

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

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Received and published: 1 February 2010

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

R: I found two major weak aspects in the manuscript: first, the calibration plot for OH has an unexpected curvature, which has not been reported for other HOx instruments. It is not described if this curvature also occurs for the second HO2 axis.

A: The referee refers to the curvature in Fig. 7. This curvature is not unexpected and mostly due to quenching with increasing water mixing ratios added to the calibration gas. When OH is increased together with humidity in the calibration gas, quenching with water has this effect in all HOx instruments based on laser-induced fluorescence. The remaining curvature not due to quenching is discussed in detail in our answer to comment 7.

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R: Secondly, the authors mention that OH concentrations linearly depend on the production rate while HO2 has a square-root dependence. In this case, the relative variability of HO2 should be smaller than that of OH, but it is not the case in Figure 13. From these two points, I suspect that the HO2 determination is not of sufficient quality and therefore that there is another possibility to explain the higher-than-expected OH, where the observed HO2 concentrations were lower than reality by some reasons and thus the high HO2 could explain the OH reproduction rate by the ordinary HO2 + NO reaction at the observed NO concentrations. The paper is publishable only after the authors successfully reject this possibility.

A: The comparatively high variability of the HO2 data is due mostly to the fact that we used 10 s data for HO2 in Figure 13, whereas 1 min data were used for OH in the same figure and for both OH and HO2 in Figure 12. We agree this is very confusing and suggest to redo Figure 13 using 1 min data also for HO2. However, it should be noted that the scatter is not only induced by variations in the production rate. In the boundary layer the mixing ratios of OH and HO2 show only a weak correlation with the OH production rate, which most likely is due to additional sources in the forest boundary layer, as we discuss in the paper. Under these conditions the relative variability of HO2 cannot be expected to be significantly smaller than that of OH. In the panels showing data from the free troposphere, we used all data above 3000m altitude, with highest altitudes at 8000m. This another reason for scatter in those panels. We suggest to restrict the data shown to altitudes between 3000 and 5000m.

Like OH, HO2 measured was actually also several times more abundant than predicted by models (see e.g. Lelieveld et al., 2008). We mention this in the abstract and propose to add a sentence in the Results as well as in the Conclusions section to further emphasize this fact. It is therefore highly unlikely that our HO2 observations are too low, and we have no reason to doubt the quality of our HO2 data.

R: 1. Which lasers (pump and dye) are used to produce 308 nm photons with 3-6 mW power?

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A: As stated in the paper, the laser system is similar to the one in the ATHOS instrument described in detail by Faloona et al. (2004). We propose to exchange the following sentence in the paper, p 15494 line 24: "From the laser system, similar to the one in ATHOS and mounted inside the Learjet cabin, the laser light was channeled to the detection module through 10m optical fibers through the wing. " for: "The laser system is similar to the one in ATHOS, and consists of a tunable dye laser (Wennberg et al., 1994), pumped by a diode-pumped Nd:YAG laser (Navigator I J40-X30SC-532Q, Spectra Physics, Mountain View, CA). The pulse frequency was set to 3 kHz. The two laser assemblies are mounted on either side of a rigid vertical plate, which was mounted on a rack inside the Learjet cabin. The laser light was channeled to the detection module through 10m optical fibers through the wing. "

R: 2. Page 15496, line 25 and Figure 2. Where do the points with $X=0.1$ and 0.4 in the upper right panel correspond to the positions in the upper left panel and in the lower panel?

A: We propose to introduce a scale in the upper left panel to clearly indicate the points.

R: 3. How did the authors measure 8 percent heterogeneous loss of OH? How about HO₂?

A: The wall loss was quantified as described by Faloona et al. (2004) by using a longer calibration tube with three equidistant windows. By situating the Hg lamp module at each of the three windows in the calibrator consecutively, a measure of the wall loss within the calibrator can be extrapolated to the inlet of the instrument. Results agreed within 3 percent for different water vapor concentrations and fluxes between 45 and 55 slm. For HO₂ the wall loss was 2 percent, significantly lower than for OH as might be expected. We propose to include this paragraph in p 15498 line 12.

R: 4. Page 15498, equation (2). Which value was used for $\sigma(\text{H}_2\text{O})$ at 184.9 nm?

A: We used $61555; \text{H}_2\text{O} = 7.2 \times 10^{-20} \text{ cm}^2$, as suggested by Heard and Pilling (2003),

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based on results by Cantrell et al. (1997) and Creasey et al. (2000). We propose to include this information in p 15498 line 7.

R: 5. Page 15500, line 25 and Figure 6. The lamp flux with the calibration tube seems to be ca. 10 percent lower than the case measured with the 3mm photolysis chamber. Can it be attributable to the lower transmission of the 185 nm light through the calibration quartz tube?

