

We thank the referee for the helpful comments and questions, which have improved the manuscript. The referee questions/comments are italicized and our replies are in different font. Changes to text in the manuscript are shown in quotation marks.

This paper describes novel measurements of glyoxal in a region where the VOC reactivity is dominated by biogenic compounds. Because of the wide suite of co-located measurements, the authors are able to make predictions using a 0-D model that is well-constrained by observations. The model is significantly biased high compared to the measured glyoxal, and the authors explore several explanations for this. One of the most interesting aspects of the paper is that model predictions of glyoxal are highly sensitive to OH. This sensitivity is not necessarily linear and depends on the generations of VOC oxidation during which glyoxal is formed as a product and also the importance of OH as a glyoxal sink, relative to photolysis.

Could the authors use the model to explore the power of the OH dependence, over a reasonable range, and test whether it is different for isoprene and MBO? While the range of values found may only be applicable to this specific location, it would be interesting to provide context for future analyses that include glyoxal.

We thank the reviewer for raising this question, as we believe it is an important result of the manuscript. In response to the reviewer's question, we have added two figures (fig. 5 and 8) with discussion in the $\frac{1}{2}$ OH model section and conclusion. To summarize our findings:

1. In our simulations, glyoxal always responds to changes in OH more strongly than glycolaldehyde, as well as formaldehyde, MVK and MACR (not shown). This is true for both the daily average values as well as the overall diurnal profile.
2. The comparatively weak glycolaldehyde response to reduced OH (in comparison to that of glyoxal) is more pronounced in the case of simulations of MBO oxidation than in those of isoprene oxidation. This is expected as glycolaldehyde is a 1st generation product of MBO but a secondary (higher generation) product for isoprene, whereas glyoxal always has a substantial contribution from secondary production.
3. For both isoprene and MBO, glyoxal is reduced more than the OH reduction.

The text in the "reduced OH radical concentrations" section now reads:

"Another means of reducing model glyoxal concentration is to alter the overall oxidation process via changes to OH radical abundance. The average reduction in glycolaldehyde and glyoxal upon reducing OH is shown in Fig. 5. In the top panel, which shows simulated MBO chemistry, glyoxal responded slightly more than linearly to reductions in OH while glycolaldehyde responded less strongly. In the bottom panel, which shows simulated isoprene chemistry, both

glycolaldehyde and glyoxal responded approximately linearly to reductions in OH, with the response in glyoxal slightly stronger. Thus we demonstrate that glyoxal concentrations are very sensitive to OH levels; results of a model run in which OH was reduced by a factor of two are presented in Fig. 6.”

The new figure (Fig. 5) that was referenced has the caption:

“The fractional reduction in glyoxal and glycolaldehyde concentration for models using either measured OH or reduced OH. The top panel shows results using only MBO chemistry, and demonstrates that glyoxal is correlated to OH concentration while glycolaldehyde (a first generation product of MBO) shows less dependence on OH. In the bottom panel, the results of isoprene oxidation for the same changes in OH concentration are shown. Here, glyoxal and glycolaldehyde (both of which are mainly higher-generation products of isoprene oxidation) approximately follow changes in OH. The change in glyoxal is slightly more than 1:1 while that of glycolaldehyde is slightly less.”

The text in the conclusion now reads:

“This demonstrates that glyoxal can be a useful local tracer of OH-driven VOC oxidation chemistry, in particular given its short photochemical lifetime. For example, the relative sensitivity of glyoxal and glycolaldehyde to changes in OH is shown in Fig. 8, which demonstrates that glyoxal is more sensitive (i.e. has a greater reduction for reduced OH) than glycolaldehyde for isoprene and MBO oxidation. The sensitivity is especially enhanced for the case of MBO, in which glycolaldehyde is a first generation product and glyoxal is a higher-generation product, but remains even for isoprene in which both are mainly higher-generation products. Thus we propose that the high sensitivity of glyoxal to OH makes it an especially useful tracer for BVOC oxidation studies aimed at investigating OH-driven chemistry.”

And the accompanying figure (Fig. 8) has caption:

“The ratio of the relative response functions Y of glyoxal to glycolaldehyde for models using either measured OH or reduced OH. These results show that for MBO chemistry, glyoxal becomes increasingly more sensitive than glycolaldehyde to OH concentration as OH decreases. In isoprene chemistry, glyoxal is always more than 1.5 times more sensitive than glycolaldehyde but the magnitude and the trend are less pronounced.”

In general the paper is well-written, however that authors should address the following issues in a revised submission for publication in ACP.

Page 13665, line 1-14 By what mechanisms are glyoxal and O_3 deposited? Maybe the lack of correlation between the two reflects differing mechanisms, e.g. glyoxal is dissolving in surface water whereas O_3 is being oxidized by BVOC (see Fares et al.,

2010). A warmer, drier night might be expected to increase ozone loss rates and decrease glyoxal loss rates. Does the loss rate of glyoxal have any dependence on RH?

