

## **Author response – Reviewer #2:**

### 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 limonic acid (C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>). 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.*

We thank the reviewer for these comments and respond point-by-point below.

### 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.*

The reviewer points out that the detected ROS may be a combination of ROS formed in the aerosol, and additional ROS formed in aqueous solution following particle collection. While recent studies have indicated that OH radicals form when SOA is dissolved in water (Badali et al., 2015; Tong et al., 2016) the proposed mechanisms involve light or transition metals, neither of which are present in the OPROSI collection system.

Organic peroxides and other related functional groups have long been shown to be a major component of monoterpene SOA (Camredon et al., 2007; Docherty et al., 2005) and in Wragg et al., (2016) we demonstrated that the assay used in our study is sensitive to organic peroxide standards. We therefore prefer to keep the title as is, and address some of the specific points about different types of ROS in response to comment 2.

*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.*

We have modified the introduction to clarify this definition of ROS (p2 lines 16–22): “Similarly, species including hydrogen peroxide and oxygen-centred radicals and ions can cause biological stress and damage (Anglada et al., 2015; Apel and Hirt, 2004). Related organic compounds including peroxides have been shown to be major SOA components (Camredon et al., 2007; Docherty et al., 2005). Together, these reactive oxygen species (ROS) are thought to be associated with the observed negative health effects of airborne particles (Verma et al., 2009).”

An OPROSI experimental subsection (2.2.3) has been added which describes the species characterised by OPROSI (p10 lines 21–25): “The fluorescence response is calibrated with  $\text{H}_2\text{O}_2$  and quantitative ROS concentrations are reported as “[ $\text{H}_2\text{O}_2$ ] equivalents”. The assay also responds to organic peroxide standards. It is likely sensitive to  $\text{HO}_x$  radicals and ions such as superoxide but we are unable to obtain suitable standards to test this directly.”

*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<sub>long</sub>] 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  $[\text{ROS}_{\text{long}}]=0.42 \times \text{MASSSOA}$  can overestimate the yield of ROS<sub>long</sub>. 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.*

By definition in Equation 2, the final  $\text{ROS}_{\text{long}}$  yield will be  $0.42 \text{ nmol} [\text{H}_2\text{O}_2] \mu\text{g}^{-1}$ . We have added discussion of possible overestimated  $\text{ROS}_{\text{long}}$  yields at the start of the experiment (p24 line 31–p25 line 2): “If some  $\text{ROS}_{\text{short}}$  were converted to  $\text{ROS}_{\text{long}}$  during the early part of the experiment, Equation 2 could underestimate the  $\text{ROS}_{\text{short}}$  contribution to  $[\text{ROS}_{\text{total}}]$  and correspondingly overestimate  $[\text{ROS}_{\text{long}}]$  early in the experiment.”

Regarding connecting the “plateaus” in Fig 5(b) and Fig 6, we are not proposing a direct link between the specific ions in Fig 5(b) and ROS, but using this as an illustration that the general aerosol composition (and gas phase composition and particle mass) is not changing significantly in the ROS plateau region.

4. In line 6-10: “We propose that ROS<sub>long</sub> 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 ROS<sub>short</sub> 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<sub>long</sub> and ROS<sub>short</sub>. 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  $\alpha$ -and  $\beta$ -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., Antñolo, 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 Shiraishi, 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.

We have added the following additional detail for ROS<sub>long</sub> (p24 lines 11-14): “We propose that ROS<sub>long</sub> are a group of relatively stable long-lived products (such as hydrogen peroxide and organic peroxides) which constitute the stable ROS at the end of the experiment and which have been shown to be major products of monoterpene ozonolysis (Docherty et al., 2005; Wang et al., 2011).”

We are not in a position to speculate more on the identity of ROS<sub>short</sub> than we already do (p24 line 15): “...radicals or otherwise short-lived compounds such as reactive peroxides...”) because unlike the long lived components where surrogate standards are available, we are unsure of the relative reactivity of the OPROSI assay towards different short-lived species.

We have cited some of the suggested references throughout the manuscript and we discuss Chen and Hopke (2010) in more detail below.

