

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⁻¹."

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 H₂O₂ in the dark than it is with H₂O₂ 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 α -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 (PHA₁ and PHA₂) since the molecular weight of the α -hydroperoxide is different from those of R₁OOH and R₂OOH. 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 α -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 HO₂ 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 HO₂ 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 μM and to 1 M. The 10 μM 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- 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 ...”

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 #2)

The manuscript describes formation of hydroperoxides via aqueous processing of H₂O₂ with methylglyoxal. Evidence for the formation of these peroxides is proposed via mass spectrometric detection of m/z assigned to peroxy hemiacetals. This finding of hydroperoxide formation via aqueous processing has not been previously considered, to my knowledge; partitioning of hydroperoxides produced in the gas-phase has been considered as the main source of condensed phase peroxides. There is much current interest in peroxides and this work presents an interesting and important contribution, especially as peroxides in aerosol may play an important role with respect to reactivity and health effects of aerosol. The work addresses a topic that fits well in the scope of ACP and generally should be published. The high O/C ratio with low unsaturation supports the formation of hydroperoxides in these experiments. The hydroperoxides themselves were however not observed, and I have some reservations whether the methods used are able to identify the peroxy hemiacetals unambiguously raising some questions whether peroxides were in fact formed. Thus, I recommend publication after my main comments below can be clearly addressed and resolved.

Main comments

R2C1) A novel and very interesting finding is the production of hydroperoxides in the condensed phase. The mechanism proposed in the manuscript is reasonable. However, the potential for formation of (hydro)peroxy compounds from non-radical reactions of H₂O₂ with either MGL via formation of alpha-hydroxy hydroperoxides, or formation of peroxy carboxylic acids via reaction of H₂O₂ with carboxylic acids, may contribute. This would not change the fact that peroxide containing compounds are made, but it does affect the mechanism and implications with respect to radical chemistry.

Response) Please see our response to R1C5.

R2C2) My main concern is that the instrumental setup used in this work is poorly suited for detection and quantification of peroxides. This is reflected in the fact that the hydroperoxides themselves were not observed, a substantial drawback. Even techniques that use components at lower temperatures than the 300C capillary (P. 17372 L.6), such as PTR-MS have been shown to destroy hydroperoxides (Liu et al. ACP, 13, 5715-5730 2013 and others). For this work a technique that can directly observe the proposed hydroperoxides is critical or use of a method that can resolve isomeric compounds, as explained in the following: Generally, there can be substantial uncertainties in assignment of chemical structures to m/z observed in ESI-MS, in particular without the use of a LC separation method. Depending on conditions, the method can produce spectra that contain large amounts of clusters of molecular species. For example, using methanol and water as a solvent it is not unexpected to see these solvents cluster with other species. This could explain the loss of methanol observed in the most of the MS/MS spectra. Another example is that there is no difference in mass between a hydroperoxide and geminal diol or between PHAstd and a cluster of MGLY and t-BuOOH (see 2b and also 2a). Given these concerns a more detailed analysis is required before the proposed m/z from the ESI spectra can be identified unambiguously as peroxy hemiacetals, i.e., the MS/MS spectra have to clearly highlight how they cannot arise from clusters or other species. This is critical as the evidence of hydroperoxide formation resides in the observation of PHA1 and PHA2.

Response) Since organic hydroperoxides (ROOHs) will decompose at the capillary temperature (250- 300 °C), as the reviewer points out, our approach is to measure peroxyhemiacetals, which won't be destroyed at this temperature. We verify peroxyhemiacetals by using an ultra high resolution FTICR-MS and FTICR-MS/MS. We see O₂ loss by MS/MS. This is expected from ROOHs, and not from geminal diol. The formation of peroxyhemiacetals from aldehydes and ROOHs through acid catalysis is well established by Ziemann's work (Tobias et al., 2000; Docherty et al., 2005).

R2C2a) For example, in Figure 4 can the authors prove that m/z 159.06278 does not (in part) correspond to a cluster of two methanol molecules with MGLY rather than a double hemiacetal of methanol with MGLY. It would be extremely helpful and important to discuss this. Using liquid chromatography (LC) this should be easily feasible as that should separate the double hemiacetal from unreacted MGLY that merely clustered with methanol (or water) in the ESI source.

