Atmos. Chem. Phys. Discuss., 8, S8152–S8158, 2008
www.atmos-chem-phys-discuss.net/8/S8152/2008/

Atmospheric
Chemistry
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Discussions

Interactive comment on “Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: airborne measurements” *by* M. Martinez et al.

Anonymous Referee #1

Received and published: 11 October 2008

General Comments

These are the first measurements of OH over a tropical rainforest, from 300m in the boundary layer up to the free-troposphere. Measurements close-by over the ocean enable the impact of biogenic emissions (in particular isoprene) on OH and HO2 concentrations to be studied.

As presented in an earlier paper this year in Nature (Lelieveld et al.), and in another paper by Kubistin et al., but not really discussed there, the OH and HO2 concentrations measured above the rainforest show large discrepancies with model calculations, which underpredict OH and HO2. This paper describes the measurements in greater detail.

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This paper represents the first description of the Mainz HORUS instrument, and justifiably it is described in some detail. Although these are the first measurements, the instrument is based on an instrument at Penn State, of which the authors have considerable experience, and the calibration method is tried and tested and used by other HOx groups around the world, although modifications in methodology have been necessary for this particular setup on the Learjet.

The paper is very well written and structured, and the results are most impressive.

The main criticism is in the description of some aspects of instrument performance and particularly in the results from its calibration. For example, to vary OH in the calibration the concentration of water vapour is changed, rather the preferable method of varying the lamp flux at 185 nm to vary OH, and repeating this over a range of H2O concentrations. Although detail is given, there are several instances where more detail is required or additional supporting statements required to either clarify the meaning or provide new evidence that there are no underlying problems with the methodology (e.g. curved calibration in fig 7). The accurate, quantitative detection of OH is perhaps one of the most difficult of all atmospheric measurements, and is even more difficult for an airborne platform where calibration under operating conditions is not always possible. Despite some of the shortcomings in my specific comments below, the authors have provided a very good description of the instrument, and have presented the data acquired during the fieldwork clearly and gained important insights.

The main conclusions of the field data are that the behaviour below 1000 m in the boundary layer is very different to that in the free troposphere (3000-5000m) above the rainforest, analysed in terms of diurnal variation, average OH and HO2 with altitude, and OH and HO2 versus OH primary production rate. This is interpreted as due to the influence of biogenic hydrocarbons (short lived) which survive in significant concentrations only in the boundary layer. There would seem to be a recycling mechanism producing OH from HO2 under NOx free conditions that is not currently understood and is not included in current atmospheric models. Further studies are needed to con-

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firm this, both within the canopy and in the boundary layer/free-troposphere above it. The major production and loss routes for OH and HO2 with altitude are also calculated using supporting data measured on the Learjet. The OH reactivity is calculated using measurements on the Learjet, and compared with the limited data available in the canopy itself.

This is a highly original submission, and contains very important new results.

Specific comments

Page 15495, line 11, the value of v (upper state) needs to be specified as zero

For the gated photon counter, what was the delay and width of the photon counting gate for the OH and HO2 channel?

Although laser-generated OH requires two photons to produce a signal, if the probe laser detecting the laser-generated OH optically saturates the transition, then the LIF signal with laser power may appear linear, although some curvature is always likely.

What was the flow of NO added to convert HO2 into OH?

For Fig 3 showing the effect on OH on pitch and roll, is this naturally occurring OH or OH generated by the in flight calibration system? (I assume the latter?)

R 1.2. Strictly a third body is required and M should be above the arrow.

What is the spatial overlap between the lamp flux field and the airflow field?

Page 15498, line 12, how is the 8% loss of OH between the calibration tube and the instrument measured. Was the lamp moved up the tube and the first order loss rate measured directly?

Did you check that the flow in the tube has a flat profile, perhaps by translating a capillary tube transversally across the flowtube, and sampling ozone generated by the lamp into the capillary. A flat ozone profile would indicate fully mixed flow.

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15498. line 12. Was the 5% reduction in flux due to O2 absorption at the centre of the tube or the integrated change from 0 to h?

15499, R3.1 to R3.2- give the yields for these two reactions next to the reactions.

When N2 is present, what % of O(1D) is removed by N2 compared to N2O? (at a certain typical value of N2O)

15500, line 1. Total flow is 5-35 slm, and N2O mixing ratio is 0-100%. Assuming that the 100% N2O flow is at the smallest total flow, that still implies a flow of 4 slm of N2O, which seems too big, or did I misunderstand? Also, at 100% N2O mixing ratio, the 185 nm absorption by N2O must be very large even for short pathlengths?

What is the expected increase in signal when switching from N2 to He, so that more O(1D) reacts with N2O to produce NO rather than being quenched to O(3P) by N2?

Line 10 . Although given below, the increase in pressure needs to be stated here.

