Response to Interactive comment by Anonymous Referee #1 on "DOAS measurements of formaldehyde and glyoxal above a South-East Asian tropical rainforest" by S. M. MacDonald et al.

The manuscript by MacDonald et al. describes DOAS based measurements of HCHO and glyoxal over a tropical rainforest. The measurements are compared to a single column model and sensitivity studies are performed to gain inside into the effect of various production and loss processes on the concentration levels of those species. Since in particular glyoxal measurements are sparse, the data set itself is of high relevance for the atmospheric chemistry community. The data analysis is sound and the paper is well written. Thus, I recommend publication after some minor revisions:

We would like to thank the referee for their comments and provide detailed responses to the points raised below. Changes in the manuscript are indicated by blue text.

Page 5909: The description of the MAX-DOAS measurements lacks some information on the data quality (detection limits). This information would be useful and should be added.

We agree and added the following sentence to the description: "Typical values for the 2σ uncertainty and 2σ detection limit are 6×10^{15} and 3.4×10^{16} for SZA < 80°, and 3×10^{15} and 2×10^{16} for SZA < 60° molecule cm^{-2}."

Page 5910: In the discussion of Fig. 7 the authors state that there is good agreement between the HCHO measurements performed by LP-DOAS and the converted slant column densities for the 2 elevation angles of the MAX-DOAS. What does good mean? A more quantitative comparison (e.g. a scatter plot) should be provided to allow the reader to judge the quality of the intercomparison.

The two DOAS instruments were sampling different air from two different viewing directions as stated in the manuscript, in combination with the very different topography, we find the correlation coefficient to be R = 0.016 and have added the following sentence: "A correlation of the LP against the MAX-DOAS data sets gave a correlation coefficient of only 0.016. Reasons for this low value include the fact that the two instruments were sampling different air masses with highly variable topography due to their differing viewing directions.'

Page 5911: The authors compare their results for HCHO with previous observations published in the literature. They mainly restrict these comparisons to groundbased observations. Nevertheless, I would recommend to compare their HCHO LP-DOAS and the vertical information gained from MAX-DOAS with our publication on airborne HCHO measurements over a tropical rainforest (Stickler et al., ACP 7, 3933-3956, 2007). The agreement seems to be quite good.

We thank the referee for pointing out this study to us. We have added the reference.

Page 5912: I understand that the height of the atmospheric boundary layer is kept constant during the model runs. Is that correct […]

This is indeed the fact and we made this clear in the revised manuscript by adding the sentence: "The vertical resolution of the model was 5 m with a boundary layer of 1 km which was kept constant throughout the model runs."

[…]and don't you expect, that the change of boundary layer height over a diurnal cycles has some influence on modeled trace gas levels? I also expect, that the actual NOx level strongly influence at

The boundary layer height was found to be consistently around 800-1000 m during the day based on LIDAR measurements at the site (Pearson et al. 2010). However, it did drop to around 200 m from around midnight to sunrise. This collapse in the boundary layer, however, coincided with periods of fog at the measurement site which resulted in fewer LP-DOAS measurements during these times. We have now pointed this out in the manuscript.

In addition to the discussion of the NO_x sensitivity of the formaldehyde yield in the paper (Page 5913 , Lines 18 - 25) sensitivity studies show that doubling the observed NO_2 produces a 30% increase in the yield of both HCHO and CHOCHO.

The larger concentrations of glyoxal through the late evening after the drop in the modelled values may be due to alternative sources of glyoxal such as monoterpenes. Measurements of monoterpenes during the two campaigns showed that they were consistently present throughout the night, unlike isoprene, and could represent a source of glyoxal in the evening. We have added to the discussion section in the manuscript.

Response to Interactive comment by Anonymous Referee #2 on "DOAS measurements of formaldehyde and glyoxal above a South-East Asian tropical rainforest" by S. M. MacDonald et al.

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:

We would like to thank the referee for their comments and provide detailed responses to the points raised below

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.

We agree with the referee's comments and have added a discussion of these potential effects in the manuscript. Sensitivity studies were conducted changing the NO_x concentration using the MCM chemical scheme and a doubling of the measured NO_x concentrations was found to cause a 30 % increase in the HCHO and CHOCHO produced. This has now been added to the manuscript discussion section.

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.

One potential reason for the glyoxal being present at significant levels into the evening and night may be due to increasing importance of alternative sources such as monoterpenes. Unlike isoprene, monoterpenes measured at the site were found to be present throughout the night and could offer are known precursors for glyoxal. We have added this explanation to the discussion section of the manuscript.

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.

