhou et al., 1999). Gaseous HONO was sampled by dissolution in a buffer phosphate solution followed by derivatization with an aqueous sulphanilamide/N-(1-naphthyl)-ethylenediamine solution (SA/NED).

A Scanning Mobility Particle Sizer (SMPS) was used to monitor aerosol total number and volume concentrations and size distributions from 10.9 to 478 nm. It consists of a Differential Mobility Analyzer (DMA, TSI, model 3080) coupled with a Condensation Particle Counter (CPC, TSI, model 3010). The non-refractory submicron particulate matter bulk chemical composition was measured using a high resolution time-of-flight aerosol mass spectrometer (AMS, Aerodyne) (Canagaratna et al., 2007; De Carlo et al., 2006). The instrument was used under standard conditions (vaporizer at 600°C and electron ionization at 70 eV) and operated in MS mode (V and W, 30s each) and PToF mode (60s). Ammonium nitrate particles were used regularly to perform standard AMS calibration procedures (including Brute Force Single Particle (BFSP~~BSFP~~) ionization efficiency calibration and size calibration). The AMS data were analyzed using the standard fragmentation table with the corrected air fragment column for our carrier gas, the default values of relative ionization efficiency and a collection efficiency of 0.5 for the organics (Squirrel ToF-AMS Analysis 1.51H and Pika® ToF-AMS HR Analysis 1.10H packages for the software Igor® Pro 6.21).

3 Results and discussion

3.1 Isoprene experiments

Figure 1 shows the time profiles of the gas phase reactants and reaction products during an isoprene photooxidation experiment performed without inorganic seed and using HONO as OH precursor. The irradiation induced a fast consumption of NO, leading to an increase of NO_2 concentrations *via* NO to NO_2 conversion (Figure 1B). Isoprene concentration decay was also observed (Figure 1A) and its lifetime due to reaction with OH ($\tau_{\text{isoprene-OH}}$) was determined considering the time needed to divide the initial isoprene concentration by a factor *e*. In all~~All over~~ our experiments, $\tau_{\text{isoprene-OH}}$ was 1.7±0.4 hour (except for I160113 and I130313 in which isoprene lifetime was 1 and 2 hours longer respectively), thus close to the atmospheric isoprene lifetime (Karl et al., 2006). During isoprene photooxidation, NO reacts with RO_2 and HO_2 radicals to form NO_2 which photolyzes~~photolizes~~ and leads to ~~an~~ ozone production, thus explaining the observation of O_3 mixing ratios reaching up to several hundred ppbv (Figure 1B). Despite these high O_3 mixing ratios, isoprene oxidation was dominated by OH radicals during all experiments, due to the higher reactivity of isoprene towards OH radicals than ozone (Karl et al., 2006).

3.1.1 Determination of OH concentrations

The OH concentrations and their time profiles were estimated from the observed decay rate of isoprene and methacrolein (using polynomial fit curves). The loss of VOC (i.e. either isoprene or methacrolein) was corrected from their reaction with ozone, photolysis and dilution, using Eq. (1):

$$[OH]_i = \frac{1}{k_{OH+VOC}}\left(-\frac{1}{[VOC]_i}\times\frac{\Delta[VOC]}{\Delta t} - k_{O_3+VOC}[O_3]_i - k_{dil} - J_{VOC}\right) \qquad (1)$$

Where $\frac{\Delta[VOC]}{\Delta t}$ is the time variation of the VOC mixing ratios, k_{OH+VOC} and k_{O_3+VOC} are the rate coefficients for reaction with respectively OH and O_3 (from Atkinson et al. (2006)), k_{dil} is the dilution rate, and J_{VOC} is the photolysis rate of the VOC. J_{VOC} was determined for MACR (J_{MACR}) using MACR absorption cross-section and quantum yields (Atkinson et al., 2006), and xenon arc lamp irradiation spectrum with 6.5 mm Pyrex® filters (Figure S1). The value for k_{dil} was determined using the air flow rate used to offset the loss of pressure due to sampling and~~, it~~ was found to be around 1.6 × 10^{-5} s^{-1}. The OH concentrations were calculated from the isoprene decay until its concentration became too low, and then the MACR decay was used. The resulting OH concentrations ranged between 1.5 × 10^6 and 6 × 10^6 molec.cm^{-3} thus showing that the protocol used (low flow of diluted NO continuously introduced) allowed to maintain an OH level in the chamber of the same order of magnitude as the one of the atmosphere during the entire experiment length (Figure 1E).

3.1.2 Isoprene gas-phase reaction products

The major first generation products of isoprene OH-oxidation were MACR, HCHO and MVK (Figure 1A, FTIR measurements), two minor first generation products (3-MF and C_5H_8O, see Figure 1D) were also detected by the PTR-ToF-MS. Plotting the concentration (dilution corrected) of each first generation products versus the reacted isoprene concentration ($[\text{product}]_{\text{corr},t} = f([\text{isoprene}]_0 - [\text{isoprene}]_t)$ during the first hour of photooxidation (i.e. when photolysis and reaction with OH of the primary products were not significant), provided linear curves. The corresponding slope gave the yield for each first-generation product. Table 2 shows that the obtained yields were in good agreement with those from the literature. Thanks to the continuous OH radical concentrations maintained throughout the experiments, the consumption of the primary products leading to the formation of compounds of higher generation was clearly seen (Figure 1A, 1C and 1D). Among these compounds, PAN, methylglyoxal, glycolaldehyde and hydroxyacetone were previously identified as major primary oxidation products of MACR and MVK (Galloway et al., 2011; Orlando et al., 1999; Tuazon and Atkinson, 1990b, 1989). Other species generally observed in isoprene photooxidation experiments as acetaldehyde, formic acid and acetone (Nguyen et al., 2011b; Paulot et al., 2009) were also observed (Figure 1C). Some other compounds were not clearly identified considering only their molecular formula given by PTR-ToF-MS measurements, but some assumptions can be made~~done~~. We measured C_5H_8O (Figure 1D), which seems to be a primary product (with a yield around 1%), it may be attributed to 2-methylbut-3-enal. The latter was identified in the gas phase by Healy et al. (2008) in the same type of experiments. The yield for this compound was determined considering only the $(C_5H_8O)H^+$ ion signal and assuming no contribution from fragmentation of higher-molecular weight products. This unsaturated C_5 carbonyl compound can be formed, like the other primary products, from OH addition to one of the isoprene double bonds, followed by oxidation of the hydroxyalkyl radical produced. Compound $C_5H_6O_2$ (Figure 1D) could correspond to methylbutandial, that was assumed to be formed by the δ-hydroxy channels including 3-MF reaction with OH (Paulot et al., 2009). It was also suggested by Paulot et al. (2009) that the δ-hydroxy channels lead to the formation of 3-oxobutanal, with a molecular formula corresponding to $C_4H_6O_2$, that we also observed (Figure 1D). Species with this molecular formula could also be hydroxy methyl vinyl ketone (Galloway et al., 2011). MPAN concentrations were detected (but not quantified) by the PTR-ToF-MS at the $(C_4H_6O_3)H^+$ ion (m/z 103) (Hansel and Wisthaler, 2000). This compound was not detected by FTIR, thus it was deduced that its mixing ratios were below the FTIR detection limit (i.e. 5ppb).

