

Review for “Multiphase composition changes and reactive oxygen species formation during limonene oxidation in the new Cambridge Atmospheric Simulation Chamber (CASC)” by Peter J. Gallimore et al.

General comments: this manuscript showed interesting results about the online composition changes of gas and particle phase products during the photolysis of limonene by using mass spectrometry. Meanwhile, they also measured the reactive oxygen species (ROS) formation by limonene SOA in water by using a fluorescent assay. Based on these experiments and mathematic modelling, the authors claimed that diffusion-limited and bulk reaction-limited scenarios might have resulted in the low loss of some low volatile compounds like 7-hydroxy limononic acid ($C_{10}H_{16}O_4$). Furthermore, the authors also claimed that stable ROS dominate the total ROS formed by limonene SOA in water especially in a long timescale during the oxidation of limonene in the Cambridge Atmospheric Simulation Chamber (CASC). Overall the results are interesting and the manuscript was written well. If my following concerns can be addressed, I would like to recommend this manuscript to be published in Atmos. Chem. Phys.

Specific points:

1. The title of “Multiphase composition changes and reactive oxygen species formation during limonene oxidation in the new Cambridge Atmospheric Simulation Chamber (CASC)” shows that the ROS in this article was generated during the limonene oxidation in CASC. However, the ROS data in Fig. 6 and 7 were relevant to the limonene SOA dissolved water solutions by using Online Particle-bound Reactive Oxygen Species Instrument (OPROSI). Even though some kind of ROS (organic peroxides etc.) could be generated during the limonene SOA formation process, the title is not accurate to describe the source of the ROS in this article.
2. In line 16-18 of page 2: “Similarly, organic reactive oxygen species (ROS), including organic peroxides and oxygen centred radicals, are thought to be associated with the observed negative health effects of airborne particles (Verma et al., 2009).” The authors introduced the definition of ROS for the first time in this article. However, they did not clarify the

difference of the term ROS used in this article from that in literatures (e.g. Klaus Apel and Heribert Hirt., *Annu. Rev. Plant Biol.* REACTIVE OXYGEN SPECIES: Metabolism, Oxidative Stress, and Signal Transduction. 55, 373-399, 2004; Josep M. Anglada et al., Interconnection of Reactive Oxygen Species Chemistry across the Interfaces of Atmospheric, Environmental, and Biological Processes. *Acc. Chem. Res.* 48, 575-583, 2015.), especially the authors should clarify the ROS species their method (OPROSI) could characterize.

3. In Fig. 6 at page 18, the author showed a plateau of ROS formation in limonene SOA water solutions ($0.42 \text{ nmol } [\text{H}_2\text{O}_2] \mu\text{g}^{-1}$). Afterwards, the authors used the equations 1 and 2 (page 19) to categorize the total ROS to short and long modes. During this analysis, the assumption of “[ROS_{long}] scales with the total particle mass in proportion to the final mass weighted ROS concentration (as do most individual aerosol components in Figure 5(b)).....” has been used. However, the plateau in Fig. 6 may be induced by a homeostasis of long and short lifetime ROS. So the used equivalence of $[\text{ROS}_{\text{long}}]=0.42 \times \text{MASS}_{\text{SOA}}$ can overestimate the yield of ROS_{long} . In the same timescale, the yield of limonene SOA is also relatively stable (Fig.3), so it is reasonable to see the plateau of EESI mass spectrum intensity in Fig. 5(b). If the authors would like to connect the plateau of Fig. 5(b) with the plateau Fig. 6, they need a response sensitivity test to confirm the ROS value indicated by the OPROSI system are real relevant to the ions showed in Fig. 5.
4. In line 6-10: “We propose that ROS_{long} are a group of relatively stable long-lived products (such as organic peroxides) which constitute the stable ROS at the end of the experiment, and $\text{ROS}_{\text{short}}$ are reactive species (possibly radicals or otherwise short-lived compounds such as reactive peroxides) species which are produced directly from ozonolysis or other early-generation reactions.” The authors should discuss more about the component of ROS_{long} and $\text{ROS}_{\text{short}}$. In addition, numerous studies indicated that limonene SOA and other precursor-generated SOA particles could show high oxidative potential and generate ROS, like: Chen, X., and Hopke, P. K.: A chamber study of secondary organic aerosol formation by limonene ozonolysis, *Indoor air*, 20, 320-328, 2010.; Wang, Y., Kim, H., and Paulson, S. E.: Hydrogen peroxide generation from α - and β -pinene and toluene secondary organic aerosols, *Atmospheric environment*, 45, 3149-3156, 2011.; McWhinney, R. D., Zhou, S., and Abbatt, J. P. D.: Naphthalene SOA: redox activity and naphthoquinone gas-particle partitioning, *Atmos. Chem. Phys.*, 13, 9731-9744, 10.5194/acp-13-9731-2013, 2013.;

Badali, K. M., Zhou, S., Aljawhary, D., Antiñolo, M., Chen, W. J., Lok, A., Mungall, E., Wong, J. P. S., Zhao, R., and Abbatt, J. P. D.: Formation of hydroxyl radicals from photolysis of secondary organic aerosol material, *Atmos. Chem. Phys.*, 15, 7831-7840, 2015.; Tong, H., Arangio, A., Lakey, P., Berkemeier, T., Liu, F., Kampf, C., Pöschl, U., and Shiraiwa, M.: Hydroxyl radicals from secondary organic aerosol decomposition in water, *Atmos. Chem. Phys.*, 16, 1761-1771, 2016. Tuet, W. Y., Chen, Y., Xu, L., Fok, S., Gao, D., Weber, R. J., and Ng, N. L.: Chemical oxidative potential of secondary organic aerosol (SOA) generated from the photooxidation of biogenic and anthropogenic volatile organic compounds, *Atmospheric Chemistry and Physics*, 17, 839-853, 2017.

5. In 2010, Chen and Hopke have measured the ROS formation by limonene SOA (Chen, X., and Hopke, P. K., *Indoor air*, 20, 320-328, 2010.) using a similar fluorescent assay system. Their study showed a maximum $\sim 0.2 \text{ nmol } [\text{H}_2\text{O}_2] \mu\text{g}^{-1}$. However, current study showed a yield of $0.2 \text{ nmol } [\text{H}_2\text{O}_2] \mu\text{g}^{-1}$, which is 2 times higher. More recently, they also found that when limonene SOA mass concentration ranged from 30.3 to 157.3 $\mu\text{g m}^{-3}$, the ROS concentration could range from 6.1 to 29.4 nmol m^{-3} of H_2O_2 (Chen, et al., *Aerosol and Air Quality Research*, 17, 59-68, 2017.), this value is also much lower than the value of $\sim 150 \text{ nmol m}^{-3}$ in Fig. 6. How to explain this?
6. In 2014, Epstein et al. indicated that photolysis can influence the abundance of peroxide in biogenic SOA (*Environ. Sci. Technol.*, 48, 11251-11258, 2014.). The authors are encouraged to discuss the potential impact of the photolysis on their ROS values.
7. Some typos should be corrected: page 5: line 3 "1/4" and 1/2", line 17 and 18: "160W", "75W". Page 9: line 15: "4mm".