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 nmol [H<sub>2</sub>O<sub>2</sub>]  $\mu$ g <sup>-1</sup>. However, current study showed a yield of 0.4 nmol [H<sub>2</sub>O<sub>2</sub>]  $\mu$ g <sup>-1</sup>, which is 2 times higher. More recently, they also found that when limonene SOA mass concentration ranged from 30.3 to 157.3  $\mu$ g m<sup>-3</sup>, the ROS concentration could range from 6.1 to 29.4 nmol m<sup>-3</sup> of H<sub>2</sub>O<sub>2</sub> (Chen, et al., *Aerosol and Air Quality Research*, 17, 59-68, 2017.), this value is also much lower than the value of  $\sim$ 150 nmol m<sup>-3</sup> in Fig. 6. How to explain this?

Thank you for bringing these relevant studies to our attention. We discuss and explain differences between the studies (p27 line 10–p28 line 5): “Chen and Hopke (2010), Chen et al., (2011) and Chen et al., (2017) studied ROS formation from the ozonolysis of limonene using a similar chemical assay with an offline sampling and sonication extraction method. Like the current study, both short-lived and long-lived ROS are reported. However,  $\text{ROS}_{\text{long}}$  yields for Chen and Hopke (2010) and Chen et al., (2017) ( $0.15\text{--}0.19 \text{ nmol } [\text{H}_2\text{O}_2] \mu\text{g}^{-1}$ ) were lower than those determined here ( $0.42 \text{ nmol } [\text{H}_2\text{O}_2] \mu\text{g}^{-1}$ ). A number of experimental differences may be important. The three other studies employed dry conditions, compared to 40% RH here. The presence of water may influence the gas-phase fate of initial products and promote ROS formation (for instance, hydroperoxides from reaction of stabilised Criegee intermediates with water (Docherty et al., 2005)) as well as potentially modifying Henry’s law partitioning of species such as hydrogen peroxide, and facilitating oligomerisation and hydrolysis reactions in the condensed phase (Gallimore et al., 2011). The higher mass loading here ( $375 \mu\text{g m}^{-3}$ ) compared to these previous studies ( $30\text{--}160 \mu\text{g m}^{-3}$ ) may be an important parameter through its influence on gas-particle partitioning and subsequent particle-phase reaction.

Chen et al., (2011) reported a correlation between  $[\text{O}_3]/[\text{VOC}]$  and  $[\text{ROS}_{\text{long}}]$  for a range of VOCs, and found higher ROS yields when ozone was in excess, presumably as a result of increased formation of oxygenated products such as peroxides. This is consistent with the higher  $[\text{ROS}_{\text{long}}]$  reported here ( $[\text{O}_3]_{\text{max}}/[\text{limonene}]_0 = 2.4$ ) compared to Chen et al., (2017) ( $[\text{O}_3]_0/[\text{limonene}]_0 = 0.45$ ). Furthermore, we proposed above that oxidation of the second (exo) double bond is partly occurring in the particle phase; this direct ROS formation in the particle may result in higher measured yields than gas phase only routes. These findings contrast with Chen and Hopke (2010) who do not see a systematic trend in  $[\text{ROS}_{\text{long}}]$  with varying  $[\text{O}_3]/[\text{limonene}]$ .

We subdivided the ROS discussion into CASC measurements (3.2.1, p23 line 2) and comparison with other studies (3.2.2, p27 line 10) to improve readability of this extended ROS section.

*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.*

Photolysis is clearly an important fate for peroxides and ROS-relevant species, as indicated by Epstein et al., (2014) and other references from point 4. However, the ROS data in Figure 6/7 were obtained under dark conditions. This is now clarified (p14 lines 18–19): “Ozonolysis was performed under dark conditions without the addition of  $\text{NO}_x$ .”

*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”.*

We have now added spaces between the number and unit in each case (p5 line 29, p6 lines 14–15, p 11 line 25).