3.1.3 Isoprene-SOA yields

Figure 2 shows a typical time profile of SOA mass and number size distributions during isoprene OH-oxidation without seed particles. In all experiments, SOA formation started when a major part (> 80 %) of isoprene was consumed, i.e. 2 hours (minimum) after the irradiation started. Particle number concentrations showed a sharp increase at the onset of SOA formation and then, a gradual decrease with a corresponding rise in average particle diameter due to coagulation (Figure 2A and 2C). SOA growth continued even after isoprene complete consumption and the aerosol mass typically reached a maximum after approximately 7-9 hours of irradiation (showing the importance of maintaining OH level during several hours). These observations are typical of a SOA formation induced from the oxidation of secondary products as observed by Ng et al. (2006).~~These observations exhibit a clear secondary products type growth (Ng et al., 2006).~~ At the end of the experiment, particle mean mass diameter was around 85 nm. Once SOA mass was stabilized, aerosol yields (Y) were calculated following Eq. (2):

$$Y = \frac{\Delta M_0}{\Delta[isoprene]} \quad (2)$$

Where ΔM_0 is the mass concentration of SOA formed and $\Delta[isoprene]$ is the mass concentration of isoprene reacted. All values were dilution corrected. The comparison of the mobility diameter (obtained from the SMPS measurements) and the vacuum aerodynamic diameter (measured by the AMS) (as described by Bahreini et al. (2005)) lead to the SOA effective density of 1.4 $g.cm^{-3}$ in good agreement with previous studies carried out in the presence of NO_x (Dommen et al., 2006; Kroll et al., 2005). Aerosol volume concentrations were converted to mass concentrations using this value.

As shown in Table 1, the isoprene-SOA yields are low and range from 0.1 to 1 %. In our experiments, the initial NO_2/NO or isoprene/NO ratios did not influence the SOA yields. Our initial NO_2/NO ratios varied from 0.01 to 5.64, and isoprene/NO, from 3.4 to 35, it is thus possible that the lower values of these ratios were already too high in our experiments to observe any impact on SOA yields (Chan et al., 2010; Zhang et al., 2012). No direct effect of the average NO_2/NO ratio (during isoprene decay), which ranged from 4 to 50, was detected. There was no obvious dependence of SOA yields on the presence of seed particles and on the OH radical precursor used. In order to explain our very low yields, especially those obtained after the manual cleaning (Table 1), we suspected an impact of the chamber walls cleanliness on our SOA yields. Two hypotheses can~~could~~ be made: (1) When manual cleaning has been performed, high cleanliness could lead to an enhanced loss of semi-volatile reaction products that would affect the late and slow SOA growth observed for isoprene experiments; (2) In other experiments, lower cleanliness could contribute to particles formation and growth.

Concerning the first hypothesis, a higher degree of wall loss of semi-volatile species would be expected, leading to a shift in the gas and particle partitioning equilibrium, resulting in lower SOA yields. Significant~~The presence of significant~~ loss of semi-volatile species on chamber walls was already observed in other studies carried out in Teflon film chambers (Loza et al., 2010; Matsunaga and Ziemann, 2010), and its influence on SOA yields was demonstrated by Zhang et al. (2014) in photooxidation experiments. Some pseudo-first order rates for loss processes of organic compounds in the CESAM chamber can also be found in Wang et al. (2011): although the dataset is limited, these values are of the same order of magnitude as those obtained with other simulation chambers. Furthermore, a SOA yield study for a well-known system (α-pinene ozonolysis) is provided in this study without any significant difference with already published values.

Nevertheless~~ in photooxidation experiments. Thus~~, if this first hypothesis would be verified, SOA yields obtained in our study would represent lower limits. On the contrary, if the second hypothesis is right, it strongly suggests that yields obtained in other studies for this very sensitive and low productive system could be overestimated since semi-volatile species adsorbed on the walls (even in small quantities) could re-partition into the reacting mixture and contribute to particle growth.

In order to rationalize our SOA yields and compare them to the literature, the aerosol yields were plotted as a function of the organic aerosol concentrations (Odum et al., 1996). Figure 3 shows a comparison between our SOA yields from isoprene photooxidation and those from previous studies (Chan et al., 2010; Chhabra et al., 2010; Dommen et al., 2006; Edney et al., 2005; Kleindienst et al., 2006; Kroll et al., 2006, 2005; Zhang et al., 2011). Also plotted on this graph are the two products yields curves for each data set determined using Eq. (3) (Odum et al., 1996).

$$Y = M_0 \left(\frac{\alpha_1 K_{om,1}}{1 + K_{om,1} M_0} + \frac{\alpha_2 K_{om,2}}{1 + K_{om,2} M_0} \right) \tag{3}$$

Where α_i is a stoichiometric factor, and $K_{om,i}$ a gas-particle partitioning coefficient, defined according to semi-volatile partitioning theory (Pankow, 1994) for the species *i*. Despite the variability of SOA yields in this study, they were well reproduced by the two products model from Odum et al. (1996), showing that this variability was not due to a change in the chemical system but rather to a variability in its initiation or in equilibria between the walls, the gas and the particle phases. While the yields from previous studies exhibit some variation~~a general dispersion~~, our yields are consistent with the lowest values found in the literature. More specifically, they are very similar to those from Dommen et al. (2006) and Zhang et al. (2011). As strongly suggested by Carlton et al. (2009), the high sensitivity of the system to experimental and/or reaction conditions leads to a high degree of variability in yields measured in the different studies of isoprene photooxidation. These differences cannot be explained by the nature of the walls since studies from the literature all use Teflon chambers (Chan et al., 2010; Chhabra et al., 2010; Dommen et al., 2006; Kroll et al., 2006, 2005; Zhang et al., 2011), or stainless steel chambers with Teflon coating (Edney et al., 2005; Kleindienst et al., 2006).

Another parameter that might influence the SOA yields is the light intensity, determined as the NO_2 photolysis rate. Among the studies cited in Figure 3 (including our study), J_{NO2} varied from 2×10^{-3} to 5.7×10^{-3} s^{-1}. Furthermore, it has been shown by Warren et al. (2008) that, for the *m*-xylene/NO_x photooxidation system, an increase in J_{NO2} of only 7×10^{-4} s^{-1} induces an increase~~extend~~ in SOA yields by a factor of 1.6. However, the comparison of isoprene-SOA yields obtained by Edney et al. (2005) with those by Kleindienst et al. (2006) who carried out experiments in the same simulation chamber under high NO_x conditions, but with different J_{NO2} (5.7×10^{-3} s^{-1} and 2.8×10^{-3} s^{-1} respectively), shows that both yields follow the same yield curve as the one modeled by Carlton et al. (2009) for high NO_x conditions (Figure 3). In contrast, it is possible that the type of light sources used in the different studies reported in Figure 3 plays a role in the SOA yield variability: the only studies who used light sources with spectra representing the solar one are those by Zhang et al. (2011) (outdoor chamber), and by Dommen et al. (2006) who used xenon arc lamps like in our study.

Although fluorescent lamps used as irradiation source in the other studies (Chan et al., 2010; Chhabra et al., 2010; Edney et al., 2005; Kleindienst et al., 2006; Kroll et al., 2006, 2005) deliver a light intensity equivalent to NO_2 photolysis rates which are close to natural light intensity, they exhibit emission spectra significantly different from the solar spectrum (with no emission in the longer wavelength regions, i.e above 400 nm). It is thus suggested that some oxidation products contributing to the aerosol formation and growth in studies using fluorescent lamps (under similar NO_x conditions), could be photolyzed in our experiments, leading to lower SOA yields. It can be noted that the photolysis of α-dicarbonyls, for example methylglyoxal and glyoxal, may occur outside the fluorescent lamp spectrum. Average photolysis wavelengths of methylglyoxal and glyoxal are at 417 and 383 nm respectively (Carter et al., 1995). This hypothesis is thus opposite to the one from Warren et al. (2008) who observed higher SOA yields using an argon arc lamp (which presents a realistic irradiation spectrum) instead of black lights. However, atmospheric chemistry of aromatics is strongly different from that~~the one~~ of alkenes~~alkene~~, it is thus not surprising to observe a different behavior concerning relation between light source and SOA yields for isoprene/NO_x system.