Response) It would be difficult to explain H₂O loss if m/z - 159.06278 is a cluster of 2 methanol molecules with MGLY (water loss from methanol is very unlikely) while one can easily propose water loss from a double hemiacetal of methanol with MGLY. Furthermore, we have run ESI-MS standards for glyoxal (GLY) and methylglyoxal (MGLY) in the mobile phases of 100 % water and 50% water/50% MeOH. We now provide these MS spectra in Supplementary Material. For GLY, in 100% water m/z^+ 117 [GLY + 2H₂O + Na]⁺ is evident. In 50% water/50% MeOH, m/z^+ 117, 131 [GLY + H₂O + MeOH + Na]⁺, and 145 [GLY + 2MeOH + Na]⁺ are evident. For MGLY, in 100% water m/z^+ 113 [MGLY + H₂O + Na]⁺ and m/z^+ 131 [MGLY + 2H₂O + Na]⁺ are evident. For MGLY in 50% water/50% MeOH m/z^+ 113, 131, 145 [MGLY + H₂O + MeOH + Na]⁺, 127 [MGLY + MeOH + Na]⁺ and 159 [MGLY + 2MeOH + Na]⁺ are evident. These peaks clearly indicate that H₂O and MeOH undergo hydration and hemiacetal formation, respectively since the number of H₂O and MeOH correspond to the number of carbonyls in GLY and MGLY molecules. Note that 2 molecules (of H₂O/MeOH) adduct to glyoxal because glyoxal stays in a dihydrated form in the aqueous phase, while 1 or 2 molecules (of H₂O/MeOH) adduct to methylglyoxal because methylglyoxal stays in both monohydrated and dihydrated forms. The equilibrium constant for hydration of methylglyoxal is very large ($K = 2700$; Olson and Hoffmann, 1989), not to say glyoxal, and the hemiacetal formation from carbonyls with alcohols has been verified by FTIR (showing the presence of C-OH peak and the absence of C=O peak) in any Organic Chemistry textbook.

We add the following in the text (line 9; page 17374):

“We are confident that m/z^+ 159.06278 is a double hemiacetal of methanol with methylglyoxal, not a cluster of methylglyoxal with two methanol molecules by the water loss in Fig. 4 and examination of ESI-MS standard runs for glyoxal and methylglyoxal in the water mobile phase with and without methanol (See Supplementary Material Fig. S5).”

R2C2b) P. 17374 discussion of PHAstd and figure 5. It would be important and helpful for the authors to disprove the possibility that the observed $m/z = 185.07802$ could (in part) correspond to a cluster (in contrast to a chemically bonded peroxy hemiacetal) of t-BuOOH, MGLY and Na⁺, which has the same exact mass. This could also explain the observation of the intense peak at 95.01041 as it would correspond to fragmentation via loss of t-BuOOH, which would be expected for the proposed cluster. One of the keys to this and discussion of the other PHAs would be a mechanism for the fragmentation with loss of methanol from PHAs, which the authors do not discuss. If I understand correctly the authors propose that Na⁺ stays attached but MeOH or O₂ are being eliminated. Both of these would require complex arrangements from PHAstd, without losing the fairly weakly bound Na⁺ (compared to a chemical bond). The authors state that HO₂ and O₂ loss are expected but do not comment on this MeOH loss, which is the second most intense m/z after the MGLY peak. Given the experimental setup and used mixture, loss of methanol from a cluster is a very straightforward explanation. The authors reference O₂ loss from soft ionization/IRMPD without any detail of whether this was for a Na⁺ cluster. It would be very helpful to reference literature for such a process or give more detail and concrete experimental results. For example, one could also propose a pathway were the t-BuOOH in the cluster eliminates methanol forming acetone, a process found in both the NO⁺ and H⁺ mode by Liu et al. ACP 13, 5715–5730, 2013. Using a separation technique before ESI detection would obviate the possible confusion between clusters and chemical bonded species. Also, elimination of methanol as a solvent would be a useful approach.

Response) The purpose of our work is to demonstrate organic peroxide formation from methylglyoxal with OH in the aqueous phase. Since organic peroxides are not detectable as a molecular ion in FTICR-MS, we focus on peroxyhemiacetals we expect to detect. So, whether $m/z+ 185$ (and other photochemical products like $m/z- 163$ and 191) is a peroxyhemiacetal or a cluster, either supports the presence of an organic peroxide (ROOH). But we expect ROOH be a fragment of peroxyhemiacetal based on the work by Tobias and Ziemann (see below). Since ROOH is not detectable due to the hot capillary, we expect to see ROOH fragment (O_2). The detailed discussion for O_2 loss is included in Supplementary Material.