The large negative data points were observed during periods of low signal to noise and have therefore been removed from the figure. In addition, large variations in shift and stretch were observed during the campaign due to unstable temperatures within the LP-DOAS container. By calculating the stretch and shift values online within the analysis program for each spectrum the number of negative points is reduced due to better fitting of the relevant species and the figure has been updated accordingly.

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.

The window to which the data was fitted was from 422-442 nm as is shown in the figure. We have now updated the manuscript to explicitly state the fitting window and therefore have kept the figure with the same wavelength interval.

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?

These residuals appear to be random structures and do not appear systematically in successive spectra; therefore we do not believe they represent an unknown species. We have now indicated this in the manuscript.

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

Markers have been added to the updated figure.

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.

During the two campaigns in Borneo large variations in the stretch and shift required to fit the spectra was observed, and resulted from the unstable temperature within the LP-DOAS container. In the analysis program the stretch and shift is applied to the reference spectrum (which was the Volkamer et al. 2005 spectrum) to align it to the measured spectrum rather than the other way round which is why such a large difference in the peak at 440 nm is observed. The figure has now been corrected so that the wavelengths are consistent with the reference spectrum.

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.

The section has been adjusted accordingly to take into account these observations.

We have produced a correlation plot with correlation coefficient 0.016. The reason for the disparity between the measurements can be due to the different viewing angles of the two instruments, which were sampling different air masses and due to the variable topography of the region. The correlation coefficient has now been stated in the manuscript.

We thank the referee for pointing out these studies and have added the references to the manuscript.

These references have been added to the manuscript.

The boundary layer height is kept constant during the model at 1 km (approximate to the day time measurements of Pearson et al. 2010 during the campaign). The boundary layer was found to decrease to around 200 m at night, however, this generally coincided with periods of fog at the measurement site when there are fewer measurements from the LP-DOAS. This has now been mentioned in the manuscript.

We thank the referee for pointing out this reference and have added this to the discussion of glyoxal yields in the manuscript.

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

The published manuscript from MacDonald et al. about DOAS measurements of formaldehyde and glyoxal in a tropical rain forest is an interesting topic which has not been investigated so far. Thus the presented observations expand significantly the amount of available data for such environments and improve our scientific knowledge. They are very important to analyse emissions of tropical rain forests. However we also found significant problems in the quality of the presented data which are in our opinion not addressed correctly in the manuscript. This includes the data processing and the derived measurement errors which seem to our understanding to be underestimated. This may not only make the presented data and their conclusion questionable, but could also lead to a misunderstanding (especially for non DOAS experts) on the quality of the data of this instrument.

We will not discuss all points of the manuscript which are addressed by the reviewers, but focus only on some aspects we want to highlight. In the following some points of the manuscript will be discussed in the order of the manuscript:

We would like to thank Denis Pöhler and Johannes Lampel for their comments. Detailed responses to the points raised are listed below.

1. P. 5908 l. 14: No information of background and lamp reference spectra is given. This is important for the measurements at these environments.

We have added the sentence: "A 400 W xenon arc lamp was used as the light source. Reference lamp spectra were recorded online at 30 s intervals using an optical bypass system allowing for measurement of light that was not exposed to the atmospheric lightpath. A similar system enabled recording of the background light by blocking the Xe arc lamp source."

2. P. 5908 l. 21-23: "An important point to note is that simultaneous measurements of glyoxal and formaldehyde are not possible by DOAS, because these species are retrieved in different spectral regions." ! This general statement for DOAS is not correct. Many DOAS instruments have either an automatic rotatable grating (thus measurements could be made first at one than at the other spectral range) or several spectrometers are used or another option could be that a spectral range is chosen in the way to cover both species. Thus it is a problem of the here used instrument, not a general DOAS instrument problem.

We agree that the sentence is misleading and changed it to: "An important point to note is that simultaneous measurements of glyoxal and formaldehyde were not possible with this specific instrument, because these species are retrieved in different, not simultaneously probed spectral regions."

3. P. 5908 l. 25-27: "IO was not included as it was below the detection limit and was therefore omitted to avoid interferences with the glyoxal retrieval; for similar reasons BrO was not included in the formaldehyde retrieval." ! Removing a trace gas from the fit even if it is below the detection limit

can be wrong. The spectral structures of this absorber can still be in the spectrum, even if they are very weak, and thus have an influence on the derived trace gas concentrations of the other gases if they are removed. Thus an additional argument should be given why IO and BrO should also be so low that they can be ignored in the evaluation.