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 windows used on the calibration tube and the photolysis chamber were of the same material. 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. We propose to replace figure 6 with a corrected version.

R: 6. Page 15501. The ground calibration was made with apertures with different sizes to cover the wide range of pressure in the chamber during flights, while the pressure out of the chamber was kept at 1 atm. The flow condition during flight, when the pressure out of the chamber is less than 1 atm, would be different from the conditions for the ground calibration even when the inside pressure is reproduced. Especially, the broadening of the air beam would be different. This must result in differences between the ground and in-flight calibrations. In addition, the thermal distribution over the rovibronic states (of OH X state) will depend on temperature and thus the relative population for a state to be excited by the laser via the selected transition would be different at lower temperatures during flights from that for the room temperature condition during the ground calibration, even when the laser probes at the region where the air beam is well thermalized. This must also result in differences between the ground and in-flight calibrations. The authors should comment on this.

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A: As the difference between pressures outside and inside the chamber is large even when flying at high altitudes, the air beam expansion behind the critical orifice should depend only on the mass flow, which is proportional to the chamber pressure. Thus the beam shape should be the same as long as the chamber pressure is the same, independently if this chamber pressure is due to a smaller orifice at ground pressure or a larger one at 200 mbar. In order to verify this assumption, we have done the in-flight calibrations. These are not absolute calibrations, but should show if there are any effects due to changing conditions during flight which are not adequately characterized on the ground. The linear relationship between the sensitivities of ground and in-flight calibrations shown in Fig. 10 shows that for altitudes between 2000 and 8000 m a.s.l., where the in-flight calibrations were performed, no significant effects exist. A different relationship was found for altitudes below 2000 m a.s.l., though also a linear one. As discussed in the paper, we do not know if the reason is a change in instrument sensitivity incorrectly characterized by the ground calibration, or a problem with the calibration source. The temperature dependency of the population of the rovibronic states of the OH electronic ground state is calculated according to Dieke and Crosswhite (1962) and taken into account. We propose to include this sentence on p 15501 line 2.

R: 7. Figure 7. The non-linearity of OH signal against the expected OH concentration could be fatal. It seems that the H₂O concentration is also changing together with the OH concentration (x-axis). What is the typical α_3 value? Is this term significant in the ambient H₂O concentration range? What is the dependence in the second HO₂ axis signal? Is it independently measured and then taken into account before deriving ambient HO₂ concentrations?

A: As is stated in the caption of Fig. 7, different OH concentrations were produced by irradiating air with varying humidity. The major part of the nonlinearity in the figure is caused by quenching of the excited OH with H₂O and is taken into account by the quenching factor Q. The effect of quenching is the same for the OH and the HO₂ measurements.

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Additional water dependencies of LIF sensitivities have been observed before (e.g. Hofzumahaus et al., JGR 1998). In our measurements, change in sensitivity due to the additional water effect on sensitivity not due to quenching ($\alpha_3 \cdot \text{H}_2\text{O}$) was a drop of 15 percent for OH and 20 percent for HO₂ in sensitivity for water mixing ratios of 2.5 percent found at the lowest altitudes compared to dry air. It was independently measured and taken into account for HO₂.

We propose to include the following sentences in p 15501 line 22: "The major part of the nonlinearity in Fig. 7 is caused by quenching of the excited OH with H₂O and is taken into account by the quenching factor Q. The change in sensitivity due to the additional water effect on sensitivity not due to quenching ($\alpha_3 \cdot \text{H}_2\text{O}$ in eq. 4) was a drop of 15 percent for OH and 20 percent for HO₂ in sensitivity for water mixing ratios of 2.5 percent found at the lowest altitudes compared to dry air. The drop due to quenching is about double this amount. "

R: 8. Figure 8, Why C₀ values for the HO₂ axis is higher than that for OH by an order of magnitude? Was the sensitivity for the HO₂ axis higher than that for the OH axis?

A: The sensitivity for the HO₂ measurement cell is lower than that for the OH cell for two reasons: approximately a factor 6 more laser power was used in the OH cell, and there is more wall loss until the air reaches the HO₂ cell (however, HO₂ loss is smaller than OH loss on the walls). The C₀ value however is just one factor contributing to the sensitivity, which is the product of several factors according to eq. 4. These factors have been determined from a best fit to the ground calibration data. This fit resulted in C₀ parameters an order of magnitude different for OH and HO₂, but also the other parameters were different for OH and HO₂, leading to sensitivity values for HO₂ about a factor 3 lower than for OH. For some parameters a difference between OH and HO₂ is physically reasonable, e.g. the dependency on density can be expected to differ due to different loss rates on the inlet walls. For other parameters, like C₀, no physical reason is evident. The fact that the values for C₀ differ by an order of magnitude indicates that the functional dependency on density, pressure or temperature may not

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be physically correct. However, the parameters used result in an adequate description of the sensitivity determined during the calibration under varying conditions, covering the whole range of densities and humidities that occurred during flights.

