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Atmospheric
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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 #1

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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.

This paper uses measurements from the GABRIEL campaign to examine the HOx budget over a tropical forest in Suriname, South America via fully constrained box model predictions of HOx compared to the observations. A significant model underprediction of both OH and HO2 which is correlated to isoprene concentrations is used as evidence of a large missing source of OH, speculated to be due to a very large OH-return during isoprene oxidation. I find this paper to be in generally good shape, but suggest some additional discussion that could strengthen it.

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Interactive Discussion

Discussion Paper

OH loss rate measurements: Sinha et al. 2008 report on OH reactivity measurements near the surface during GABRIEL and suggest that the OH reactivity due to isoprene and its products, acetone and acetaldehyde makes up as little as 35% of the total measured reactivity. This requirement for additional OH reactivity would greatly exacerbate the missing source that you find is needed in this study. A comment on this is necessary.

Isoprene flux: Assuming that the measurements for OH are accurate, and that the chemistry in the box model is similar to that used in global models, the much higher-than-modeled OH concentrations would result in a significantly decreased isoprene lifetime, which suggests that larger fluxes of isoprene are required relative to what is currently assumed in global models. Is this larger flux realistic? This issue is investigated with a global model in Butler et al., but some discussion here of the realism of changes in our understanding of the isoprene flux would be beneficial.

I am confused about the different conclusions drawn by this paper and the Butler et al. paper with respect to the required OH return in order to explain observations. This paper suggests that an OH source stronger than the OH loss from isoprene is required ($>$ 100%), while the Butler et al study suggests an OH return of 40-50% during isoprene oxidation is required. These are significant differences. Some clarification here would be useful.

Table 4 reports a fairly low sensitivity of HOx predictions to a factor of 2 change in CH2O, but nowhere in the paper is it stated what concentrations of CH2O were observed. What were the uncertainties and LOD for the CH2O measurement? For all of the standard runs and sensitivity runs, it appears that CH2O has been constrained to the observations. CH2O is in steady state during daylight hours, and is photochemically formed from methane and NMHC oxidation. As a result, the HOx source/loss pathways from hydrocarbon oxidation flow directly through CH2O, and by constraining the model to observed values, the HOx cycling process as described by the chemical mechanisms is essentially short-circuited. (e.g., Figure 13 would more accurately reflect the cycling if CH2O were shown to be produced from the RO2+NO reaction in additional to photolyzing to form HO2.) This is a particularly important point when we are talking about isoprene oxidation, which is a strong production term for CH2O. Additionally, by unconstraining CH2O, you would add a very useful diagnostic to your analysis.

It would be instructive to compare how the model does in predicting CH2O for the standard runs (predicted OH) relative to OH set at observed values. Does the greatly decreased lifetime of isoprene produce CH2O outside of the range of uncertainty in the measurements, or is it consistent with them? The sensitivities shown in Table 4 would also seem to be more fully represented if CH2O is calculated, allowing the chemistry to follow the full mechanistic production and loss pathways.

Additional reference (Section 4.3): Thornton et al. (2002) (reference included at bottom of review) found that the observations from the SOS campaign in the Nashville area could only be reproduced by their model if they included a decrease in the peroxide formation rate (RO2+HO2->ROOH) by about a factor of 10 via either rate reduction or changes to product yield. This earlier study should also be included in your discussion of this possibility for the GABRIEL study.

Rate constants: The rate constants listed in the MECCA Chemical Mechanism supplement appear to be outdated (JPL 2003). In particular, several rates that directly impact OH concentrations have been updated and published in subsequent JPL recommendations (JPL 2006). Because this paper is focusing on the HOx budget, the most recent recommendations should be used, or if you are using the updated rates already, the supplement should be corrected.

For example:

O1D + H2O -> 2OH JPL2003=2.2E-10, JPL2006=1.63E-10exp(60/T)

O1D + N2 -> O3P+N2 JPL2003=1.8E-11exp(110/T), JPL2006=2.1E-11exp(115/T)

O1D + O2 -> O3P+O2 JPL2003=3.2E-11exp(70/T), JPL2006=3.3E-11exp(55/T)

In addition, OH + CO has changed from JPL 2003 to 2006.

References: Thornton et al. (2002), Ozone production rates as a function of NOx abundances and HOx production rates in the Nashville urban plume, J. Geophys. Res., 107, 4146, doi:10.1029/2001JD000932.

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