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 ºC), 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 germinal 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 PAHstd, without loosing 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 methylgyoxal 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 (O2). The detailed discussion for O2 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 O2 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 framgentation besides O2 loss. But we do expect O2 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 hydroperoxids 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 O2 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 O2 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 [$R_2OOH - O_2$] 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 $PHA_2$ 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 $PHA_2$ analysis, we cannot rule out the possibility that $m/z^-$ 59.01377 [$R_2OOH - O_2$] 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 $PHA_2$ 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 HOx 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 peroxihemiacetal formation that was used in the model determined?

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