We propose to include the following sentence in p 15501 line 16: "This parameterization may not be physically correct, but accurately describes the sensitivities observed." and the following sentence in p 15502 line 2: "The sensitivity for HO₂ was about a factor 3 lower than for OH due the combined effect of higher laser power used in the OH detection cell and lower wall loss of HO₂."

R: 9. Page 15503, Does in-flight calibration really produce same amount of OH and HO₂ at the inlet of the instrument? What is the typical time for the air to travel between the radical production zone and the inlet pinhole of the instrument? Can the authors assume no chemical loss during the travel? Likewise in the ground calibration, do the authors need to take into account any chemical losses of OH and HO₂ other than heterogeneous loss of OH?

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.

Air speed in the shrouded inlet is 15-20 m/s (see Fig. 2) The distance between the lamp and the instrument nozzle is about 60 mm, so the travel time is less than 4 ms. This is very short even compared to the shortest ambient air OH lifetimes of 100ms (see Fig. 16). Heterogeneous OH loss on the wall is prevented by the shrouded inlet, as discussed in section 2.2.

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." and the following sentence in p 15496 line 27: "The

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velocity is still high enough to prevent any significant chemical losses while the air passes through the shrouded inlet."

R: 10. Page 15503, is the lamp switched on only for 2 min? If so, did the photon flux become stable during such a short period?

A: We used the OH signal to determine when the lamp flux had reached a stable value. On switching on the lamp, the OH signal increased during approximately 30s. After that, no significant trend was detectable. This was the case even at low ambient temperatures, as the lamp was heated.

R: 11. Page 15503, line 23. Are the authors sure that the optics for the HO₂ axis were not contaminated?

A: No we are not. We therefore assume that similar corrections would apply to HO₂ as for OH, and take into account the error derived from not applying these corrections in the paper. This is why we state a lower accuracy for HO₂ than for OH.

R: 12. Somewhere in section 2, the authors should specify the detection limit of OH and HO₂. Also, the authors should specify how efficiently HO₂ is converted to OH by adding NO.

A: The average detection limits for 1min integration times and a signal-to-noise ratio of 2 varied with altitude and ranged between 0.04 ppt in the boundary layer and 0.02 ppt at 8 km altitude for OH, and around 0.08 ppt for HO₂. We propose to include this sentence at the end of section 2.1.

R: 13. Page 15505, line 12. It is understandable that OH concentrations are low in the model with high isoprene concentrations. But why HO₂ concentrations can also be low?

A: Under low-NO_x conditions, the main sink for HO₂ is the reaction with peroxy radicals, and NMHC oxidation enhances peroxy radical formation.

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R: 14. Page 15505, line 20. UTC minus 3“h”

A: ok

R: 15. Page 15506, line 21. Do the authors assume that the sink of OH has little diurnal variation even when it is dominated by the OH reaction with isoprene?

A: We propose to reword the text as follows: “This source varies strongly throughout the day mainly due to changing photolysis rates. If the sinks of OH are less variable, which is usually the case in the absence of variable local emissions, a linear correlation of OH with the OH production rate from ozone photolysis is expected.” As we indicate in the same paragraph, the correlation is weak in the boundary layer, where isoprene is high.

R: 16. Page 15506, lines 24- 26. The authors should add references suggesting the correlation between HO₂ and the square root of the production rate.

A: Penkett, S.A., Monks, P.S., Carpenter, L.J., Clemitshaw, K.C., Ayers, G.P., Gillett, R.W., Galbally, I.E., and Meyer, C.P., Relationships between ozone photolysis rates and peroxy radical concentrations in clean marine air over the Southern Ocean, *J. Geophys. Res.*, 102, 12805-12817, 1997.

Bloss, W. J., Lee, J. D., Heard, D. E., Salmon, R. A., Bauguitte, S. J.-B., Roscoe, H. K., and Jones, A. E., Observations of OH and HO₂ radicals in coastal Antarctica. *Atmos. Chem. Phys.*, 7, 41718211;4185, 2007.

R: 17. Page 15506, line 28- page 15507, line 1. Can we expect the comparable slope for different altitude ranges by plotting mixing ratios by some reasons, or was it just fortuitous?

A: As long as the composition of the atmosphere is similar in those altitude ranges and reaction rates don't differ due to changes in temperature and pressure, similar mixing ratios of OH can be expected. This seems to be the case for the altitude ranges between 3 and 5 km and below 1 km over the ocean.

