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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.

**M. Martinez et al.**

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We have marked questions by the reviewer with “R:” and our answers with “A:”.

R: 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.

A: To vary the lamp flux is not as simple as it may appear. The lamp flux calibration is complex and its uncertainty is a major part of the total uncertainty of our measurements. If the lamp flux is varied by changing the current, the lamp emission may change non-linearly. The use of filters would require to calibrate the lamp flux for each filter. We therefore prefer to keep the lamp emission constant, even if this means varying other parameters simultaneously with OH concentration

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

A: True.

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

A: The delay of the photon counting gate was 164 ns and the width was 436 ns, for both the OH and the HO2 channel.

R: 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.

A: A conservative calculation based on the laser power put into our White cells, the number of passes and the area illuminated in the detection volume yields an upper limit of 5% for the excitation.

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

A: The NO flow was 5-10 sccm, somewhat variable with cabin pressure. However, the HO2 signal dependence on the NO flow has been characterized and is constant within 10% between 5 and 13 sccm NO flow.

R: 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?)

A: It is naturally occurring OH and this is indeed not clear from the text. We suggest to

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introduce this information both in the text and in the figure caption.

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

A: ok

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

A: We propose to include this information on p 15497 line 20: 35mm x 16 mm x 16 mm.

R: 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?

A: Yes, see Answer to Ref. 2 Point 3.

R: 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.

A: Only 1 ppb of ozone is produced by our calibrator even if pure oxygen is used. Instead, we used our instrument to measure the OH and HO2 profile. The results showed that the concentrations do not change more than 15% across the cross sectional area. We propose to include this information on p 15498 line 11.

R: 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?

A: It was the integrated change as given in eq. 2, accounting for rapid mixing in the turbulent flow.

R: 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)

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A: Rate constants according to Sander et al., 2006:

R3.1 k1 = 2.8*10(-36) *M

R3.2 k2 = 2.6 *10(-11)

R3.3 k3 = 4.4*10(-11)

R3.4 k4 = 7.2*10(-11)

R3.5 k5 < 1*10(-12)

At 18% N2O in N2, 50%of the O1D is removed by N2 (R3.1+R3.2).

R: 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?

A: We used up to 15 slm of N2O. We don't understand the question: How is this too big ?

R: Also, at 100% N2O mixing ratio, the 185 nm absorption by N2O must be very large even for short pathlengths?

A: The 185 nm absorption by N2O is up to 60 % integrated over the 3mm height of the photolysis chamber, as stated on p 15500 line 8.

R: 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?

A: At 18% N2O in N2, 50%of the O1D is removed by N2 (through reactions R3.1 and R3.2). In addition, the sensitivity of the TECO detector is about 50% higher for NO when He is used as a carrier gas in comparison to N2. We propose to include this information on p 15500 line 4.

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

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A: During our calibrations the absolute pressure reached up to 2.5 bar at 35 slm total flow. We will include this information in the paper.

R: 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.

A: We agree (see response to R. Commane's comments).

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

A: The detection limit of the Eco Physics NOx box was 27 ppt for our measurements. We will include this information on p 15500.

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

A: There was an error in the evaluation leading to this figure that has now been corrected (see response to Ref.2). The values in the new plot agree within error limits, even though the measurements with the calibration tube at low N2O mixing ratios yield about 10% larger values. We propose to include this last sentence on p 15500.

R: 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.

A: We propose to add the following text on p 15502 line 13: "For instance, the ground calibration at different internal pressures is based on the assumption that the heterogeneous loss of OH or HO2 on the surface of the nozzle during entry is not a function of size. The validity of this assumption can be checked with the in-flight calibration, as well as temperature dependencies, which are otherwise solely based on calculations. "

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

A: The H2O mixing ratio was varied between 0 and 3.6% (H2O mixing ratios found during flights reached up to 3%). The sensitivity over this range dropped by 20% for OH and by 27% for HO2 in excess of the drop due to quenching. The correction of this additional dependency on the H2O mixing ratio was applied on the sensitivity measured at 1.5% H2O mixing ratio. See also answer to Ref. 2 Point 7.

R: Line 17 Was T changed during any laboratory calibrations?

