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 presents measurement and modeling results of glyoxal as part of the BEARPEX 2007 campaign in the Sierra Nevada mountains, a site where biogenic VOCs dominate the photochemistry. As a result, measurements of glyoxal at this site can be used as a test of models of biogenic VOC chemistry. The authors present the results of a 0-D model that is constrained by the suite of measurements during the campaign. In general, the model overpredicts the observed concentration of glyoxal by a factor of 2-5. Several sensitivity tests are presented in order to attempt to determine the cause of this discrepancy. The authors find that the modeled glyoxal is highly sensitive to the concentration of OH in the model, and a reduction in the OH concentration by a factor of two below the measured values brings the modeled glyoxal (and the modeled HO2) into better agreement with the measurements.

Overall this is a very interesting paper that addresses current issues concerning the chemical mechanism of BVOC oxidation in the atmosphere. The paper is generally very well written and the results are appropriate for ACP. The authors should address the following comments prior to publication:

1) One of the main implications the paper is that the measured OH during BEARPEX 2007 may be too high by a factor of two based on OH measurements during BEARPEX 2009. Unfortunately there is very little discussion of this in the paper or in the Supplementary Materials. As a result, it is not clear whether the interference measured in 2009 could have been similar in 2007.
A)Were the OH concentrations measured in the "traditional way" in 2009 similar to the concentrations measured in 2007?

The reviewer raises a good point. The "traditional" OH measurements for 2009 were quite similar to those of 2007, when comparing days with similar air temperature. We compared a period in 2009 which had daily average, maximum, and minimum of T=24.6°C, 30°C and 19.5 °C, respectively to a period in 2007 with daily average, maximum, and minimum T=23.6°C, 29.1°C and 19.0 °C, respectively. In 2009, the daily average "traditional" OH was 7% lower and the average maximum OH was 7% higher than that reported for the comparable period in 2007.

B)Were the concentrations of other compounds similar?

It is difficult to make a direct comparison of other compounds due to incomplete overlap of data within and between BEARPEX2007 and BEARPEX2009. The NO_2 data taken is quite similar (within 20%) and the VOC data appear broadly similar but there is not enough data to be definitive at this point. However, as the region is dominated by BVOCs and as temperatures and conditions were similar we expect similar BVOC emissions.

An expanded discussion of the OH measurements would give more confidence that the factor-of-two reduction in OH is realistic.

The PSU group is currently preparing a complete report on OH from BEARPEX and such a discussion is beyond the scope of this manuscript. We are not attempting to model OH, but rather demonstrate the large sensitivity of glyoxal to OH and that a reduction is the most effective way of addressing model over-prediction and improve agreement between model and measurement. The factor-of-two reduction in OH used here is meant to be illustrative of the sensitivity of glyoxal to OH concentrations. We chose 0.5x OH and 2x OH (not shown) as part of the sensitivity analysis and not to match the report by the PSU group that OH measurements at BEARPEX 2007 may sometimes be too high by a factor of ~2.5. However, the improvement in agreement of glyoxal as well as other species such as HO_2 upon the reduction of OH by a factor of two indicates that such a factor is reasonable.

2) Did the authors run their model without constraining OH (or by constraining the model to the observed HO2 concentrations) to see if the model predicted OH leads to modeled glyoxal concentrations more consistent with the measurements? This would provide additional information that would help to justify the factor-of-two reduction in OH.

We did not attempt to use our model without constraining OH. It has been shown that modeling OH in BVOC influenced regions, in particular in isoprene influenced regions, is challenging [Lelieveld et al. 2008; Hofzumahaus et al. 2009] and our model was not designed for this. The reviewer is correct in that this could be an interesting study, but it would be beyond the scope of the presented work as it would require a different model.

3) It has been recently reported that measurements of HO2 by titration to OH in LIF instruments may be sensitive to hydroxylalkyl peroxy radicals (Fuchs et al., Atmos. Meas. Tech., 4, 1209-1225, 2011). Is it known whether the PSU instrument is sensitive to this interference? If so, the measured values may reflect both HO2 and some RO2 radicals, and thus care should be taken in comparing them to the modeled HO2.

The PSU group is working on a more complete analysis of OH and HO_2

measurements, which will address this concern. At this time we have no specific information on the possibility that the HO_2 measurements were influenced by hydroxylalkyl peroxy radicals. We have however adjusted our text to include this possibility.

The new text reads:

"A potential instrumental artifact which would influence this analysis is the possibility of a positive bias in HO_2 measurements due to interference by hydroxylalkyl peroxy radicals [Fuchs et al. 2011]. As no specific information is available for the BFRS site in 2007 concerning this interference, no correction was attempted. However, it is possible that this affects our model-measurement comparison of HO_2 and hence care should be taken in using the model-measurement agreement of HO_2 as a metric for success in representing oxidation."

4) The measured OH concentrations were lower during the cold period. Did the authors attempt to model the cold period glyoxal constrained to the observed OH? Could the presumed interference in the OH measurement be lower during the cold period?

As we had not directly investigated this effect we ran some new simulations with MCM v3.2, using only isoprene and MBO chemistry and neglecting loss of glyoxal to aerosol. For the hot period sample days we investigated (day of year 251-253) the model over-predicted glyoxal by a factor of 4.1, during the day and at night, whereas for the cold period sample days (day of year 256-258), the model only over-predicted glyoxal by a factor of 1.5 during the day, but a factor of 2.75 at night. Thus, the reviewer is correct that the over-prediction is less during the cold period during the day, potentially as the measured OH concentrations are much lower. In contrast, the night time values are close to those in the hot period.

However, we do not want to discuss the cold period extensively for the following reason: Our model mainly focuses on BVOC oxidation. BVOCs dominate during the hot period and thus our model is appropriate for this time. During the cold period BVOC concentrations are quite low and it is likely that effects of transport and anthropogenic VOCs become more important and thus our model might not be appropriate for this period.

5) Page 13668 lines 10-15: The authors state that an "unphysical" rate constant for the RO2 + HO2 reaction would need to be employed in order to reduce the modeled glyoxal concentrations noticeably. What would be the unphysical rate? Much greater than gas kinetic rate constant?

The unphysical rate constant for HO2 + RO2 has been clarified as being faster than gas kinetic. The new text reads:

“In order for low NO_x chemistry to lower glyoxal noticeably unphysical (i.e. faster than gas kinetic) rate constants for the RO_2 + HO_2 reaction had to be employed.”

Similarly, the authors should clarify the “unphysical” dilution rate constants.

We have clarified the point regarding the dilution rate constant. The new text reads:

“Decreasing glyoxal concentrations noticeably by increased mixing with background air via vertical dilution required a dilution rate constant much larger (~ 5x) than that used in other studies [Perez et al. 2009; Dillon et al. 2002], which is unlikely to be correct.”

6) Page 13688, line 19: This discussion is a bit confusing. Are the chamber measurements consistent with a glyoxal yield of 0.29? Thus a reduction of the yield to 0.045 to match the observations would not be consistent with the chamber measurements?

We have adjusted the text to clarify this point:

“however, a reduction to a yield of 0.045 (~15% nominal) was required to achieve agreement with average glyoxal measurements. In addition, the nominal yield of 0.29 in the model was calculated from chamber experiments of MBO oxidation which included glycolaldehyde measurements, following BEARPEX 2007 with no observable change in instrument performance and hence should be optimized for this study.”

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

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