

Interactive
Comment

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

D. Pöhler

denis.poehler@iup.uni-heidelberg.de

Received and published: 17 April 2012

Comments to:

Atmos. Chem. Phys. Discuss., 12, 5903–5937, 2012

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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:

1. P. 5908 l. 14: No information of background and lamp reference spectra is given. This is important for the measurements at these environments.
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.
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. However arguments should be given why BrO was still used in the MAX-DOAS evaluation p.5909 l. 16!
4. P 5908-5909: The spectral fit ranges are not explicitly mentioned (only the measured

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

spectral range). They can only be read from Fig. 3.

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

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

7. P. 5910 I. 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 values agreeable with zero. As this is not always the case it indicates that the measurement error is likely underestimated.

8. P. 5910 I. 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.

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

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

11. P. 5912 I. 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 retro-reflector 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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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.

12. P. 5914 I. 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.

13. P. 5915 I. 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.

14. P. 5915 I. 6-p.5916 I. 5: “the HCHO/CHOCHO ratio” → As can be seen in Fig 4 concentrations of especially HCHO vary strongly from day to day and period to period. Thus any analysis of the ratio of the two values which are not taken at the same time seem to be scientifically inaccurate and do not have a value.

15. P. 5927 Fig3: Please clarify that these are LP-DOAS evaluations. The other fitted absorbers should also be shown. This plot shows the potential problems of the measurement itself.

a) Why the spectral analysis of Glyoxal is not performed at the strongest absorption band at around 455nm. The strong water absorptions (440-450nm) can be excluded and would not influence the analysis at this absorption line. Here only an analysis with three time's weaker lines below 442nm is made where the fit itself is not very good (Fig.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

3). Including this line should reduce the fit error and reduce cross sensitivities.

b) Why does the HCHO fit window does not include more of the strong HCHO absorptions below 325nm?

c) It looks like the measured spectra are smoothed (red line) as they contain no high frequency noise. However if this is the case this has a significant influence on the retrieved measurement error as smoothing makes the pixel dependent from each other and thus the fit underestimates the fit error see Stutz and Platt, 1996.

d) Strong residuum structures can be found in the spectra almost in the same order like the absorption structures (especially for CHOCHO). Several structures of the reference cannot be found in the same way in the measured spectra (HCHO and CHOCHO). Thus it is not obvious from the presented fits that these absorbers can be found in these spectra especially with such a good accuracy like stated. Thus the given results seem not to be reliable; especially the detection limit may be much higher. This increases the question of how reliable are the data if typical concentrations are lower than these in the presented fit.

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

References: Stutz, J. and Platt U., Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least-squares methods, Appl. Opt., 35 (30), 6041-53, 1996.

Written by Denis Pöhler and Johannes Lampel

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 5903, 2012.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)