A: No, all our ground calibrations are at ambient temperature. This is one of the reasons for the in-flight calibration. However, as the instrument was inside the wingpod together with the pumps, the temperature in the measurement cells never fell below 283 K, even when outside the air temperature was down to 250 K at 8 km altitude.

R: 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?

A: g1 was 164 ns, g2 was 600 ns. We propose to include this information on p15501 line 20. At 300K and 4.5 mbar, which are typical values during flight in the boundary layer where H2O is largest, quenching with 2.5% of water vapour leads to 40% decrease in signal, quenching with 3.6% of water vapour leads to 52% decrease in signal. See also answer to Ref. 2 Point 7.

R: Line 22. Density rather than pressure?

A: Yes, will be corrected.

R: 15502, line 6, data are plural

A: Will be corrected with “ . . . humidity data were available. When they were not . . . ”.

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

A: Certainly not. We propose to eliminate a seriously flawed “and therefore more accurate”.

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R: 15503. Line 5. How much OH can be made by the in flight calibration system. Can an estimate to be given.

A: As shown in Figs. 9 and 10, up to 4x10(8) OH and HO2 were produced, mostly depending on ambient H2O mixing ratio. The in-flight calibration was designed as a relative calibration. Therefore it was not necessary to map the actinic flux field of the lamp inside the inlet, which is not simple to do.

R: 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)

A: The highest levels of 2-4x10(8) were produced in the boundary layer, were atmospheric HO2 was also highest with concentrations of 7-15x10(8). So HO2 was indeed significant compared to atmospheric levels, but too small for a useful calibration. We propose to reedit the paragraph to “OH was produced during calibration periods of about 2 min, in concentrations typically higher than ambient by more than an order of magnitude, so the variability of the calibration signal due to changes in ambient OH was negligible. This was not the case for HO2, which is usually a factor 10 to 100 higher than OH in the troposphere, whereas the lamp produces equal amounts of OH and HO2. The HO2 produced during calibration was always less than atmospheric HO2 and comparable in magnitude to its natural variability during the calibration period. Therefore the in-flight calibration was used only to characterize the OH sensitivity of the instrument. ”

R: Line 15. Why does the presence of oil lead to curvature?

A: It does not. As is explained in the paper, contamination events lead to scatter, as they cause changes in sensitivity between flights and ground calibrations.

R: 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?

A: We would expect to see similar scatter in HO2 if the in-flight calibration for HO2 had

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provided data of sufficient quality, which it didn't. Similar, but not equal, as the effect on sensitivity will vary depending on where exactly how much oil deposits. See also our answer to R. Commane's last comment and to Ref. 2 point 11.

R: 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?

A: Could be. However, the water vapour effect described by Hofzumahaus et al. (1996) lead to an increase in sensitivity at H2O mixing ratios <0.3%, whereas in our measurements the change in sensitivity occurred at 1.5%. It could also be an effect of pressure or temperature, or a combined effect like condensation of water on a calibration lamp window (though this would have had to be very reproducible every time we calibrated in the boundary layer, which seems unlikely). So far we have not managed to find out.

R: 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).

A: The TUV code does not have cloudiness factors as a function of wavelength. Crawford et al. (JGR 2003) have shown that the effect of cloud cover on the actinic flux is up to 40% different at 320 nm compared to 420 nm depending on cloud cover and if the sun is occluded or not. In addition, the difference is positive in one case and negative in

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the other. As the GABRIEL campaign took place during the dry season, it was mostly sunny with low cloud cover, so the overall effect for our data is much smaller.

R: 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.

A: We propose to include the following sentence at the end of section 3.3: “Other species not measured on the Learjet could contribute to increase this number, as indicated by very high total OH reactivities of the order of 100/s measured during GABRIEL within the canopy (Sinha et al., 2008). ”

R: 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 modeled OH and could be mentioned in this discussion, Carslaw et al., Atm Env 35, 4725, 2001.

A: We propose to include this reference as well as other references about the measurements in forested areas which were also underestimated by the model (Tan et al, 2001; Martinez et al., 2003).

R: Table 1. Kinetic rate coefficients rather than just rates?

A: ok

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

A: We will change the value for the accuracy to 1 sigma in the text.