## References

- Anglada, J. M., Martins-Costa, M., Francisco, J. S. and Ruiz-lo, M. F.: Interconnection of Reactive Oxygen Species Chemistry across the Interfaces of Atmospheric, Environmental, and Biological Processes, *Acc. Chem. Res.*, 48, 575–83, doi:10.1021/ar500412p, 2015.
- Apel, K. and Hirt, H.: REACTIVE OXYGEN SPECIES: Metabolism, Oxidative Stress, and Signal Transduction, *Annu. Rev. Plant Biol.*, 55, 373–99, doi:10.1146/annurev.arplant.55.031903.141701, 2004.
- 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(14), 7831–7840, doi:10.5194/acp-15-7831-2015, 2015.
- Camredon, M., Aumont, B., Lee-Taylor, J. and Madronich, S.: The SOA/VOC/NO<sub>x</sub> system: an explicit model of secondary organic aerosol formation, *Atmos. Chem. Phys.*, 7, 5599–5610, 2007.
- Chen, F., Zhou, H., Gao, J. and Hopke, P. K.: A Chamber Study of Secondary Organic Aerosol (SOA) Formed by Ozonolysis of d-Limonene in the Presence of NO, *Aerosol Air Qual. Res.*, 17, 59–68, doi:10.4209/aaqr.2016.01.0029, 2017.
- Chen, X. and Hopke, P. K.: A chamber study of secondary organic aerosol formation by limonene ozonolysis, *Indoor Air*, 20, 320–328, doi:10.1111/j.1600-0668.2010.00656.x, 2010.
- Chen, X., Hopke, P. K. and Carter, W. P. L.: Secondary Organic Aerosol from Ozonolysis of Biogenic Volatile Organic Compounds: Chamber Studies of Particle and Reactive Oxygen Species Formation, *Environ. Sci. Technol.*, 45(1), 276–282, 2011.
- Docherty, K. S., Wu, W., Lim, Y. Bin and Ziemann, P. J.: Contributions of organic peroxides to secondary aerosol formed from reactions of monoterpenes with O<sub>3</sub>, *Environ. Sci. Technol.*, 39(11), 4049–4059, doi:10.1021/es050228s, 2005.
- Epstein, S. A., Blair, S. L. and Nizkorodov, S. A.: Direct Photolysis of  $\alpha$ -Pinene Ozonolysis Secondary Organic Aerosol: Effect on Particle Mass and Peroxide Content, *Environ. Sci. Technol.*, 48, 11251–58, 2014.
- Gallimore, P. J., Achakulwisut, P., Pope, F. D., Davies, J. F., Spring, D. R. and Kalberer, M.: Importance of relative humidity in the oxidative ageing of organic aerosols: case study of the ozonolysis of maleic acid aerosol, *Atmos. Chem. Phys.*, 11(23), 12181–12195, doi:10.5194/acp-11-12181-2011, 2011.
- Tong, H., Arangio, A. M., Lakey, P. S. J., Berkemeier, T., Liu, F., Kampf, C. J., Brune, W. H., Poschl, U. and Shiraiwa, M.: Hydroxyl radicals from secondary organic aerosol decomposition in water, *Atmos. Chem. Phys.*, 16(3), 1761–1771, doi:10.5194/acp-16-1761-2016, 2016.
- Verma, V., Ning, Z., Cho, A. K., Schauer, J. J., Shafer, M. M. and Sioutas, C.: Redox activity of urban quasi-ultrafine particles from primary and secondary sources, *Atmos. Environ.*, 43(40), 6360–6368, doi:10.1016/j.atmosenv.2009.09.019, 2009.
- Wang, Y., Kim, H. and Paulson, S. E.: Hydrogen peroxide generation from a- and b-

pinene and toluene secondary organic aerosols, *Atmos. Environ.*, 45(18), 3149–3156, doi:10.1016/j.atmosenv.2011.02.060, 2011.

Wragg, F. P. H., Fuller, S. J., Freshwater, R., Green, D. C., Kelly, F. J. and Kalberer, M.: An automated online instrument to quantify aerosol-bound reactive oxygen species (ROS) for ambient measurement and health-relevant aerosol studies, *Atmos. Meas. Tech.*, 9, 4891–4900, doi:10.5194/amt-9-4891-2016, 2016.