We agree that methanol loss is also possible from t-BuOOH in MS/MS. However, this fragmentation (loss of a β -carbon and an OH) does not work for R1OOH and R2OOH since water loss (by the loss of a β -H and an OH) is not observed.

Also, regarding the discussion of PHAstd, p. 17374 line 29. Loss of O_2 from t-BuOOH. This requires some clarification. I was under the impression that the parent m/z for the MS/MS was PHAstd and not t-BuOOH. How can there be loss of anything from t-BuOOH in the MS/MS if the m/z of the PHAstd, in which the t-BuOOH has reacted to a different chemical species, was selected unless the parent is the cluster of t-BuOOH, MGLY and Na^+ proposed above. In addition, the signal at 81.06971 is small and it would be useful to discuss the role of all the other m/z compared to $m/z = 81.06971$ one.

Response) Peroxyhemiacetal formation was observed by Tobias and Ziemann (2000) using a thermal desorption particle beam mass spectrometer (TDPBMS). TDPBMS is an electron impact, and in MS spectra peroxyhemiacetals share corresponding organic hydroperoxide fragments. We expect the same fragmentation in FTICR-MS/MS, showing a fragment of an organic peroxide. We do not know what all the other peaks are. Perhaps they suggest other fragmentation besides O_2 loss. But we do expect O_2 loss for t-BuOOH and the small intensity does not always mean low abundance; abundance per mole varies with structure.

Lastly, t-BuOOH is not the best compound to use for peroxyhemiacetal work. It is sterically hindered which hinders formation. Also, it only has a t-Butyl group which may cause its nucleophilicity to be completely different from the nucleophilicity of hydroperoxides formed in atmospheric water, which are highly functionalized.

Response) For organic hydroperoxide standard, only t-BuOOH and cumene hydroperoxide are commercially available. We selected t-BuOOH because it was smaller and simpler for MS analyses to study peroxyhemiacetal chemistry. Due to the difficulty and efforts, we did not attempt to synthesize organic hydroperoxides. However, methylglyoxal is a small molecule and is expected to react with a hydroperoxide group in t-BuOOH. It is possible that water solvent changes the nucleophilicity of t-BuROOH, resulting the change of the rate. However, a recent study by Badali et al. (2015) shows that OH production rate of t-BuOOH ($6.5e-10$ M/s) by photolysis is not much different from that of SOA ROOH ($9-11e10$ M/s). Thus, the solvent effect seems to be minor.

R2C2c) Section 4.2 would benefit from more extensive discussion. The discussed m/z do match the chemical formulae of PHA1 and PHA2. However, it would be useful to find stronger evidence how the MS/MS spectra can actually prove that they structurally correspond to PHA1 and PHA2. Observation of MGLY Na^+ could for example result from MGLY Na^+ clustering with one of the many other compounds in the mixture (see next point). Like for the $m/z 81.06971$ discussed above, the statement that 59.01377 results from loss of O_2 from R1OOH is rather confusing as R1OOH is not present, unless the parent ion corresponds to a cluster with R1OOH. Observation of the $m/z = 59.01377$ fragment only shows that acetate is formed but the process is unclear. It cannot result from O_2 elimination from R1OOH as the corresponding negative ion, $m/z = 91.00316$, was not selected as the parent ion for fragmentation.

Response) See our response to R2C2b.

R2C2d) Contrary to the discussion, in Fig. 7b, 159.02946 results from loss of CH₃OH from the parent mass, 191.05540, not loss of O₂ from PHA₂. It appears a parent mass different from PHA₂ was selected for fragmentation again highlighting the possibility of formation of methanol clusters from the solvent. I believe the authors were referring to m/z = 87.00832 when discussing m/z of 59.01377 for PHA₂, which results from loss of C₄H₈O₃ from the parent m/z of 191.05540, the latter corresponding to C₇H₁₂O₆ (a cluster of methanol with C₆H₈O₅?).