3.1.4 Isoprene-SOA composition

The time profiles of elemental ratios (O/C, H/C and OM/OC) are shown in Figure 4. The organic mass to organic carbon ratio (OM/OC) was calculated using the equation from Aiken et al. (2007). In our experiments performed without seed particles, the very small size of the formed SOA did not allow any reliable detection by the AMS before approximately two hours of SOA formation (Figure 4A). However, the use of ammonium sulfate seed particles for two experiments (I080411 and I110411) allowed an earlier detection (Figure 4B). This Figure shows that O/C and OM/OC ratios increased during the first hour of SOA formation while H/C decreased, thus exhibiting oxidation processing during the particle formation. After two hours of SOA formation, all these ratios reached a plateau that remained stable until the end of the experiment. The comparison between different experiments performed under different conditions (seeds/no seeds, HONO/NO_x…) (Figures 4A and 4B) reveals that the final O/C, H/C and OM/OC values were highly reproducible. Thus the observed variability of the SOA yields in our experiments was likely disconnected to the elemental ratios. This reproducibility also shows that all our experiments were performed in the same chemical system. Table 3 shows that the average elemental ratios (O/C, H/C and OM/OC) and their associated estimated uncertainties (as determined by Aiken et al. (2008)) are in good agreement with previous studies who carried out isoprene-SOA formation under high-NO_x conditions (Aiken et al., 2008; Chhabra et al., 2010; Nguyen et al., 2011a). Furthermore, the stability of the evolution of our elemental ratios is in very good agreement with the observations by Chhabra et al. (2010). These authors related these observations to the findings by Surratt et al. (2006) who pointed out that an important pathway for isoprene-SOA formation under high NO_x conditions occurs *via* the reactivity of MACR and MPAN that were detected in the present study. Therefore, we hereafter investigate the MACR-SOA formation under identical conditions as those performed with isoprene, and we compare the two systems.

3.2 Methacrolein experiments

Typical time profiles of gas-phase compounds in a MACR photooxidation experiment (M240512 in Table 1) without seeds and with NO_x as OH source is shown in Figure 5. Compared to isoprene experiments, ozone production was slower and reached lower maximum concentrations (Table 1), and NO consumption was slower (compare Figure 5B and Figure 1B), thus denoting a slower oxidation process.

3.2.1 MACR gas-phase organic reaction products

Formaldehyde, hydroxyacetone, methylglyoxal, MPAN and CO (Figure 5A, 5C and 5D) were observed in our study as the major primary MACR-oxidation products in the presence of NO_x. The variability in initial NO_x levels impacted primary yields, values obtained were thus different between experiments. Table 4 shows that their yields were in good agreement with previous studies, except for hydroxyacetone which showed yields four times lower in our study. Small hydroxyacetone yields could not be explained by wall loss in our chamber considering its low decrease in concentration after its production period (i.e. after 6 hours of reaction in Figure 5D). The $(C_2H_4O)H^+$ signal at m/z 45 measured by PTR-ToF-MS showed a primary production (Figure 5C), it was attributed to acetaldehyde with a yield of 2-6 %. The origin of this primary behavior is difficult to explain since it implies an H transfer which is complicated in gas chemistry (Figure S4~~S3~~). The presence of fragments of higher molecules contributing to this signal (like methylglyoxal; Müller et al. (2012)) cannot be excluded. Unfortunately, the presence of acetaldehyde in the chamber could not be verified by FTIR measurements since the maximum concentrations observed throughout all experiments were below its detection limit (i.e. 20 ppb). Furthermore, a release from the walls is unlikely since acetaldehyde was not observed in control experiments (i.e. irradiation of a N_2/O_2 mixture (80 % / 20 %)).

3.2.2 MACR-SOA yields

SOA formation from MACR photooxidation was usually observed between 10 minutes and one hour after the start of irradiation, depending on the OH level in the system. Since SOA production in these experiments began earlier than in isoprene experiments (less than 25% of MACR was consumed before the start of the SOA formation), MACR can be considered as a more direct SOA precursor (compare Figure 6A with Figure 2A). In all experiments, SOA mass concentration reached a plateau between 5 and 8 hours after the onset of irradiation. These mass concentrations were calculated using an effective density of 1.4 g.cm~~m~~$^{-3}$ which was obtained from the comparison of the mobility diameter and the vacuum aerodynamic diameter (Bahreini et al., 2005). Table 1 shows that our SOA mass yields varied between 0.6 % and 4 %, thus four to six times higher than in isoprene experiments. Except for experiment M250113, the use of HONO as OH precursor led to higher yields (at least twice higher) than in experiments using NO_x as OH source. This observation is directly linked to higher OH concentrations obtained at the beginning of the experiment when HONO was used (Figure S5~~S4~~). Table 1 shows that the cleanliness of the walls did not affect the MACR-SOA mass yields, as opposed to isoprene experiments. It seems to suggest that the state of cleanliness of the walls would have a smaller impact on SOA yields when more direct SOA precursors are used: the extent of semi-volatile wall losses ~~extent~~ could be limited by the fast SOA production. The use of inorganic seed particles did not affect our SOA mass yields. Except for M240512 and M250512, initial NO_2/NO ratios were below 1, so these ratios are probably too low to make any conclusion about the influence of this ratio on SOA mass yields (Chan et al., 2010). At the end of MACR experiments, we observed particles with higher size than in isoprene experiments (compare Figures 6B and 6C with Figures 2B and 2C) with mean mass diameters ranging between 100 nm and 180 nm.

Figure 7 shows a comparison of our MACR-SOA mass yields and the corresponding two products yield curves with the literature. For this comparison, fewer studies than for isoprene experiments are available, but it can be seen that, for MACR experiments too, SOA yields exhibit a fairly large variation.~~general dispersion.~~ In their study, Chan et al. (2010) used two different OH sources (leading to a change in initial NO_2/NO ratio) that affect SOA yields, resulting in two different yield curves. In our experiments, considering the differences observed between yields obtained with the two OH sources (which lead to similar initial NO_2/NO ratio),~~,~~ two yield curves were also modeled. Like for isoprene experiments, our SOA yields are among the lowest values from the literature, i.e. comparable to those obtained by Zhang et al. (2012) in which an outdoor chamber was used (with NO_x as OH source), thus strengthening the hypothesis of an impact of light sources used on SOA yields.

3.2.3 Composition of MACR-SOA

SOA mass spectrum obtained by AMS measurements (Figure S6B~~S5B~~) showed no significant variation over the experiment. Its comparison with the mass spectrum of SOA from isoprene photooxidation (Figure S6A~~S5A~~) exhibits a high degree of similarity which strongly suggests that methacrolein is a principal intermediate in SOA formation from isoprene photooxidation in our experimental conditions, as observed by previous studies performed in the presence of NO_x (Kroll et al., 2006; Surratt et al., 2006). Temporal variations of elemental ratios are presented in Figure 8. Experiments carried out with seeds showed that O/C and OM/OC ratios increased quickly during the first hour of SOA formation and then stabilized. Obtained ratios after stabilization were reproducible and no clear influence of OH source or of the presence of seeds was observed. Table 3 shows that these average values are in good agreement with elemental ratios from Chhabra et al. (2011), considering measurement uncertainties given by Aiken et al. (2008). Elemental ratios for MACR-SOA were very~~really~~ close to those measured for isoprene-SOA, confirming the role of MACR in SOA formation from isoprene photooxidation.

4 Atmospheric implications and conclusion

In the present study, gas-phase products and SOA formation from isoprene and MACR photooxidation were investigated in a stainless steel simulation chamber equipped with realistic artificial light sources (Figure S1). A~~ very~~ good agreement with the literature was observed for the gas-phase products and particularly for primary oxidation product~~products~~ yields.

