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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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General comments: The authors describe details of a newly-developed airborne instrument HORUS to measure OH and HO2 radicals installed in a wingpod of a Learjet. The ground and in-flight calibration methods are presented. The basic features of the OH and HO2 observed by the instrument during the GABRIEL campaign are illustrated, including diurnal variations, altitude dependence, forest-ocean contrast, and the dependence on the primary production rate of the radicals. On the basis of the steady state analysis, the authors conclude that unknown conversion from HO2 to OH must be present to explain the higher-than-expected OH levels over the forest.

The description of the instrument is new and the conclusion is important, shedding light into unexplored photochemistry over the tropical rainforest. However, I found two major weak aspects in the manuscript: first, the calibration plot for OH has an unexpected

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curvature, which has not been reported for other HOx instruments. It is not described if this curvature also occurs for the second HO2 axis. 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.

Specific comments:

1.Page 15495, line9. Which lasers (pump and dye) are used to produce 308 nm photons with 3-6 mW power?

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?

3.Page 15498, line 12. How did the authors measure 8% heterogeneous loss of OH? How about HO2?

4.Page 15498, equation (2). Which value was used for sigma(H2O) at 184.9 nm?

5.Page 15500, line 25 and Figure 6. The lamp flux with the calibration tube seems to be ca. 10% 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?

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

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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.

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 a3 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?

8.Figure 8, Why C_0 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?

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?

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?

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

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contaminated?

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.

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?

14.Page 15505, line 20. UTC minus 3"h"

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?

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

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?

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

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?

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

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?)

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22.Page 15508, lines 3-5. Did the author assume that the photolysis of organic peroxide yields two molecules of HOx radicals?

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?)

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?

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

26.The first part of conclusion, describing similarity to Ren et al. (2008), should be a part of discussion. The sentence "Furthermore, atmospheric chemistry transport models tend to strongly overestimate isoprene in the boundary layer over forests, consistent with an 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 model's overestimation where isoprene concentrations are overestimated.

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.

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

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.

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

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