The first statement by Pöhler and Lampel is not fully correct since also the opposite can be observed. A known example is the OClO cross section: When included in a fit, it always results in the positive detection of OClO even though not present in the atmosphere. In addition, GC-MS measurements of the halocarbons $CHBr_3$, CH_2Br_2 and CH_3I were all <2 ppt during the first campaign and during the second campaign CH_2Br_2 and CH_3I were consistently <1 ppt and hence levels of IO and BrO are predicted to be below the detection limit. Including them in the spectral analysis resulted large negative values hence it is valid to ignore these species in the evaluation to avoid artificial optical densities. Hence we have removed the sentence from the revised manuscript completely.

However arguments should be given why BrO was still used in the MAX-DOAS evaluation p.5909 l. 16!

BrO is a stratospheric trace gas which also has a free troposheric column and hence has to be included in the MAX-DOAS fit for complete removal.

4. P 5908-5909: The spectral fit ranges are not explicitly mentioned (only the measured spectral range). They can only be read from Fig. 3.

The spectral fit ranges have now been explicitly mentioned in the experimental techniques section with the following sentences: "The spectral fitting window used was from 422-442 nm and the reference spectra fitted in this region were glyoxal (Volkamer et al., 2005a), NO_2 (Vandaele et al., 1998) and H_2O (Rothman et al., 2003)." And "Formaldehyde was measured in the near-UV from 316 - 358 nm and the spectral fitting range used was from 324 – 356 nm." For the MAX-DOAS measurements the following sentence is added: "Along with the HCHO absorption cross section, the other species fitted in the window from 336 – 357 nm were BrO, NO_2, O_3, O_4, and a Ring spectrum."

5. P. 5909 l. 1: The Absorbers O4 and possibly also HONO are missing in the HCHO retrieval window (316-358nm).

O4 was included in the MAX-DOAS analysis as stated on page 5909 line 16. HONO was not included in the LP-DOAS analysis due to interference with the NO_2 spectrum which resulted in large negative values and hence was excluded from the final analysis.

6. P. 5909 l. 15: Any statement which reference for the MAX-DOAS measurement was used is missing. An example of the MAX-DOAS fit is missing.

We have added the sentence: "The zenith spectrum from each scan is used as a reference." and also included a fit example.

7. P. 5910 l. 10-13: "It should be noted that the negative concentration values in Fig. 4 resulted from the DOAS fitting procedure to poor quality spectra, which usually resulted from reduced visibility." ! Even if visibility is poor, the derived measurement error should still make the derived negative

The large negative concentrations observed were during times of low signal to noise and these data points have now been removed from the figure. In addition, large variations in shift and stretch were observed during the campaign due to unstable temperatures within the LP-DOAS container. By calculating the stretch and shift values online within the analysis program for each spectrum the number of negative points is reduced due to better fitting of the relevant species and the Figure has been updated accordingly.

8. P. 5910 l. 10-13: "A geometrical conversion of the slant column densities for the 2 elevation angle assuming the formaldehyde is uniformly distributed in a layer 250m above the canopy gives good agreement with the LP-DOAS formaldehyde measurements (Fig. 7)." ! To use the whole potential of MAX-DOAS measurements, the authors should think about a vertical profile retrieval for aerosol and trace gases. With the presented approximation, radiative transfer is completely ignored. It thus gives here in this form not more information than already presented with the LP-DOAS measurements.

As was pointed out by Pöhler and Lampel in their introduction "Thus the presented observations expand significantly the amount of available data for such environments and improve our scientific knowledge." we would rather leave our MAX-DOAS data in the manuscript since this approximately doubles the HCHO data. Further, a full inversion was applied to data of one day which was relatively cloud-free and the mixing ratios close to the surface of the retrieved profile agreed well with the geometric conversion within the uncertainties. The applied inversion code using the radiative transfer model SCIATRAN was successfully compared in the study by Wittrock et al. (to be submitted in 2012). A full inversion is not possible for all data since patchy clouds were always present and contaminated the higher elevation angles. Therefore, we decided to analyse only the 2° elevation angle for the HCHO. As for the extra information that this data provides: We can best reproduce the LP mixing ratios with a 250m shallow layer as stated in the manuscript. This obviously provides an estimate of the vertical mixing and therefore is valuable additional information. We have clarified that by adding a sentence "A full inversion of the slant columns using radiative transfer is not possible for all the data due to the constant presence of patchy clouds contaminating the higher elevation angles, however, using one relatively cloud free day a full inversion was applied which gave good agreement with the geometric conversion."

9. P. 5911 l. 19-24: By comparing to satellite observations the large uncertainty of these satellite values should be stated.

We agree and added the sentence: "The errors in the monthly averaged satellite HCHO slant columns were typically around 2.5×10^{15} cm^{-2}."

10. P. 5912 l. 8: "boundary layer height of 1 km" ! Why this fixed value is used and what is the explanation by choosing this height.