Comparing the SOA mass formed during isoprene experiments performed before and after manual cleaning of the chamber walls suggested~~highlighted~~ an impact of the state of cleanliness of the walls on the nucleation step. While this hypothesis has not been verified with other hydrocarbons or ~~oxidized species~~ commercially available oxidized species, it is suggested~~considered~~ that more oxidized species could be adsorbed on clean walls, preventing the initial nucleation step.~~cluster to be formed.~~ It must also be noted that such an effect has not been observed with~~for~~ other chemical systems (such as α-pinene ozonolysis) in the same chamber (Wang et al., 2011). This may be due to the fact that ~~being much smaller,~~ the molecules produced during isoprene oxidation are much smaller and hence need to be much more oxidized to undergo partitioning and therefore~~hence may be~~ more sensitive to wall effects. This delay in ~~triggering~~ particle formation could lead~~eventually led~~ to a deficit in the ~~overall~~ SOA mass ~~obtained~~ because of the potentially higher proportion of isoprene oxidation products adsorbed to the clean chamber walls.~~less surface was available for semi-volatile condensation.~~ Nevertheless, the partitioning of the semi-volatile compounds was reproducible within several experiments spanning over more than three years as shown by the high level of internal consistency of the measured data on the ~~as it can be seen from the well-defined tendency of the~~ Odum plots (Figure 3).~~Figure 3).~~ Furthermore, it is striking to see that the SOA yield may vary significantly when measured~~be in significant disagreement while being obtained~~ in similar chambers with similar protocols (for example~~like between~~ Kroll et al. (2005)~~ and Dommen et al. (2006) studies)~~ and Dommen et al. (2006)) and be~~being~~ in good agreement in two different chambers (Dommen et al. (2006)~~(like between Dommen et al. (2006) study~~ and this work). This ~~is~~ somewhat contradicts the existence of ~~in contradiction with~~ a possible wall effect~~ of the walls~~ proposed above.

Our results~~Results~~ for the particle phase show that SOA yields from isoprene and MACR photooxidation are in good agreement with the lowest values reported in~~of~~ the literature. They correspond~~, corresponding~~ to experiments carried out with natural irradiation or with artificial irradiation with an emission profile ~~that emits a wavelength spectrum~~ more similar to the solar spectrum (e.g.~~like~~ xenon arc lamps~~ used in our study~~) than the fluorescent lamps used in other studies.~~,~~ It was thus suggested that the use of fluorescent lamps as irradiation sources would not activate~~could avoid~~ photolysis reactions requiring ~~occurring in the~~ longer wavelengths, such as those which break down~~wavelength region that concern some~~ oxidation products (e.g.~~such as~~ methylglyoxal). These oxidation products would otherwise contribute~~)~~ ~~contributing~~ to~~ the~~ aerosol formation and growth, thus leading to a decrease in SOA mass yields when xenon arc lamp or natural light were used. The differences in light sources ~~used~~ between environmental chambers may thus be able to explain partially~~help explaining~~ the variability in SOA mass yield ~~variability~~ observed for identical compounds. SOA mass yields from isoprene and MACR in the atmosphere could therefore be overestimated by experiments carried out in simulation chambers equipped with fluorescent lamps. Further experiments and analysis are needed to determine the influence of the irradiation~~wavelength~~ spectrum on SOA formation from isoprene and MACR photooxidation like experiments carried out~~made~~ by Warren et al. (2008) on the *m*-xylene/NO_x photooxidation system. Therefore, according to our~~If the~~ results~~ in the present study are further confirmed~~, isoprene and MACR SOA mass yields in the atmosphere could be lower than most of current chamber studies suggest. Finally, this study highlights the need for additional work on the photochemical fate of SOA components.

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Table 1 Experimental conditions and results

Experiment[a,b]	**[VOC]$_0$ ppb**	**OH source**	**[NO]$_0$ ppb**	**[NO$_2$]$_0$ ppb**	**[HONO]$_0$ ppb**	**[O3]$_{max}$ ppb**	**T °C**	**V[e]AS, 0 µm^3.cm^{-3}**	**ΔM_0[f] µg.m^{-3}**	**SOA mass yield**
					Isoprene					
I150211	473	NO$_x$	119	32	/	347	18.1	/	8.4	0.006
I160211	500	NO$_x$	14	79	/	546	16.4	/	4.7	0.003
I170211	485	NO$_x$	22	55	/	397	16.6	/	1.6	0.001
I050411	465	NO$_x$	110	4	/	495	20	/	12.4	0.010
I060411	458	NO$_x$	135	5	/	300	21.1	/	7.3	0.006
I080411	465	NO$_x$	109	3	/	286	20.8	16.2	5.5	0.004
I110411	462	NO$_x$	127	5	/	359	21.9	12.9	6.2	0.005
I150512	452	NO$_x$	101	< 1	/	174	21.4	/	7.8	0.006
I160512	445	NO$_x$	117	< 1	/	175	20.6	/	7.4	0.004
I210512[g]	442	NO$_x$	110	< 1	/	183	22.2	/	< 0.1	0
I220512	444	NO$_x$	111	< 1	/	113	21	/	0.3	0
I230512	439	NO$_x$	21	76	/	131	24.3	/	0.1	0
I160113[g]	846	HONO	143	27[d]	15	122	21.5	/	< 0.1	0
I280113[g]	833	HONO	88	45[d]	125	201	18.3	/	2.8	0.001
I130313[g]	840	HONO	66	< 1[d]	45	54	17.5	/	2.4	0.001
I250313[g]	802	HONO	137	48[d]	121	81	19.7	/	0.15	0
					Methacrolein					
M120411	474	NO$_x$	117	4	/	145	19	14.8	17.4	0.013
M130411	480	NO$_x$	123	4	/	130	20.8	13.5	13.9	0.010
M240512	457	NO$_x$	19	84	/	97	24.2	/	9.5	0.008
M250512	405	NO$_x$	26	100	/	46	24	/	5.0	0.005
M280512	403	NO$_x$	n.m.[c]	80	/	59	23.8	/	9.4	0.009
M180113[g]	735	HONO	88	25[d]	124	94	19.8	/	58.8	0.03
M210113[g]	927	HONO	118	81[d]	150	123	19.4	/	65.8	0.032
M230113[g]	396	HONO	67	5[d]	125	51	19.6	/	27.3	0.028
M250113[g]	445	HONO	39	8[d]	60	31	18.8	/	7.8	0.007
M110313[g]	400	HONO	107	38[d]	91	17	21.8	/	44.8	0.042

[a] All experiments were carried out at RH <5%.

[b] Experimental IDs starting with "I" indicate isoprene photooxidation experiments and experimental IDs starting with "M" indicate methacrolein photooxidation experiments.

[c] Not measured.

[d] Corrected from HONO interference.

[e] Volume concentration of ammonium sulfate seed.

[f] SOA mass concentration using an effective density of 1.4 g.cm^{-3} (see text).

[g] Experiment with manual cleaning the day before.

Table 2 Yields of first~~First~~-generation oxidation products ~~yields~~ during isoprene photooxidation compared with previous studies. Values in parentheses are 2-sigma uncertainties.

Compound	Yield	Reference
Formaldehyde	**0.75 (±0.11)**	**This work**
	0.63 (±0.10)	Tuazon and Atkinson (1990a)
	0.57 (±0.06)	Miyoshi et al. (1994)
	0.59 (±0.12)	Sprengnether et al. (2002)
Methacrolein	**0.30 (±0.09)**	**This work**
	0.22 (±0.05)	Tuazon and Atkinson (1990a)
	0.25 (±0.03)	Paulson et al. (1992)
	0.22 (±0.02)	Miyoshi et al. (1994)
	0.27 (±0.04)	Sprengnether et al. (2002)
	0.22 (±0.006)	Galloway et al. (2011)
	0.27 (±0.03)	Karl et al. (2006)
Methyl vinyl ketone	**0.27 (±0.08)**	**This work**
	0.32 (±0.07)	Tuazon and Atkinson (1990a)
	0.36(±0.04)	Paulson et al. (1992)
	0.32 (±0.05)	Miyoshi et al. (1994)
	0.44 (±0.06)	Sprengnether et al. (2002)
	0.30 (±0.01)	Galloway et al. (2011)
	0.41 (±0.03)	Karl et al. (2006)
3-Methylfuran	**0.033 (±0.014)**	**This work**
	0.048 (±0.006)	Tuazon and Atkinson (1990a)
	0.04 (±0.02)	Paulson et al. (1992)
	<0.001	Sprengnether et al. (2002)

Table 3 Average elemental ratios of SOA from isoprene and MACR photooxidation. Values in parentheses reflect the measurement uncertainty as determined by Aiken et al. (2008).

