

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 N₂/O₂ 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 N₂/O₂ 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 ((C₂H₄O)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 (C₂H₄O)H⁺ signal at m/z 45 measured by PTR-ToF-MS (Müller et al. (2012), we propose to replace "acetaldehyde" by "(C₂H₄O)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.

Response: 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

Response: 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:

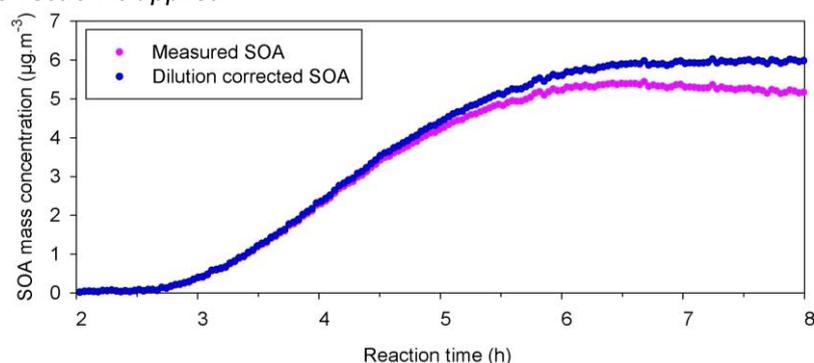


Figure R1: Time profile of SOA mass concentration during an isoprene experiment (I150211; table 1)

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.

Response: 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).

Response: 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?

Response: 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)

Response: Control experiments, i.e. irradiation of a N₂/O₂ mixture (80 % / 20 %) did not show any gaseous release nor formation of SOA in the chamber.

5D/ or an issue of data analysis?

Response: 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.

Response: 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.

Response: There was an inversion in the legend, this error has been corrected and it now reads:

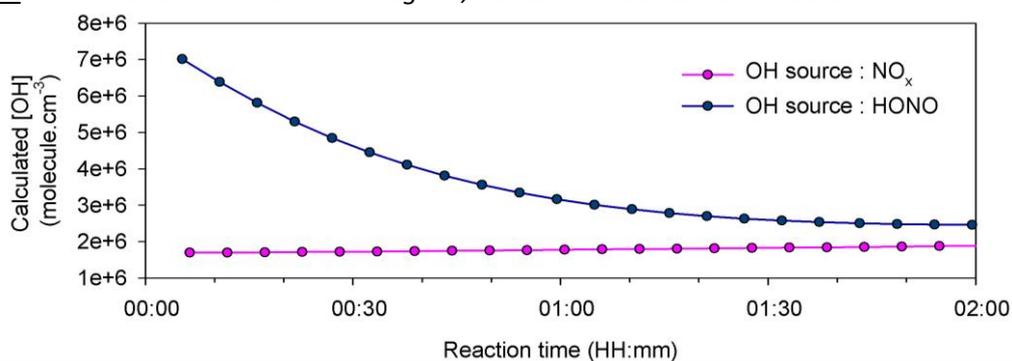


Figure S4 Time profiles of calculated OH concentrations during MACR photooxidation experiments performed with HONO (blue curve; M230113) and NO_x (pink curve; M240512) as OH source.

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

Response: 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.

References

- Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, *Environmental Science & Technology*, 42, 4478-4485, 2008.
- Bao, L., Matsumoto, M., Kubota, T., Sekiguchi, K., Wang, Q., and Sakamoto, K.: Gas/particle partitioning of low-molecular-weight dicarboxylic acids at a suburban site in Saitama, Japan, *Atmospheric Environment*, 47, 546-553, 2012.
- Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer, *Atmospheric Chemistry and Physics*, 10, 4111-4131, 2010.
- Chhabra, P. S., Ng, N. L., Canagaratna, M. R., Corrigan, A. L., Russell, L. M., Worsnop, D. R., Flagan, R. C., and Seinfeld, J. H.: Elemental composition and oxidation of chamber organic aerosol, *Atmos. Chem. Phys.*, 11, 8827-8845, 2011.
- Dommen, J., Metzger, A., Duplissy, J., Kalberer, M., Alfarra, M. R., Gascho, A., Weingartner, E., Prevot, A. S. H., Verheggen, B., and Baltensperger, U.: Laboratory observation of oligomers in the aerosol from isoprene/NO_x photooxidation, *Geophysical Research Letters*, 33, L13805, 2006.
- Healy, R. M., Wenger, J. C., Metzger, A., Duplissy, J., Kalberer, M., and Dommen, J.: Gas/particle partitioning of carbonyls in the photooxidation of isoprene and 1,3,5-trimethylbenzene, *Atmospheric Chemistry and Physics*, 8, 3215-3230, 2008.
- Kawamura, K., Okuzawa, K., Aggarwal, S. G., Irie, H., Kanaya, Y., and Wang, Z.: Determination of gaseous and particulate carbonyls (glycolaldehyde, hydroxyacetone, glyoxal, methylglyoxal, nonanal and decanal) in the atmosphere at Mt. Tai, *Atmospheric Chemistry and Physics*, 13, 5369-5380, 2013.

- Loza, C. L., Chan, A. W. H., Galloway, M. M., Keutsch, F. N., Flagan, R. C., and Seinfeld, J. H.: Characterization of Vapor Wall Loss in Laboratory Chambers, *Environmental Science & Technology*, 44, 5074-5078, 2010.
- Matsunaga, A. and Ziemann, P. J.: Gas-Wall Partitioning of Organic Compounds in a Teflon Film Chamber and Potential Effects on Reaction Product and Aerosol Yield Measurements, *Aerosol Science and Technology*, 44, 881-892, 2010.
- McMurry, P. H. and Rader, D. J.: Aerosol Wall Losses in Electrically Charged Chambers, *Aerosol Science and Technology*, 4, 249-268, 1985.
- Müller, M., Graus, M., Wisthaler, A., Hansel, A., Metzger, A., Dommen, J., and Baltensperger, U.: Analysis of high mass resolution PTR-TOF mass spectra from 1,3,5-trimethylbenzene (TMB) environmental chamber experiments, *Atmos. Chem. Phys.*, 12, 829-843, 2012.
- Platt, S. M., El Haddad, I., Zardini, A. A., Clairotte, M., Astorga, C., Wolf, R., Slowik, J. G., Temime-Roussel, B., Marchand, N., Ježek, I., Drinovec, L., Močnik, G., Möhler, O., Richter, R., Barmet, P., Bianchi, F., Baltensperger, U., and Prévôt, A. S. H.: Secondary organic aerosol formation from gasoline vehicle emissions in a new mobile environmental reaction chamber, *Atmos. Chem. Phys.*, 13, 9141-9158, 2013.
- Wang, J., Doussin, J. F., Perrier, S., Perraudin, E., Katrib, Y., Pangui, E., and Picquet-Varrault, B.: Design of a new multi-phase experimental simulation chamber for atmospheric photochemistry, aerosol and cloud chemistry research, *Atmos. Meas. Tech.*, 4, 2465-2494, 2011.
- 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.
- Zhang, H. F., Lin, Y. H., Zhang, Z. F., Zhang, X. L., Shaw, S. L., Knipping, E. M., Weber, R. J., Gold, A., Kamens, R. M., and Surratt, J. D.: Secondary organic aerosol formation from methacrolein photooxidation: roles of NO_x level, relative humidity and aerosol acidity, *Environ. Chem.*, 9, 247-262, 2012.
- Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, *Proc. Natl. Acad. Sci. U. S. A.*, 111, 5802-5807, 2014.