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Atmospheric
Chemistry
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Discussions

Interactive comment on “Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: comparison of measurements with the box model MECCA” *by* D. Kubistin et al.

Anonymous Referee #3

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Review of "Hydroxyl Radicals in the tropical troposphere over the Suriname rainforest: comparison of measurements with the box model MECCA" by Kubistin et al.

General. This paper describes comparisons between a zero-dimensional (i.e. without transport) photochemistry model and airborne measurements of hydroxyl and perhydroxyl radicals. The model is constrained by measurements of controlling species from this study and earlier studies. The radical measurements are significantly greater than the model values. Several possible changes to the model that might improve the agreement are examined.

This analysis is interesting and very important to the interpretation of atmospheric free

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radical measurements. This paper is likely publishable, but I believe several important issues need to be resolved before it is. Below, I describe several issues that I identified in this version of the paper. There may be other issues, so I suggest all of the co-authors critically review the content and logic of this paper.

Specific (1) Several papers have been written about the GABRIEL campaign, including at least three papers on measurements and modeling relevant to the present paper (Martinez et al., Butler et al., and Stickler et al.). While these papers are referenced, it would be useful if the conclusions of those papers were discussed relevant to the conclusions of the present paper. The present paper should be able to stand on its own, but should also give the reader an idea of how the approaches used in this paper are similar and different from these other papers, and other similar published analyses of free radical measurements. It should also be clear what the present paper adds to the analysis. Why write another paper on the comparison of radical measurements and models? While it may be true that these are the first OH and HO2 measurements in a tropical forested environment, there have been many studies in isoprene rich regions that are relevant. These previous studies should be quantitatively compared to the results of the present one.

(2) The important variables that control OH and HO2 are discussed in the paper, but their values are not given. While they may be reported in other papers, it is absolutely crucial that they be reported in this paper as well. It may be that reporting median values and their ranges for the four cases discussed in the paper is sufficient, or it may be that more detailed descriptions are needed. Referee #1 mentions formaldehyde specifically in this regard, and I wholeheartedly agree. I also agree that formaldehyde and peroxides should be modeled constrained by the observations and using the steady state assumption.

(3) It is also important to realistically assess the role of measurement uncertainties in the radical measurement-model comparisons. These uncertainties include the radical measurements themselves, but also the controlling variables. Among the rele-

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vant topics, the paper should discuss possible interferences in LIF instrument in the isoprene-rich (and associated oxidation products) forested environment. For example, is there any chance that artifacts are formed within the instrument from isoprene-ozone chemistry? Is there a chance that isoprene measurements are in error? Are there interferences in the measurements of formaldehyde? What are the likely errors in the cloud corrections of j(O1D) using changes in j(NO2)? What are the errors caused by unmeasured but likely present species (e.g. glyoxal, acetaldehyde, glycoaldehyde, hydroxyl-acetone, etc.)?

(4) The possible errors in the kinetic and spectroscopic parameters were not addressed in this paper. It would not be hard to run the model for a few conditions in the Monte Carlo mode, changing these parameters over their expected range of uncertainties.

(5) Several issues are put forward that improve the measurement-model differences. None by themselves are sufficient to bring the two into agreement, but why not combine all of them and see what happens? There might be several problems with the chemistry that conspire to cause the measurement-model differences.

(6) The model mechanism and solver should be checked carefully. I developed a simple steady state model in an Excel spreadsheet. It doesn’t have detailed isoprene chemistry, but rather increases the amount of methane equivalent to the isoprene reactivity. This produces copious amount of formaldehyde and peroxides (which would be other carbonyls and organic hydroperoxides in a detailed isoprene scheme) which are calculated using the steady state assumption as well. At about 1-2 ppb equivalent isoprene, the model yields OH values of about 4 x 106 cm-3 and HO2 values of about 1 x 109 cm-3, in close agreement with the low altitude over-land measurements. At 6 ppbv equivalent isoprene, the OH drops to 2.2 x 106 cm-3, and HO2 increases to 1.3 x 109 cm-3. These measurement-model differences are likely within the uncertainties in the measurements and the model.

Technical comments: Page 15241, line15-16. Should "irradiation intensity" be "radiation intensity".

Page 15243, line 3. "topical" should be "tropical".

Page 15243, line 11. It states that *all* species relevant for fast photochemistry were measured, but later some VOCs were inferred. Also, apparently NO2 was not measured. Perhaps the statement should be that "many important species relevant for fast photochemistry were measured".

Page 15244, line 25. The reason for the selected ozone column should be discussed (i.e. average for the flight days, average for the month, or whatever).

Page 15245, line 1. As stated above, I am concerned about scaling j-value changes from clouds and aerosols that are predominately in the UV-B region to j(NO2) that is weighted toward the UV-A.

Page 15245, line 20. The symbolism for the deposition rate isn't really described. As I understand it, 1.35 x 10-5...-4 s-1 means ranging 1.35 x 10-5 to 1.35 x 10-4 s-1. I would suggest just spelling this out in the text. Do these small deposition rates have any impact on the radical levels?

Page 15246, line 17. It is stated that the underestimation of OH is an indication of the inadequacy of the hydrocarbon chemistry scheme. Couldn't this also be indication of problems with the measurements or both?

Page 15247, line 5. "ranging from 0 and 3" should be "ranging from 0 to 3".

Page 15253, line 21. The statement that "OH recycling via reaction of HO2 is weak compared to primary production" is worrisome. Even in low NO environments, the recycling of OH is important. I calculate (for NO=13 pptv) recycling rates that are about twice the primary production.

Page 15254, line 23. My little model for the forest afternoon case gives [HO2]/[OH] = 241, close to the observed value of 234, if I use an equivalent isoprene of 2 ppb. For the forest morning case, it gives a ratio of 132, using equivalent isoprene of 0.5 ppb, compared to the observed value of 127. I don't think lack of understanding in OH-HO2 cycling is a serious problem. It may be that isoprene measurements are the problem.

Page 15255. In order to under recycling in the forested troposphere, don't you want to run the model so it agrees well with the radical observations? The calculations in section 4.5 were run with the model base case. Wouldn't it be better to run them with the OH and HO2 constrained?

Page 15256, line 7. Suggest changing "independently" to "independent".

Page 15258, line 1. Change "combing" to "combining".

Page 15268. The results for the reference run just don't seem to make sense. To obtain such low OH values, I suggest there is a mistake in one or more rate coefficients, or species concentrations, or parameter (i.e j-values, deposition velocities). I can only get my little model OH to go below 1 x 106 cm-3 if I increase the equivalent isoprene to 30 ppbv or more.

Figures 10,12,14,16, and 17. I suggest a logarithmic scale on the ratio plots, so the values at ratios less than unity are clearer.

Figure 15 caption. Suggest "Comparison" rather than "Deviation".

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 15239, 2008.