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R: 18. Figure 13. Are all the dataset obtained during the campaign are plotted? Or only data for selected flights are used?

A: The plot includes the complete dataset from all flights in the specified altitude ranges.

R: 19. Figure 13, if HO₂ has a linear correlation with the square root of the radical production rate in FT, the relative variation of HO₂ should be smaller than that of OH. However, it seems not in Figure 13; HO₂ is fluctuating much between 10 and 40 ppt. Why is it?

A: It is due to using 10 s data for HO₂ in Figure 13, whereas 1 min data were used for OH in Figure 13 and for both OH and HO₂ in Figure 12. We agree this is confusing and suggest to redo Figure 13 using 1 min data also for HO₂.

R: 20. Page 15507, line 25 and Figure 14. What was the dominant wind direction, from ocean to land?

A: Throughout the campaign southeasterly trade winds transported Atlantic air over the Guyanas. We suggest to include this sentence on page 15493 line 29 and to add “as the air is transported over the forest by the southeasterly trade winds” in line 22 page 15507.

R: 21. In section 3.1, I wondered how uniform J values were over ocean and forest regions (with more convection and more clouds over the continent, and thus lower J values?)

A: It is true that there were more clouds over the continent, leading to somewhat lower J values: $6.3 \times 10^{-5} \text{ s}^{-1}$ compared to $7.5 \times 10^{-5} \text{ s}^{-1}$ over the ocean averaged for noontime data. OH production from O₃ photolysis however was very comparable (0.36 ppt/s), because the lower J values were compensated by somewhat higher O₃ over the forest (18.5 ppb compared to 14.7 ppb over the ocean). We propose to include this information on page 15506 line 19.

R: 22. Page 15508, lines 3-5. Did the author assume that the photolysis of organic

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peroxide yields two molecules of HOx radicals?

A: Yes, because only the sum of peroxides was measured and we preferred to calculate an upper limit rather than to underestimate the OH production. We propose to include this information in section 3.2.

R: 23. In section 3.2, the measured HCHO concentrations are used in the analysis. The authors should mention its measurement technique and refer to the description (Ganzeveld et al?)

A: A summary of the species measured and the measurement techniques used during Gabriel can be found in in Stickler et al., 2007, referenced in the introduction. We will include another reference to this paper here.

R: 24. For Figure 16, were MACR and MVK separately measured and their reactivities were summed? Or were they measured as a sum by a PTR-MS instrument and some reactivity weighting was assumed to calculate OH loss rates?

A: MVK and MACR were measured as a sum by a PTR-MS instrument and the mean of their reactivities was used to calculate OH loss rates. We propose to include this information in section 3.3.

R: 25. For Figure 16, only midday data are used?

A: Data from all flights were used for this figure, we will mention this explicitly in the caption.

R: 26. The first part of conclusion, describing similarity to Ren et al. (2008), should be a part of discussion.

A: Why? This paragraph is about how our conclusions fit into the picture with previous findings, therefore we think it should be part of the Conclusions section.

R: The sentence "Furthermore, atmospheric chemistry transport models tend to strongly overestimate isoprene in the boundary layer over forests, consistent with an

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underestimate of OH" (page 15510, lines 24-26) is misleading. The authors discuss underestimation of OH under the conditions where isoprene concentrations are constrained to the observed concentrations, which is nothing to do with the model8217;s overestimation where isoprene concentrations are overestimated.

A: We propose to rephrase this sentence to better explain our meaning: "Furthermore, atmospheric chemistry-transport models using isoprene emission inventories tend to overestimate isoprene in the boundary layer over forests. To get around this problem, isoprene sources have been reduced in models by a factor of two or more (von Kuhlmann et al., 2004; Jöckel et al., 2006). OH mixing ratios higher than can be explained with current chemistry schemes could solve this discrepancy. "

R: 27. Page 15511, line 17. Why do the authors need to invoke HO2 interference? HO2 needs to be rather increased to explain the observed high OH concentrations. And moreover, the origin of HO2 interference, if any, could have different origin from the OH interference, because NO is added.

A: An OH interference alone cannot explain all our results. As explained above, HO2 measured was actually also several times more abundant than predicted by models. We mention this in the abstract and proposed to add a sentence in the Results section to further emphasize this fact. We will also mention this here.

R: 28. Figure 17 left panel, OH loss needs to be more than estimated in the FT over the ocean?

A: No, they agree within the variability of the data.

R: 29. The authors relate the missing source of OH with isoprene. Why don't they plot the missing source strength as a function of isoprene concentration? This diagram would be more convincing than Figure 18.

A: Yes indeed. We propose to replace Figure 18.

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