In agreement with another comment given by R. Commane, the effect of quenching of electronically excited NO2* in the NOx box by N2O needs to be addressed.

15500, line 23. What is the DL of the Eco Physics NOx box?

Line 25. It is not sufficient to say reasonable agreement, this needs to be quantified.

Page 15501. Line 7. There is an implicit assumption in changing the cell pressure using different pinhole sizes that the heterogeneous loss of OH (or HO2) on the surface of the nozzle during entry is not a function of size. Some further discussion of this.

Line 10. Over what range of water vapour was this studied? How much did the sensitivity change over the range studied?

Line 17 Was T changed during any laboratory calibrations? Equation (5) What is the theoretical reduction in signal due to quenching due to water vapour with the integration gates used? Can g1 and g2 be given?

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Line 22. Density rather than pressure?

15502, line 6, data are plural

Line 12. Does it necessarily follow that a more time intensive calibration necessarily means it is more accurate?

15503. Line 5. How much OH can be made by the in flight calibration system. Can an estimate to be given. Fig 9 suggests that about 1x10(8) was produced by the lamp? This is close to atmospheric HO2 levels? (contrary to statement in line 5)

Line 15. Why does the presence of oil lead to curvature? If oil does contaminate the optics, would you not expect to see this also in the HO2 channel and see the same effect on sensitivity in this channel?

15504. Validity of the calibration for boundary layer versus the free-tropopshere is discussed. The instrument sensitivity seems to follow two regimes. One big change between the BL and FT is the amount of water vapour. Could there be a water vapour effect which is not captured properly in the calibration. The different temperatures of the BL and FT, combined with the different water vapour loadings, could lead to changes in the physical nature of the supersonic expansion, and possible changes in the degree of sequestering of radicals by clusters of water vapour that form in the jet. Other groups have seen water vapour dependencies which are inconsistent with just collisional quenching of OH by water vapour. Could it be a water vapour effect?

15508. Does the TUV code have cloudiness factors as a function of wavelength? The ratio of measured to calculated J(NO2) (due to clouds or other scattering) may need a correction in order to calculate other J mainly controlled by different wavelengths (e.g. J(O1D).

15509 . OH sinks. The total reactivity in the BL is calculated to be ˜ 7-9 s-1, dominated by isoprene. The results of Shina et al (one of the references given), although limited in temporal coverage, indicated a reactivity of up to 100 s-1 in the canopy. This should be given here as well as just in the conclusions.

15510. Lines 15 onwards. There are some earlier field measurements within a forest in northern Greece which showed measured OH to be considerably higher than modelled OH and could be mentioned in this discussion, Carslaw et al., Atm Env 35, 4725, 2001.

Table 1. Kinetic rate coefficients rather than just rates?

Table 2. The text discussed 2 sigma, but the table uses 1 sigma , need to be consistent.

Fig 3. need to be labelled as (a) and (b). Is this natural OH (and assuming it is constant) or OH made in by the in flight calibration system? I assume the latter as would not know if ambient OH was constant.

Fig 5. There appears to be a trend in the N2 data, with the photon fluxes changing (decreasing) with both total flow and N2O, although there seems no systematic effect for Helium. More discussion of this I think is needed. Add to this caption that these expts were done in the 3 mm chamber.

Fig 6. The flux measured for the open squares at 10% and 20% N2O seem to be about 20% different (and outside the error bars except for one point). Any comment on this? Add that these expts were done with the better Eco Physics NOx box.

Fig 7. The range of OH is quite a bit higher than ambient. Why is this plot curved? There should be some discussion about this. The humidity was varying (increasing it to make more OH), and so the sensitivity may also be varying with [OH], leading to the curvature. This is not the best way to vary OH , varying the flux at a constant humidity would be expected to give a linear plot of signal versus OH, and give a more appropriate sensitivity factor. This could be repeated for different water vapour concentrations across the ambient range encountered. 140 ppt of OH is 3.25 x 10(9) , need a statement to justify ruling out radical radical reactions leading to the curvature. (OH+HO2). For this plot what are the lines? Are these fits to the expressions developed in the text or just guides to the eye joining up the points? The pinhole sizes used to generate the different internal pressures should be given also in the caption.

Fig 8. What is the error for each point? The solid and dashed line shows the mean and standard deviation of all the points. Which internal pressure was this plot derived from? Presumably the same internal pressure for all points.

Fig 9. It is worth noting that the OH observed in the range 1-4x10(8) is less than the lowest OH concentration used in the calibration in figure 7 (25 ppt which is 6.25 x 10(8)).

Fig 10. Is the left group of points for higher altitudes, whereas the right hand group is for low altitudes. Mention this in the caption.

Fig 11. Are the linear and curved lines the calculated linear and quadratic dependence for OH or HO2 versus P(OH). The caption needs to say exactly what the lines refer to.

Figure 14. Shade is a better word than colour for the caption?

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 15491, 2008.

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