Daytime measurements of the boundary layer height during the campaign found that it varied from around 800 – 1000 m during the day. The boundary layer did drop to around 200 m at night from around midnight to sunrise, however, this generally coincided with the periods of fog frequently

observed at the measurement site so fewer LP-DOAS measurements were available during these times. This point has now been mentioned in the manuscript.

11. P. 5912 l. 24-26: "Second, the light path was not horizontal over the forest canopy, but at an angle of 3 producing a vertical displacement of 180m between the retroreflector array and the LP-DOAS (Fig. 2)." ! For analyzing the data the minimum, maximum and average height above the canopy (or ground) would be relevant. Thus it has to be taken into account that there are also trees at the mountain side. Especially the isoprene measurements (and other measurements at the FAGE container) at 5m on the mountain cannot be defined as 185m altitude, as this is not the height of these measurements above the ground. A more accurate analysis of the measurement height would be nice.

Assessing the exact height of the canopy is naturally difficult (also since this is changing during the duration of the campaign) as is described in more detail in the sentences followed by the one quoted by Pöhler and Lampel. And although there were trees on the side of the mountain, the FAGE measurements were made above the canopy.

We have clarified this by adding the sentence: 'The isoprene measurements used for the diurnal profile in the model were recorded at 5 m on the FAGE container, which was positioned in a clearing on top of the hill at Bukit Atur above the level of the trees, and were therefore assumed to be at 185 m above the canopy in the model'

However, even accurate knowledge of the canopy height below the light paths would not improve the simulations since the terrain is in general highly variable. Obviously, a 1D model will not be able to reproduce this and it is also not the aim of this study.

12. P. 5914 l. 19-21: "The formaldehyde also mostly resides below 250m, which validates the assumption used in Fig. 7 to compare the MAX-DOAS slant column at 2 elevation angle with the LP-DOAS." ! Comparison of LP-DOAS and MAX-DOAS data should be made using mixing ratios retrieved for the later from radiative transfer analysis. The MAX-DOAS concentrations will have with these simplified assumptions larger uncertainty. Comparing these value like done is thus not very precise.

As mentioned in response to point 8 above, the geometric conversion of the MAX-DOAS slant columns to mixing ratios was found to be consistent with those retrieved from the full inversion on one day of measurements. Therefore, we feel it is valid to compare these values with those of the LP-DOAS.

13. P. 5915 l. 3-5: "However, it should be noted that convection is not treated explicitly in this 1-D model, although it is likely to increase the vertical and horizontal inhomogeneity of the chemistry in this environment." ! How convection can be ignored in such an environment? This should have a significant influence and would result in a much higher vertical mixing.

Sensitivity studies were conducted changing the value of the eddy diffusion coefficient to increase vertical mixing as explained in the manuscript (Page 5914, Line 23) and showed that doubling the coefficient only had a modest effect on the observed HCHO and CHOCHO (13% and 11% decrease respectively). The sentence has now been altered to "However, it should be noted that a detailed description of convection is not done explicitly in the model".

We do not agree since this is an average and the standard deviations have been calculated from the measured mixing ratios and are indicated on the figure so that the comparison can be made.

The absorption band of glyoxal at 455 nm was not used in the analysis due to overlap with the strong emission lines from the xenon arc lamp in this region. Including this band causes the residual being dominated by the Xe emission and hence could lead to overestimation of the glyoxal concentrations. Indeed, sensitivity tests were done on artificially constructed spectra by including this stronger absorption band and results suggested that excluding it was more reliable, albeit with a modest increase in the detection limits and errors. This can be seen through the large errors on the results. However, it can also be seen than the presence of glyoxal above these large detection limits is without a doubt even if we ignore the largest band. It should also be noted that although the absorption is lower in the window we have chosen, the differential structures are still large enough to allow for detection. The water structures were also well fitted and we did not see a large interference even in the artificially constructed spectra due to difference in absorption structures.

The window was chosen to fit BrO, HCHO and O_4 and as a result some of the HCHO structures had to be sacrificed.

This is indeed the case, however, although errors may be underestimated, the reported errors are 2 σ errors and detection limits which should give a good measure of the error in the results and beyond that positive detections are still observed. It should be noted that this is only the case for the LP-DOAS data, of which some days have been analysed without filtering and the mixing ratios do not show a difference.

The maximum optical density and root mean squared of the residual are 0.0015 and 7.1×10^{-5} respectively, less than the optical density of the glyoxal. The accuracy of the results is calculated using the data itself and the statistics backup their reliability.

e) Can the residual structures visible in the plot be found in other independent spectra or are they random structures?

The structures appear to be random and do not arise systematically in other independent spectra which has been stated in the manuscript.