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Atmospheric Chemistry and Physics Discussions

Interactive comment on "DOAS measurements of formaldehyde and glyoxal above a South-East Asian tropical rainforest" *by* S. M. MacDonald et al.

Anonymous Referee #2

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This manuscript contains new and very interesting results within the context of isoprene oxidation and glyoxal. In particular, glyoxal in a tropical rural environment is of great interest, as is the ratio of formaldehyde to glyoxal and little previous information exists on these topics for tropical environments. Thus, the scientific topic is certainly appropriate for ACP.

The manuscript is suitable for publication after addressing the following points:

1. The formaldehyde yield from Jenkin et al. 1998 (only a direct yield) is in the absence of NOx, and the authors argue that OP3 corresponds to low NOx conditions. This is certainly valid. However, low NOx conditions in laboratory experiments do not necessarily reflect ambient low NOx conditions. Specifically, the Jenkin et al. 1998 work reflects high RO2/HO2 ratios, which is evidenced by the low hydroperoxide yields. These

conditions will favor products formed by RO2+RO2 reactions, such as formaldehyde. Thus, it is not apparent whether the Jenkin et al. HCHO yield (31.5-34%) is applicable for the conditions of OP3, as such high RO2/HO2 ratios are not expected under ambient low NOx conditions. In addition, the Jenkin yield only accounts for the direct formaldehyde production, whereas secondary production can be substantial. These two last points need to be discussed.

2. P. 5910 L. 7. The fact that glyoxal reaches a maximum after isoprene has dropped to zero whereas formaldehyde does not appear to have this behavior is very interesting and it would be helpful to discuss potential reasons.

3. P. 5910 L. 10-12. The short comment by Pohler et al. goes into much more detail. However I agree that the detection limit and accuracy of the data requires further discussion. The explanation given in this section for the negative concentration values is helpful but does not detract from the fact, that this has implications for the detection limit and/or accuracy. If values of negative 1 ppb are consistently observed this means either the detection limit has to be more than 1 ppb or the accuracy is worse than 1 ppb. This in turn has implications for the interpretation of the data. I agree with Pohler et al. that it would be helpful to further address this point, as it is central to the manuscript.

4. Figure 3 shows a glyoxal DOAS spectrum in the lower inset. I have four comments with respect to this figure.

A. P. 5908 L. 23 states that CHOCHO was measured from 412-454 nm. Within the context of the comments of Pohler et al., either this figure needs to be modified to show the same data/time over the whole spectral range, i.e., to 454 nm, or an additional figure needs to be added.

B. The residuals for glyoxal are substantial for this spectrum (420-435 nm range). Is this an unknown species, which would be very interesting. If the cross section were similar to glyoxal it would be at substantial concentrations. Can the authors discuss this further?

C. Please add markers in addition to the smooth lines to indicate location of data points.

D. The maximum of the absorption cross section in the 440 nm region for reference spectra, such as Volkamer et al. 2005 is a little longer than 440 nm. However, in figure 3 the maximum is around 439.3 nm. Can the authors show figure 3 using the now widely used Volkamer et al. reference spectrum? I am surprised by such a big difference in wavelength and an explanation would be helpful.

5. P. 5911 L. 8. The measurements of Huisman et al. 2011 appear to have had very similar isoprene concentrations (about 2 ppb, see Fig.1 of that paper) as well as methyl butenol, which has a high glyoxal yield. The section should be adjusted accordingly. However, likely the NOx conditions were quite different from the work reported here. I could not readily find the isoprene concentrations in Munger et al. 1995, Lee et al. 1998 or Sinreich et al. 2007.

6. Figure 7: Showing a correlation plot with correlation coefficient would be helpful and provide more quantitative information.

Technical comments:

7. P. 5905 Line 20: Additional measurement techniques for glyoxal have reported ambient data:

A. Washenfelder et al. 2011 have reported glyoxal measurements using incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS) in the LA basin.

B. Huisman et al. 2011 have reported glyoxal measurements using laser-induced phosphorescence. This is mentioned later, but is better mentioned at this point, as it appears to be a list of techniques.

8. P. 5906 Line 22. The work of Volkamer et al. 2009 should be added as a reference as it is important for this point, as well as Galloway et al. 2011a.

9. P. 5912 L. 8. I probably just missed this, but it would be useful to briefly discuss

treatment of the variation in the boundary layer in the model.

10. P. 5915 L. 13. A more recent discussion of glyoxal yields from isoprene is given in Galloway et al. 2011b. The authors report total yields between 8-11% in good agreement with the values used here.

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