Response) In Fig. 6, we expect PHA₂ appears at m/z 191.01998. However, in MS/MS analyses, we couldn't isolate this peak due to its small intensity. There exist not only m/z 191.02000 in MS/MS, but m/z 191.05540 as a prominent parent ion. And the difference between m/z 191.05540 and m/z 159.02946 would indicate MeOH loss. However, m/z 159.02946 suggests C₆H₇O₅ (within the uncertainty of -2.7 ppm), which indicates O₂ loss from PHA₂ (m/z 191.02000). We admit that PHA₂ analysis is not as clear as PHA₁ analysis due to the low intensity of m/z 191.02000 and the presence of m/z 191.05540. However, we do not agree that C₇H₁₂O₆ could be a cluster of methanol with C₆H₈O₅ because it is difficult to expect the C₆H₈O₅ product from MGLY-OH photooxidation. The major C₆ product is a 2, 3-dimethyltartaric acid [C₆H₁₀O₆] formed via organic radical-radical reactions. To form [C₆H₈O₅] from [C₆H₁₀O₆], dehydration is required. But it is structurally forbidden to form a carbonyl (ketone) because both OH groups are attached to tertiary carbons. But we agree that m/z 59.01377 [R₂OOH – O₂] could be the fragment from m/z 191.05540 [C₇H₁₁O₆]. We now include m/z 191.02000 in Figure 7b and add the following in the text (line 20; page 17375):

“m/z 191.02000 is PHA₂ while m/z 191.05540 is prominent as a parent ion. Due to the small intensity we were unable to isolate m/z 191.02000 from m/z 191.05540 for MS/MS analyses. Therefore, for the PHA₂ analysis, we cannot rule out the possibility that m/z 59.01377 [R₂OOH – O₂] could be the fragment from m/z 191.05540 [C₇H₁₁O₆].”

R2C2e) Similarly, the discussion of the positive mode in figure 8 could indicate cluster of MGLNa⁺ with some other compounds existing in the solution.

Response) We now add the following in the text (line 27; page 17375):

“Note that for the PHA₂ analysis in the positive mode, again, we cannot rule out the possibility that methylglyoxal [m/z⁺ 95.01040] could be the fragment of m/z 215.05151 [C₇H₁₂O₆Na]⁺.”

R2C3) Figure 6: It would be helpful to discuss the role of the peroxy hemiacetals in context of this figure. There are a large number of m/z observed in the boxed region. In fact, the proposed peroxy hemiacetal m/z do not correspond to the most intense peaks and they represent a very small fraction of the signals. It would be helpful to discuss the importance of the proposed peroxy hemiacetals if they only are a minor component.

Response) It is clear from Figure 6 and our previous work that aqueous MGLY photooxidation yields many products. However, the potential for this chemistry to form ROOH and PHA was previously unrecognized, and therefore is the focus of this work. It is also worth remembering that the FTICR-MS ion abundance per mole depends on the solution composition and ion structure. Modeling or other types of chemical analysis are needed to determine the relative abundance of products.

Minor comments:

R2Ca) Chemical nomenclature: With respect to point 2 above the authors on p. 17374 line 2 and 5 mention “solvation of methylglyoxal” with methanol. Solvation describes formation of a complex via intermolecular forces and not formation of a chemically-bonded hemiacetal. I don't think the authors

mean to imply that m/z 159.02678 corresponds to a cluster species and not the double hemiacetal or related species. In addition, and related to Figure 9: The nomenclature in figure 9 is unconventional: “DeMGLY” is in fact what should be referred to as MGLY (methylglyoxal) and not dehydrated methylglyoxal, and “MGLY” is in fact hydrated methylglyoxal. I would encourage the authors not to redefine organic nomenclature. However, it makes the statement at the beginning of this point confusing as I am not sure which form of methylglyoxal is meant. I would also encourage the authors to refer to ROOH compounds as organic hydroperoxides to distinguish them from ROOR type peroxides.

Response) We modify the sentence (line 2-5; page 17374) as following:

“undergoes hydration with water and hemiacetal formation with MeOH...”

The reviewer’s point would be more reasonable for the gas phase. Since in the aqueous phase methylglyoxal undergoes hydration and the aldehyde moiety in methylglyoxal is rarely present. So, we call hydrated methylglyoxal MGLY. And the reaction with organic peroxides occurs when MGLY is dehydrated (i.e., the reaction requires the aldehyde moiety). We use DeMGLY to emphasize that dehydration must occur for the formation of peroxyhemiacetals. Besides, if we used nomenclature as the reviewer suggested, what would be the right word for “methylglyoxal” in line 25 on page 17373?

We already state that organic peroxides are herein particularly organic hydroperoxides (ROOH) in line 1 on page 17367.

R2Cb) Abstract: The whole first paragraph is more suitable for an introduction to a paper than to an abstract presenting new findings. The paragraph describing the work and new findings is shorter than the intro paragraph. However, this is a style aspect. I would encourage the authors to be more specific about the actual experimental findings in the abstract.

Response) As the reviewer points out, this is a matter of style. We believe the importance of organic peroxide formation in the condensed-phase during aqueous photooxidation should be addressed in the abstract.

