

We thank the reviewers for careful reading and helpful comments that improve the quality of the manuscript. Reviewer comments have been copied followed by our responses in bold.

Anonymous Referee #1)

The authors present mass spectral evidence for the formation of peroxyhemiacetals forming in aqueous solution when methylglyoxal is either mixed with a commercial organic hydroperoxide or when a methylglyoxal/hydrogen peroxide solution is photolyzed at 254 nm. The mass spectral approach is to use electrospray ionization coupled to an FT-ICR mass spectrometer, so that very high mass spectral resolution is obtained along with MS-MS spectra. To my knowledge, this is the first evidence for the formation of peroxyhemiacetals forming in the aqueous phase via reactions of organic hydroperoxides formed also in the aqueous phase. Ziemann has shown that peroxyhemiacetals may form via uptake of gas phase peroxides. This is an interesting observation but I have a few comments that need to be addressed before it can be published.

R1C1) Title. I find the title a little bit baffling because it does not include the word peroxyhemiacetal. This class of compounds is what is observed in the experiments and will likely lead to SOA. As written, the focus of the title is on peroxides and OH but I don't think that the novelty of the paper lies in the experimental inference of peroxide or OH formation occurring in the aqueous phase, i.e. it is not surprising that they form and the authors have no direct evidence that they do. I suggest the title be changed to: "Laboratory evidence for peroxyhemiacetal formation in the aqueous phase".

**Response) We accept including the word, "peroxyhemiacetal." But this compound is evidence of organic peroxide, which was formed by photooxidation in the aqueous phase. Furthermore, organic peroxide is expected to generate OH radical through UV photolysis. Although we did not measure an OH concentration from organic peroxide products during irradiation, we simulated it using our kinetic model. We also provided OH simulation results (Fig. S1 and S3). We change the title to:  
"Laboratory evidence of organic peroxide and peroxyhemiacetal formation in the aqueous phase and implications to aqueous OH."**

R1C2) First sentence of Abstract: I don't agree that aqueous phase chemistry in aerosols is well accepted as an important SOA formation mechanism. This is still a hypothesis lacking compelling evidence from the field that can place it quantitatively on a scale with other SOA formation mechanisms. This is not to say that it is not interesting and does not occur, just that our understanding is not at this level as yet.

**Response) Now it reads:**

**"... is considered a potentially important atmospheric pathway to produce..."**

R1C3) The reference to Ehn et al, Nature, 2014 is lacking in the Introduction, as a motivation for the likely presence of organic hydroperoxides in aerosol and cloud water.

**Response) We included this reference in line 11 on page 17370:**

**"... , and form SOA (Tobias and Ziemann, 2000; Ehn et al., 2014)"**

R1C4) Page 17370, Line 23 – The Henry's Law constants for the organic hydroperoxides will be very highly dependent on their structure, and will not all fall in the range of 100 to 1000 M/atm.

**Response) Now it reads:**

**"Henry's law constant up to 1000 M atm<sup>-1</sup>."**

R1C5) Page 17371, Line 10 – The use of high concentrations of 20 mM of hydrogen peroxide will lead to the formation of hydroxyhydroperoxides of methylglyoxal in solution (see Liu et al., ACP, 2102; Zhao et al., ACP, 2013). How will this class of compounds affect the chemistry? Will they

photolyze to form OH, for example? Will they react with methylglyoxal to form peroxyhemiacetals?

**Response) These hydroxyhydroperoxides and corresponding peroxyhemiacetals with methylglyoxal have different m/z's from our organic peroxides and peroxy hemiacetals. Moreover, control experiments by Tan et al. (2010) show that methylglyoxal degradation is much slower with H<sub>2</sub>O<sub>2</sub> in the dark than it is with H<sub>2</sub>O<sub>2</sub> in the UV light. Therefore, we do not expect the formation of hydroperoxides by Liu et al. and Zhao et al. We include the following sentences in Line 13.**

**“Liu et al. (2012) and Zhao et al. (2013) found that  $\alpha$ -hydroperoxides can form when methylglyoxal reacts with hydrogen peroxide in the dark. However, this reaction cannot explain the formation of the identified peroxy hemiacetals in this work (PHA<sub>1</sub> and PHA<sub>2</sub>) since the molecular weight of the  $\alpha$ -hydroperoxide is different from those of R<sub>1</sub>OOH and R<sub>2</sub>OOH. Moreover, according to control experiments by Tan et al. (2010) methylglyoxal degradation is much slower with hydrogen peroxide in the dark than it is with hydrogen peroxide in the UV light. Therefore, we do not expect the formation of the  $\alpha$ -hydroperoxide in our photooxidation experiment.”**

R1C6) Perhaps I missed it, but I do not recall seeing the pH of the solutions described.