R: 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.

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A: It is ambient OH, and as said in the caption we show averages of changes in data where there was a fast change in pitch or roll within 10s. OH is not constant for each individual case but on average, as shown by the 1sigma standard deviations. In average the change in ambient OH should be 0 unless the change is induced by different angles of the aircraft, since there should be no correlation between changes of natural OH with the angle of the aircraft.

R: 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.

A: The data using He as a carrier gas are much more numerous and show no trend. The apparent trend in the 5 data points measured with N2 is within the 1 sigma error and therefore not significant, but the values are equal to the ones found using He within errors. The data shown were measured in the lab shortly after the GABRIEL campaign. Later measurements of the lamp flux showed no trend when using either N2 or He as a carrier gas.

R: Add to this caption that these expts were done in the 3 mm chamber.

A: Ok

R: 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.

A: There was an error in the evaluation leading to this figure that has now been corrected. This error had to do with the absorption by N2O, and had a larger effect on the calibration tube measurement than on those done with the photolysis chamber.

The values in the new plot agree within error limits, even though there seems to be an increase at low N2O mixing ratios measured with the calibration tube. We do not have an explanation for this increase.

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We propose to replace figure 6 with a corrected version (see also answer to point 6 raised by Ref. 2.)

R: Fig 7. The range of OH is quite a bit higher than ambient. Why is this plot curved?

A: We propose to introduce the following sentence in the caption: “The curvature is produced by quenching with water. ” See also answer to point 7 by Ref. 2.

R: 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.

A: If the lamp flux is varied by changing the current, the lamp emission may change non-linearly. The use of filters would require to independently measure the lamp flux for each filter. We therefore prefer to keep the lamp emission constant, even if this means varying other parameters simultaneously with OH concentration.

R: 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).

A: Photolysis of H2O produces equal amounts of OH and HO2. In the ground calibrator, the air speed in front of the lamp is 3.7 m/s, and the distance to the nozzle is about 30 mm, resulting in a travel time of less than 10 ms. Up to 150 ppt OH and HO2 are produced by the lamp, so the reaction with HO2 is the main chemical loss of OH. The lifetime for this reaction is about 2.5 s, much longer than the travel time, and losses due to this reaction amount to <1%. We propose to include the following sentence in p 15498 line 11: “Due to the short transit time of the air between the lamp and the instrument inlet of less than 10 ms, chemical losses are negligible. ”

R: For this plot what are the lines? Are these fits to the expressions developed in the

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text or just guides to the eye joining up the points?

A: The lines are the best fits using eq. 4. We will include this information in the caption.

R: The pinhole sizes used to generate the different internal pressures should be given also in the caption.

A: Information about the pinhole sizes used is given in the text on p. 15501 line 6 (0.7 mm to 1.5 mm). We will mention that the different pressures were produced with different pinhole diameters in the caption.

R: 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.

A: The parameter C0 describes the dependency of the sensitivity on the optics and the detector sensitivity, as described on p. 15501. The dependency on pressure is described by other parameters in eq. 4. Thus the values of C0 plotted in Fig. 8 were derived from all calibrations performed on the same day at all pressures used using eq. 4. The error for each point can on principle be derived from the fit, but the variability of the values is a good measure for the error. C0 should be constant during a campaign, as long as the instrument setup is not changed. Problems during the campaign with the pump as described in the text lead to variations of C0 which were later corrected using the in-flight calibrations, as described in section 2.3.3, where the errors of the resulting total sensitivity are given.

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

A: We propose to include the following text at the beginning of section 2.3.3: “The ground calibrations during GABRIEL were made using HOX concentrations close to ambient HO2 concentrations but 2 orders of magnitude higher than ambient OH concentrations. The concentrations during in-flight calibrations were considerably lower, though still more than an order of magnitude higher than ambient OH. ”

R: 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.

A: To make this clearer, we propose to mention that less OH is produced by the in-flight calibrator at higher altitudes due to lower ambient humidities also in the caption, even though this is already being explained in the text.

R: 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.

A: We assume the referee means Fig. 12. We propose to add “The lines show fits through the data assuming linear dependence on P(OH) for OH and on the square root of P(OH) for HO2. ”

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

A: ok

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