O/C	OM/OC	H/C	Reference
		Isoprene	
0.60 (± 0.19)	**1.92 (± 0.12)**	**1.43 (± 0.14)**	**This work without seeds**
0.65 (± 0.20)	**1.99 (± 0.12)**	**1.39 (± 0.14)**	**This work with seeds**
0.41 (± 0.13)	1.75 (± 0.10)	/	Aiken et al. (2008)
0.62 (± 0.19)	2.00 (± 0.12)	1.46 (± 0.15)	Chhabra et al. (2010)
0.83	2.26	1.55	Nguyen et al. (2011a)
		Methacrolein	
0.61 (± 0.19)	**1.93 (± 0.12)**	**1.43 (± 0.14)**	**This work without seeds**
0.72 (± 0.22)	**2.07 (± 0.12)**	**1.32 (± 0.13)**	**This work with seeds**
0.54 (± 0.17)	1.87 (± 0.11)	1.53 (± 0.15)	Chhabra et al. (2011)

Table 4 Yields of first~~First~~-generation oxidation products ~~yields~~ during methacrolein photooxidation compared with previous studies.

Compound	Yield	Reference
Formaldehyde	**0.3-0.6**	**This work**
	0.4-0.7	Orlando et al. (1999)
Methylglyoxal	**0.02-0.06**	**This work**
	0.08 (0.002)	Tuazon and Atkinson (1990b)
	< 0.12	Orlando et al. (1999)
	0.08 (0.004)	Galloway et al. (2011)
Hydroxyacetone	**0.01-0.1**	**This work**
	0.41 (0.03)	Tuazon and Atkinson (1990b)
	0.47 (0.05)	Orlando et al. (1999)
	0.39 (0.017)	Galloway et al. (2011)
Carbon monoxide	**0.45-0.85**	**This work**
	0.51 (0.04)	Tuazon and Atkinson (1990b)
	0.6-0.8	Orlando et al. (1999)
MPAN	**0.06-0.17**	**This work**
	0.04-0.30	Orlando et al. (1999)

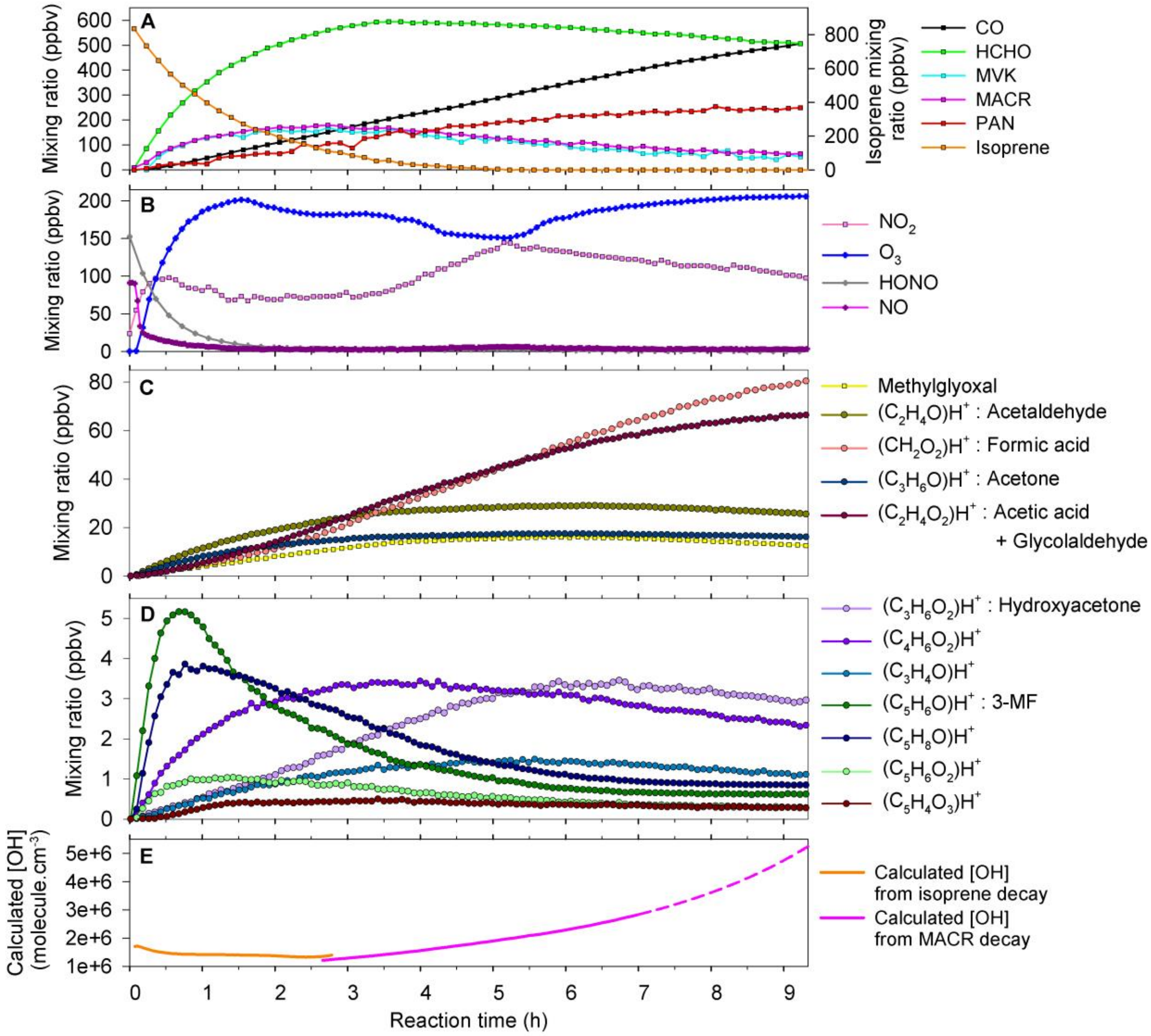


Figure 1. Time profiles of gas-phase measured compounds and calculated OH concentrations during isoprene photooxidation (experiment I280113) performed with no seeds and with HONO as OH source. PTR-ToF-MS measurements are represented by circles, and FTIR measurements, by squares. Calculated [OH] is represented by a dotted line after 7 hours of irradiation due to low MACR mixing ratios which implies less precision in the calculation as the contribution from other VOCs is not negligible.