We agree with the reviewer that the lack of correlation likely reflects differing mechanisms and have adjusted the text accordingly. We do however not observe a correlation with RH. The text now reads:

“Thus there is some degree of variability between the relative deposition rates of both glyoxal and O₃ on different nights, likely arising from the different processes which control the loss of each compound, such as reactions of O₃ with biogenic VOC [Fares et al. 2010] or loss of glyoxal to surfaces. We do not observe a relationship between RH and deposition rate of glyoxal, but this is not necessarily conclusive as we have only six points (corresponding to six nights).”

Page 13665 Line 20-22. This sentence is a little unclear as written, since it seems that the issue is that the production is slow, rather than that it exists at all. Perhaps end with “as according to the model there was nighttime glyoxal production, albeit at a slow rate of xx.”

We have clarified the wording. The text now reads:

“The photochemical model described in section 4 required a deposition rate which was double that inferred here to match the observed loss rate. This difference arises from the incorrect assumption in this analysis that no glyoxal is produced at night; in fact the average predicted nighttime production rate during the hot period is approximately 10% of the average noontime production rate.”

We also added the following to the discussion of reduced OH:

“While this analysis will focus on daytime chemistry, we note that nighttime production of glyoxal in the model is mediated almost entirely by OH, which may lead to changes in the deposition velocity needed in the model, but will not change the observed rate described in Sect. 3.2.”

Page 13666 Line 22 - When introducing the model mechanism, it would be useful to convey more clearly that the mechanisms are consistent with chamber measurements of glyoxal yield made using the same instrument (e.g. Chan et al., 2009 and Galloway et al., 2011). This is mentioned/IMPLIED later in the text and in the conclusions, but would be valuable for readers to know at the outset.

We have followed the referee’s advice and clarified this section. The text now

reads:

“After this equilibration, any species for which measurements were available were again set to match observation. This model was able to match glyoxal data taken by the Madison LIP Instrument in an identical operational configuration taken at the Caltech Environmental Chambers for experiments of isoprene and MBO oxidation (the dominant precursors of glyoxal at BFRS) under both NO rich and NO poor conditions [Galloway et al. 2011].”

Figure 4 – Would the time-of-day dependence of the predicted glyoxal from the MBO-only curve (not plotted) better match the observations? Could that offer some insight into what the problems are with the model?

The MBO only curve is very similar to that of the isoprene + MBO curve, and does not include any new features. The text of Figure 4 now includes the following statement:

“The form and magnitude of MBO alone is similar to that of ISOP + MBO.”

Page 13668, line 10 – Can this point be stated more clearly? Do you mean that because the chemistry is in the low NO_x regime, the main way to reduce higher generation oxidation products is the increase HO_x-HO_x chain termination reactions, but that it requires unphysically large rate constants to have an impact? When you say “In addition, the model employed here matched low NO_x chamber studies of MBO and isoprene very well (Galloway et al., 2011)”, what aspects of the model match the chamber studies – certainly not the glyoxal production.

The reviewer has surmised correctly that "unphysical" rate constants refer to faster than gas-kinetic rates.

The text now reads:

“In order for low NO_x chemistry to lower glyoxal noticeably, unphysical (i.e. faster than gas kinetic) rate constants for the RO₂+ HO reaction had to be employed. We did not alter the HO_x+HO_x termination rate.”

We have also clarified the text in response to the reviewer's question concerning the aspects of model agreement with chamber studies:

“This model was able to match glyoxal data taken by the Madison LIP Instrument in an identical operational configuration taken at the Caltech Environmental Chambers for experiments of isoprene and MBO oxidation (the dominant precursors of glyoxal at BFRS) under both NO rich and NO poor conditions

[Galloway et al. 2011].”

Page 13670, lines 10-26 - This section is somewhat difficult to follow. Given that the OH measurements are so important, can more information be provided about the technique in the Supplemental section? Since the ‘PSU group’ is among the co-authors of this paper, can more information be given about whether the instrument was operated in the same manner in the 2007 and 2009 campaigns. Is it reasonable to assume that an across-the-board factor of two decrease is an appropriate correction?

The reviewer’s question is timely. We communicated with the PSU group, who indicated that they are still working on their analysis and that it is too early to recommend such an across-the-board factor. No specific information on a correction factor for BEARPEX 2007 is possible as the new measurement technique was not yet operational at that time. Despite our inability to provide this information, we believe our results are useful: our goal here is not to determine OH, or to assess the fitness of OH measurements; rather we demonstrate that glyoxal is sensitive to OH concentrations and can be useful as a way to gauge the conditions of oxidation in the atmosphere.