**Response) Although pH has not been measured, the model can accurately predict. We included pH simulation results (Fig. S4) in Supplementary Material.**

R1C7) Figures: It would be helpful to the reader if all the key peaks were labelled on the Figures. This is done in some cases but not others.

**Response) Now they are labelled.**

R1C8) Figure 1: It is not clear what is meant for the products formed from the second reaction (i.e. that with three consecutive arrows).

**Response) It was meant to show only the first generation products and to skip intermediate products. Now three arrows are separated.**

R1C9) Control Experiments: What is the spectrum of a solution of methylglyoxal with hydrogen peroxide present and no illumination? What is the spectrum of methylglyoxal with illumination and no hydrogen peroxide? These need to be provided in the Supplementary Information.

**Response) Control experiments for methylglyoxal were published previously (Tan et al., 2010 in Supporting Information).**

R1C10) I find the wording in the modeling section confusing. In particular, is the HO<sub>2</sub> in the condensed phase arising mostly via uptake from the gas phase or via production in the condensed phase?

**Response) It is arising via production in the condensed phase. Now it reads: “The concentration of HO<sub>2</sub> photochemically formed in the aqueous phase was estimated to be...”**

R1C11) In the modeling, a 1 M concentration of methylglyoxal is quite high. Could the authors provide a modeling scenario with smaller values, or at least address how the results would scale with the concentration?

**Response) Yes, we have provided model runs at two methylglyoxal concentrations. The**

reviewer just missed it. To make it easier to see that we have provided model runs at low concentrations, we have divided this paragraph (Section 5.1) into three paragraphs. We ran the model with methylglyoxal set to 10  $\mu\text{M}$  and to 1 M. The 10  $\mu\text{M}$  run represents cloud-relevant conditions. The 1 M run is intended to simulate the situation in wet aerosols, where concentrations of total dissolved organic matter (OM) are expected to be 1-10 M. In this case, we are using methylglyoxal as a surrogate for all dissolved OM. We select methylglyoxal to represent organic matter (OM) in wet aerosol and OM concentrations are expected to be 1-10 M. Although OM is a complex mixture, the rate constants for individual organic compounds with OH in the aqueous phase are expected to be similar ( $\sim 1\text{e}9$  M/s).

R1C12) Page 17378, Section 5.3. Note that Badali et al., ACP, 2015 have recently demonstrated that OH radicals are formed photolytically in SOA solutions. This should be referenced here and probably in the Introduction too.

**Response)** We appreciate the reviewer's suggestion of referencing Badali et al. because this work is closely related to our work. We not only reference it, but argue that higher OH yields from SOA solutions than expected from the organic peroxide components in SOA could occur because of photochemical (secondary) formation of organic peroxides in the solution during the experiments. In their work, there should exist plenty of aldehyde products from ozone reactions and we expect these aldehydes to form organic peroxides during photolytic experiments as we have demonstrated here (i.e., photochemical formation of organic peroxides from methylglyoxal in the aqueous phase).

We add the following in the introduction (line 22; page 17370).

“And a recent lab study (Badali et al., 2015) demonstrates that OH radicals are photolytically formed from the solutions of SOA from terpene ozonolysis and OH formation is likely due to photolysis of organic peroxides.”

We add the following in the introduction (line 26; page 17370)

“Badali et al. (2015) measured OH radical formation from photolysis of terpene- $\text{O}_3$  SOA solutions and organic peroxide standard solutions (t-butyl hydroperoxide and cumene hydroperoxide). However, photolysis of the terpene SOA generates twice as much OH as is generated from a comparable amount of organic peroxide alone (i.e., standards). Since there should exist plenty of aldehydes formed from ozone reactions, we argue that organic peroxides could also be formed in the SOA solution during the photolytic experiments.”

We modify the sentence in Section 5.3 (line 8-9; page 17378) as following.

“Note that Badali et al. (2015) confirmed OH formation from photolysis of solutions of organic peroxide SOA and measured OH formation rates are comparable to an estimation by Arakaki et al. (2013), which is  $\sim 10^{-14}$  M OH in atmospheric waters and ...”