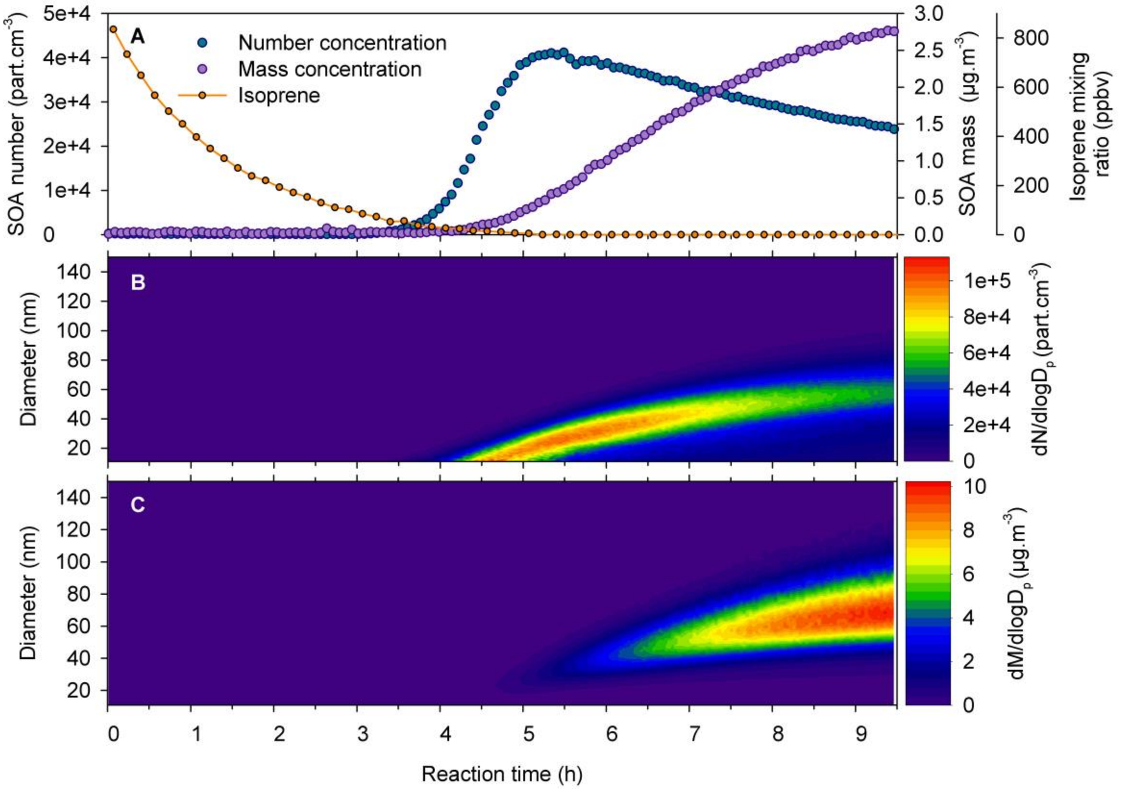


Figure 2. Time profiles of measured (A) SOA mass and number concentrations, (B) number size distribution and (C) mass size distribution during isoprene photooxidation (experiment I280113) performed with no seeds and with HONO as OH source. A particle~~particule~~ density of 1.4 g.cm~~µg.m~~$^{-3}$ was assumed (see text).

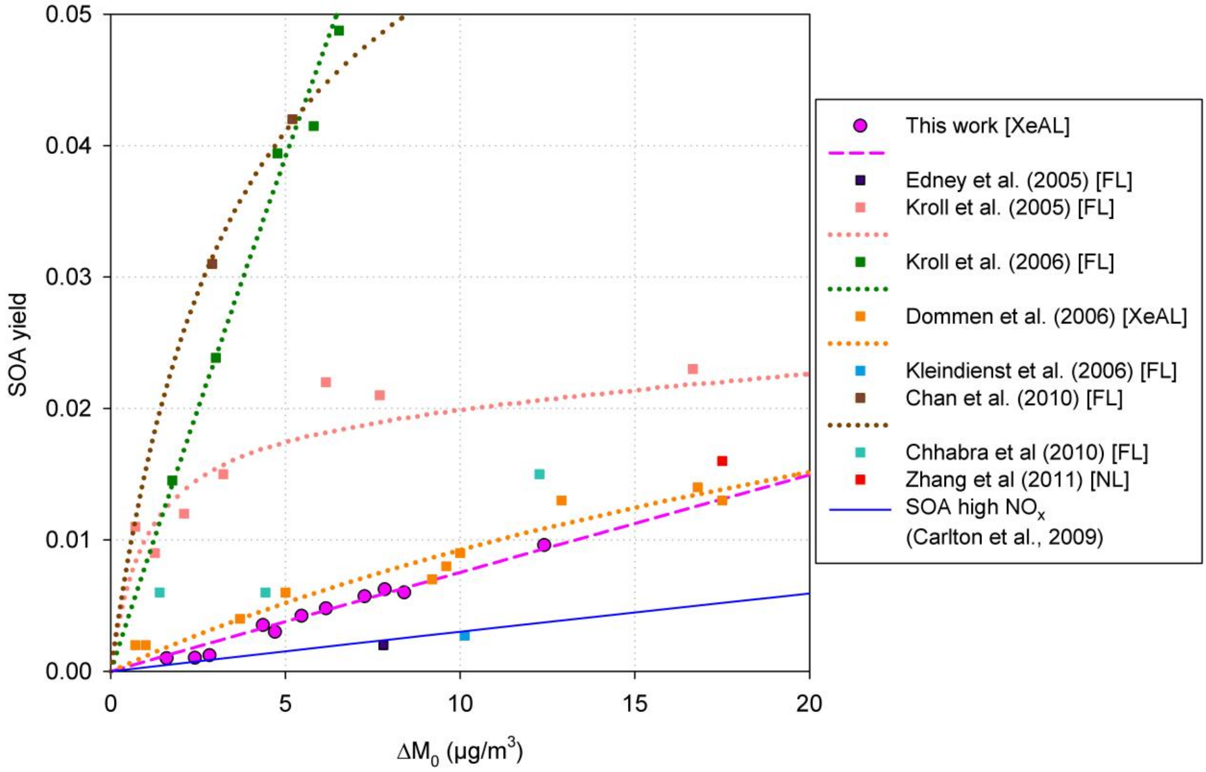


Figure 3. SOA mass yield curves from various isoprene photooxidation experiments in the presence of NO_x from the literature compared with the present study. An effective density of 1.4 g.cm^{-3} was used (see text) for conversion to mass of all our volume-based measurements. Light sources used are specified in square brackets (XeAL: xenon arc lamps; FL: fluorescent lamps; NL: natural light). The parameters of our two products yield curve (Odum et al., 1996) are as follows: $\alpha_1 = 0.508$; $K_{om,1} = 7.4 \times 10^{-4}$; $\alpha_2 = 0.509$; $K_{om,2} = 7.4\times 10^{-4}$.

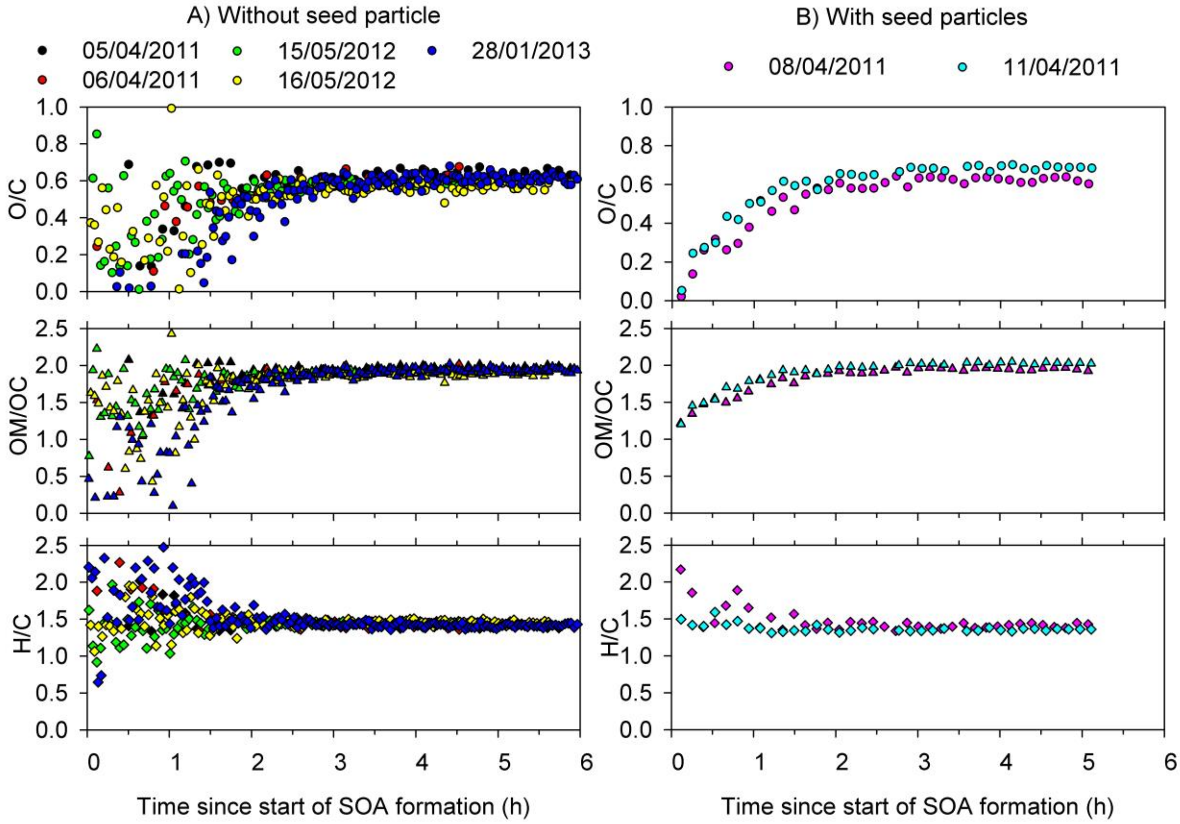


Figure 4. Time profiles of O/C, OM/OC and H/C ratios for seven different isoprene photooxidation experiments performed A) without seed particle; B) with ammonium sulfate seed particles.

