

Interactive comment on “Photochemical modeling of glyoxal at a rural site: observations and analysis from BEARPEX 2007” by A. J. Huisman et al.

Anonymous Referee #2

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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

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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. Were the OH concentrations measured in the “traditional way” in 2009 similar to the concentrations measured in 2007? Were the concentrations of other compounds similar? An expanded discussion of the OH measurements would give more confidence that the factor-of-two reduction in OH is realistic.

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.

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.

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?

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

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?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 13655, 2011.

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