Page 13670, lines 19-22 I think the sentences “The implied lower OH concentration refers to the OH concentration experienced over the lifetime of glyoxal and not necessarily the OH concentration at the measurement site. However, there is no reason to expect the OH concentrations to be substantially different.” would flow more naturally at the end of preceding paragraph (line 10), since these statements not really related to potential over-measurement of OH.

We have followed the reviewers advice to reword this statement. The text now reads:

“The implied lower OH concentration refers to the OH concentration experienced over the lifetime of glyoxal and not necessarily the OH concentration at the measurement site. However, there is no reason to expect the OH concentrations to vary substantially in space over the distance relevant to the glyoxal lifetime.”

We also clarified a point regarding the corroboration of methods, which was unclear. The text now reads:

“at present, none of the other methods we employed to reduce glyoxal are corroborated in scientific literature.”

Section 4.2.3 In the truncated Lagrangian run, what values are used for OH?

We have clarified this. The text now reads

“We construct a truncated-Lagrangian model in which the Lagrangian model run is initialized when an air-mass with very low glyoxal and glycolaldehyde concentrations (1×10^5 molecule cm^{-3}) enters the MBO emitting area, where it experiences the chemical environment (OH, O_3 , photolysis, etc.) measured at or calculated for the BEARPEX site.”

Page 13671, line 21 Rather than “the edge of the MBO-emitting region”, do you mean the edge of the isoprene-emitting region, since you are talking about losing glyoxal formed from isoprene in this sentence?

The phrase "the edge of the MBO-emitting region" has been replaced by "the zone where isoprene emissions give way to MBO emissions"

P13672, line 5 – Why would you expect the impact on glyoxal to be larger than the impact of glycolaldehyde? If glyoxal has other sources, I would expect the impact to be smaller. Why is the impact bigger for glyoxal and glycolaldehyde: because other precursors are also affected, because there is a feedback on the modelled OH, ...?

We thank the reviewer for pointing this out. This is an important point and we have clarified the section. The new text to reads:

“The effect on glyoxal (which the model predicts is largely an oxidation product of glycolaldehyde) is more pronounced, as production of glyoxal from MBO requires two reactions with OH while glycolaldehyde production from MBO needs only one. MBO is the dominant precursor of glycolaldehyde and glyoxal in this simulation. As glyoxal is a secondary product its appearance has a lag compared to that of glycolaldehyde. Due to the limit model run time, this makes the effect on glyoxal more pronounced than for glycolaldehyde.”

Concentrations of OH were set using the measurements of the PSU group; there is no feedback effect on OH in this simulation.

Supplemental, Line 83 – even ozone was assumed to have a zero background concentration? That seems like a poor choice, though I am not sure it will have a big influence on your results.

We thank the reviewer for raising this point as we did not make this clear.

Species which were used to constrain the model, such as NO₂, OH and O₃, were not subject to the dilution term. We have adjusted the text accordingly:

"Primary VOCs and other species such as OH, NO₂ and O₃ were driven to match observations and thus were not subject to this dilution."

Reference section – it seems that the page on which the reference appears is listed after each reference – is this intentional?

We have communicated with the editor and received a reply that this is not a problem.

In addition to the changes detailed in the responses to the reviewers, we note a change to the abstract of our manuscript. The altered 2nd paragraph of the abstract emphasizes our view that glyoxal can be used as a tracer of OH-driven oxidation of biogenic volatile organic compounds, to distinguish it from a means of assessing OH measurement, which is not what we were attempting--a topic often raised by the anonymous referees. Our expanded analysis of the sensitivity of glyoxal to changes in OH in response to the reviewer comments (as compared to other oxidation products of biogenic volatile organic compounds) serves to show that glyoxal is well suited for such analysis.

References:

Chan, A. W. H., Galloway, M. M., Kwan, A. J., Chhabra, P. S., Keutsch, F. N., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Photooxidation of 2-methyl-3-buten-2-ol (MBO) as a potential source of secondary organic aerosol, Environ. Sci. Technol., 43, 4647–4652, doi:10.1021/es802560w, 2009.

Fares, S., McKay, M., Holzinger, R., Goldstein, A.H. Ozone fluxes in a Pinus ponderosa ecosystem are dominated by non-stomatal processes: Evidence from long-term continuous measurements, Agricultural and Forest Meteorology, 150, 420-431, 2010.

Galloway, M. M., Huisman, A. J., Yee, L. D., Chan, A. W. H., Loza, C. L., Seinfeld, J. H., and Keutsch, F. N.: Yields of oxidized volatile organic compounds during the OH radical initiated oxidation of isoprene, methyl vinyl ketone, and methacrolein under high-NO_x conditions, Atmos. Chem. Phys. Discuss., 11, 10693–10720, doi:10.5194/acpd-11-10693-2011, 2011.