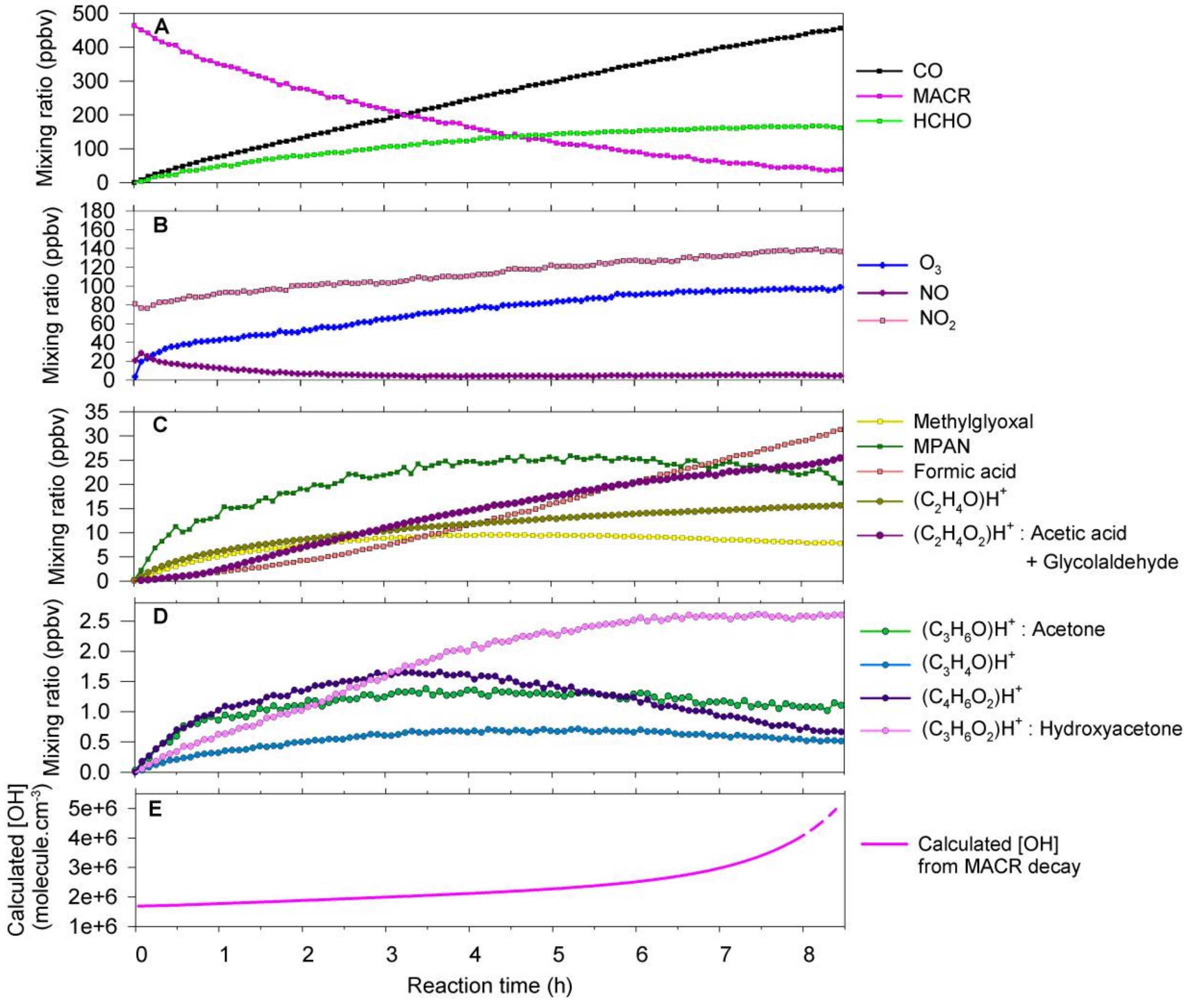


Figure 5. Time profiles of gas-phase measured compounds during MACR photooxidation (experiment M240512) performed without seed particles and with NO_x as OH source. PTR-ToF-MS measurements are represented by circles, and FTIR measurements, by squares. Calculated [OH] is represented by a dotted line after 8 hours of irradiation due to low MACR mixing ratios which implies less precision in the calculation as the contribution from other VOCs is not negligible.

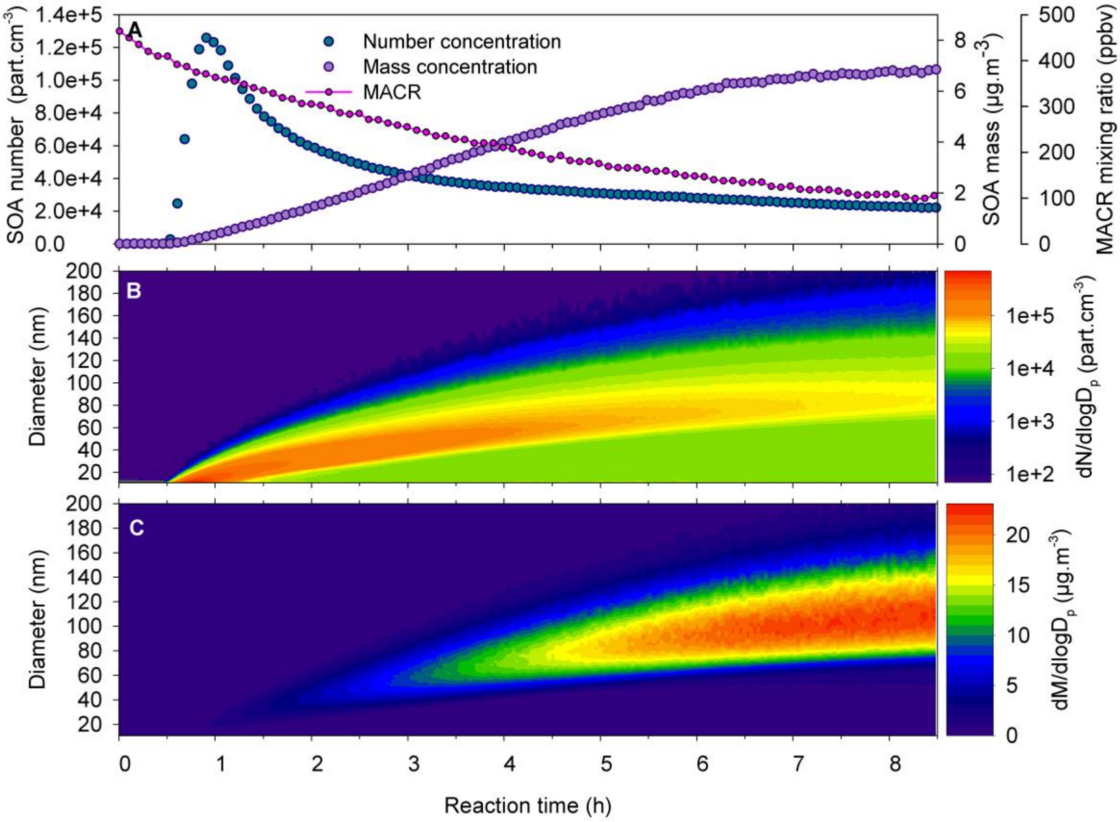


Figure 6. Time profiles of measured (A) SOA mass and number concentrations, (B) number size distribution and (C) mass size distribution during MACR photooxidation (experiment M240512) performed without seed particles and with NO_x as OH source. A particle~~particule~~ density of 1.4 g.cm~~µg.m~~$^{-3}$ was assumed (see text).