R2Cc) P. 17368 first sentence and abstract. I do not believe that the role of aqueous SOA formation is clearly proven or well accepted. It certainly represents a strong hypothesis based on lab experiments. In fact, a little later on P. 17369 Line 3 the authors state “potentially”. Hence, I encourage the authors to weaken this statement.

Response) Please see our response to R1C2

R2Cd) P. 17368 L. 17 Which peroxides form epoxides. As plural is used this statement is going beyond IEPOX and some references for these would be very helpful.

**Response) Now it reads:
“epoxides (i.e., IEPOX)...”**

R2Ce) P. 17369 L. 11. As the aqueous SOA is a hypothesis I recommend phrasing as “may explain . . .”.

**Response) Now it reads:
“... may explain ...”**

R2Cf) P. 17369 line 13-15. In the first sentence an oxidant is mentioned (OH). In the second sentence reactions are mentioned. These cannot really be directly compared as they are not the same thing. I think the authors are implying that oxidants other than OH and non-radical reactions play a role in

aerosol. It would be helpful to clarify what is meant here.

Response) We modify the second sentence (line 12-15) as following:

“In the high solute concentrations in wet aerosols, however, besides OH radical reactions a more complex system of organic radical and non-radical reactions occurs...”

R2Cg) P. 17370 Line 13. Do the authors mean flux or emission. They are clearly related but not really the same. I also assume that they are referring to non-methane VOCs?

Response) Now it reads:

“Monoterpenes have a global emission second only to isoprene among non-methane VOCs ...”

R2Ch) P. 17370 Line 18. The authors are correct that ROOH can be an OH source. However, I recommend weakening the statement, as this is only true for functionalized peroxides. For example CH₃OOH has a very slow photolysis rates and does not contribute as an OH source because of this (in fact this is why 250nm lamps and not solar radiation is used to photolyze H₂O₂). In contrast, the abstraction of the hydroperoxy H can make hydroperoxides even act as catalytic HO_x sinks. Ditto for the statements on line 20-22.

Response) We add “In general” at the beginning of the sentence.

R2Ci) P. 17370 Line 22-23. The Henry’s law constants of organic peroxides can be very low, e.g., with a large organic rest, or for ROOR with unpolar R groups. The Henry’s law constants of hydroperoxides can be higher but that will greatly depend on structure. I recommend weakening the statement.

Response) Please see our response to R1C4.

R2Cj) It would be helpful to show the mass spectra of blank solutions and those after processing of MGLY without H₂O₂ as well as those of MGLY that has been equilibrated with H₂O₂ without photochemical processing. The authors mention these but there is no harm in adding a comparison in the supplement.

Response) Please see our response to R1C9.

R2Ck) P. 17374 line 26. I would have thought there must be some literature on the fact that hydroperoxides decompose on heated surface and not just a personal communication.

Response) Now we add a reference:

“...peroxides (Karasch et al., 1950; M. Soule and E. Kujawinski, personal communication, 2013).”

R2Cl) P. 17374 line 26: I believe many of the current CI-API-TOF MS methods are able to ionize hydroperoxides without much problem, e.g., using I⁻ as a reagent ion.

Response) Now it reads:

“in the ESI method, it is difficult ...”

R2Cm) How was the rate constants for peroxyhemiacetal formation that was used in the model determined?

Response) The rate constant for peroxyhemiacetal formation was assumed to be the same as $1\text{e-}3\text{ M}^{-1}\text{s}^{-1}$, which was the acid catalysis rate constant on the aerosol surface (Lim and Ziemann, Phys. Chem. Chem. Phys., 2009). We used $1.6\text{e-}4$ for the reverse reaction rate constant from

the unpublished data by Tran and Ziemann (2006). Now we include this in Supplementary Material (below Table S1).

R2Cn) P. 13747 line 28029. I am not sure that “much more stable” compounds correspond to “(less volatile)” compounds. For example CH₄ is much more stable but also much more volatile. Do the authors mean stability (decomposition) or vapour pressure (volatility). It would in fact be useful to see vapour pressure estimates based on structure activity relationships. Some of the peroxy hemiacetals may not be very low volatility as they have few OH groups.

Response) We mean both. Besides, we do not expect that vapor pressure of peroxy hemiacetals could be higher than those of their parent organic peroxides. “... are much more stable and lesser volatile...”

R2Co) Title: OH formation seems to have no relationship with this manuscript, as there is no experimental work on OH formation from (hydro)peroxides.

Response) Please see our response to R1C1.