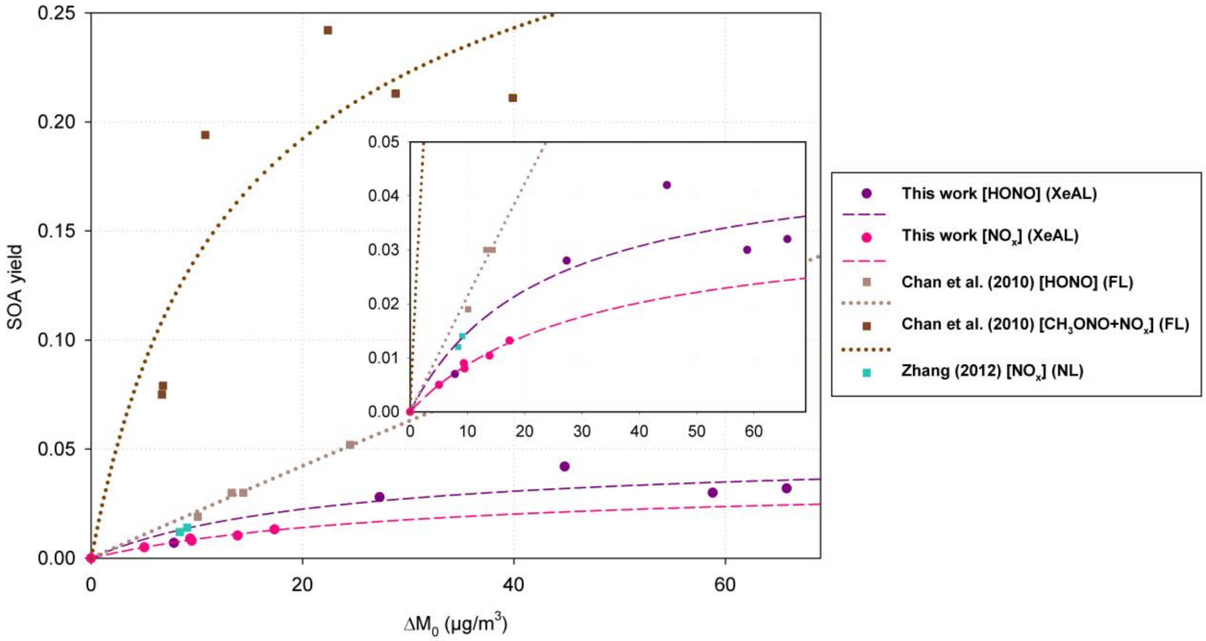
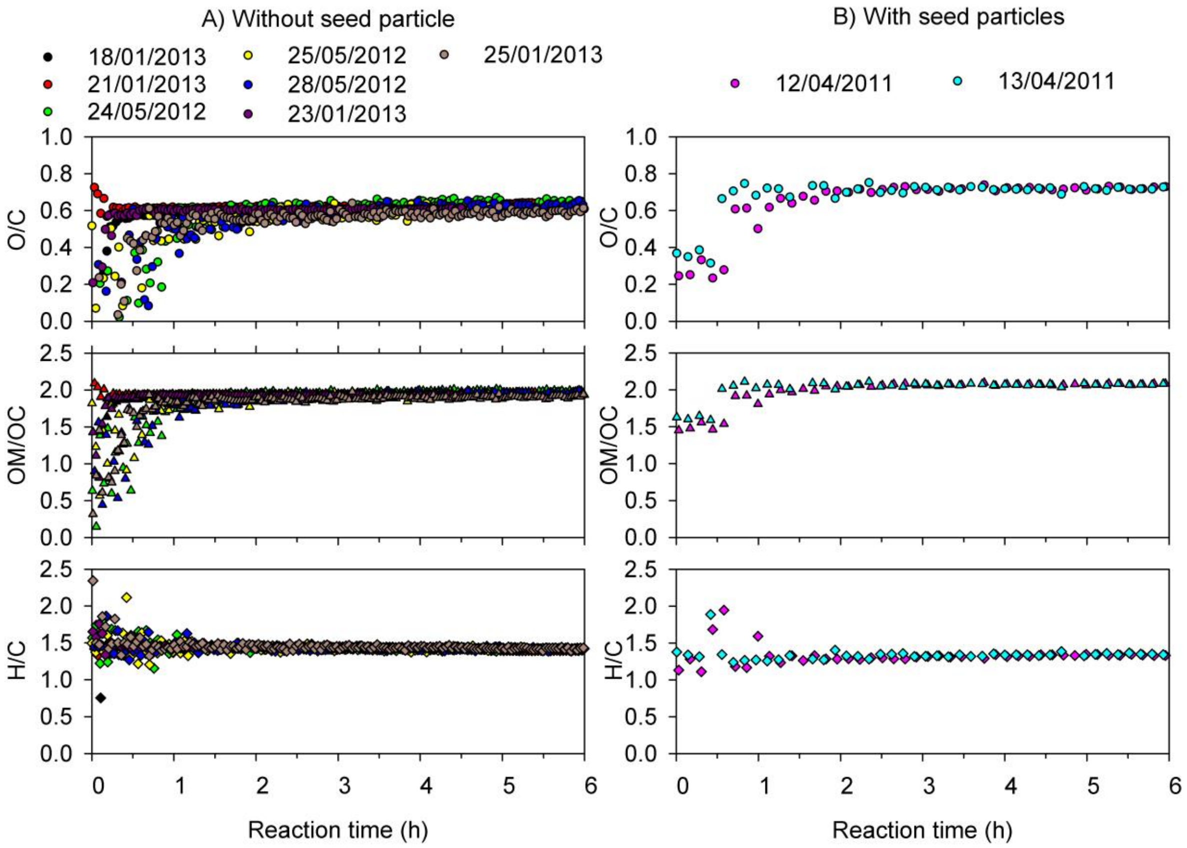


Figure 7. SOA mass yield curves from MACR photooxidation experiments in the presence of NO_x carried out by Chan et al. (2010) and Zhang et al. (2012) compared with the present study. An effective density of 1.4 $g.cm^{-3}$ was used for conversion to mass of all our volume-based measurements. Molecules in square brackets are OH sources used. Light sources used are specified in brackets (XeAL: xenon arc lamps; FL: fluorescent lamps; NL: natural light). The parameters determined for the two products model (Odum et al., 1996) in our study are, for experiments with NO_x as OH source: $\alpha_1 = 3.6 \times 10^{-2}$; $K_{om,1} = 3.2 \times 10^{-2}$; $\alpha_2 = 2.6 \times 10^{-11}$; $K_{om,2} = 1.63 \times 10^{-9}$. For experiments with HONO as OH source, these parameters are: $\alpha_1' = 4.83 \times 10^{-2}$; $K_{om,1}' = 4.35 \times 10^{-2}$; $\alpha_2' = 6.2 \times 10^{-2}$; $K_{om,2}' = 8.47 \times 10^{-10}$.



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2 Figure 8. Time profiles of O/C, OM/OC and H/C ratios for nine different MACR
3 photooxidation experiments performed A) without seed particle; B) with ammonium sulfate
4 seed particles.

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