

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.

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We thank the referee #1 for the very helpful comments on our paper. Our replies to the comments are listed below.

- OH loss rate measurements of Sinha et al.(2008):

Sinha et al.(2008) performed OH reactivity measurements within the canopy about 35 m above the ground during GABRIEL. 35 % of their measured total OH reactivity is due to reaction of OH with isoprene, MVK+MACR, acetone, acetaldehyde and methane. The missing fraction of the total reactivity is possibly due to unmeasured reactive compounds. One of the most different conditions between our aircraft measurements and the OH reactivity measurements of Sinha

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et al.(2008) are the different sampling sites. Highly reactive unmeasured compounds, emitted from the rainforest, might only play a significant role inside the canopy and might be too short-lived to reach the sampling area of the aircraft above ~ 300 m. Further measurements are needed. We will include a short comment on this in our paper.

- Isoprene flux:

Higher OH concentrations lead to a decrease of the isoprene lifetime and therefore to larger isoprene fluxes for global model applications. The description of the isoprene flux in global models is still an open question. Ganzeveld et al.(2008), who compared the GABRIEL data with a single column model, have described the problem: "A common problem of large-scale atmospheric chemistry models [...] is that simulations based on the commonly applied Guenther et al.(1995) emission algorithm generally result in a large overestimation of the C_5H_8 mixing ratios in the boundary layer over tropical forest (e.g., Houweling et al.(1998)). Simulated maximum mixing ratios can exceed 10 - 15 ppbv compared to observations usually below 5 ppbv. Consequently, a commonly applied approach in global atmospheric chemistry studies is to use a substantially smaller flux, ranging from 220 to 350 TgC yr⁻¹ (Brasseur et al.(1998), von Kuhlmann et al.(2003)), compared to 500 TgC yr⁻¹ according to Guenther et al.(1995)." Butler et al.(2008) also noticed the problem: "A common solution in global atmospheric chemistry models has been to reduce the flux of isoprene by about one half (eg. Pozzer et al.(2007)). This leads to an inconsistency between isoprene flux estimates based on a multitude of laboratory and field observations (Guenther et al.(1995), Guenther et al.(2006)) and many of the current state of the art atmospheric chemistry models." Therefore the high measured OH concentration are not inconsistent with the isoprene flux in the global models and higher OH-concentration might lead to more "realistic" isoprene fluxes in the models.

- Difference between the study of Butler et al.(2008) and our box model results:

Butler et al.(2008) introduced a definition of the OH recycling as the total number of OH radicals produced during all steps of the oxidation of isoprene to longer lived end products, divided by the total number of OH radicals consumed during this process. To describe the OH observations, a OH recycling of 40-50 % are needed. In our studies we did not calculate this number of OH recycling, since the box model simulations were constrained by the measurements. Therefore the modelled concentrations from species inside the isoprene mechanism (eg. MVK+MACR) are modified. A better comparison with the global model runs of Butler et al.(2008) is the artificial reaction of



They derived the best agreement for $n = 2$ for simulating isoprene and OH-concentrations inside their uncertainties. As the isoprene flux is a critical part in global models, as mentioned above, an additional degree of freedom exists for the global model simulations. Butler et al.(2008) obtained agreement for OH concentrations for $n = 3$, even though the observed isoprene concentrations were not reproduced. For our box model simulations $n = 3.2$ was calculated, which is in good agreement with their study.

- HCHO measurements:

The HCHO measurements are discussed in more detail in Stickler et al.(2007), in which the measured HCHO concentrations are shown for the boundary layer as a function of longitude. The mean value during daytime is (1.15 ± 0.86) ppbV in the boundary layer over the tropical forest (Lelieveld et al.(2008)). The detection limit of the HCHO measurements is 0.25 ppbV, with a precision of 25 % and a total uncertainty of 27 %.

A variation of the HCHO concentration by a factor of 2 is therefore larger than the measurement uncertainties. Although the impact for the OH concentrations

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is 103 % and 136 % for HO₂, it is not sufficient to explain the discrepancies between observations and simulations.

We constrained our box model simulations to the observed HCHO concentrations to get an estimate for the situation which was present during our measurements. We also did simulations with unconstrained HCHO to model the HO_x concentrations. The OH concentration of simulation with "free" HCHO lead to 1 % more OH on average for the boundary layer over the rainforest in the afternoon. 4 % more HO₂ radicals were produced on average compared to the basic run. Therefore we do not see a large effect in relation with the HCHO concentrations.

The focus of Fig. 13 is the OH and HO₂ radicals. We can include the additional pathway RO₂ + NO → HCHO, but Fig. 13 is meant to show a simplified reaction scheme. The chemical reaction mechanism of the box model has to be taken for detailed analysis.

- Box model results for HCHO:

In our studies we concentrated in the box model results of OH and HO₂. Stickler et al.(2007) focussed on HCHO and performed simulations with the same box model, constrained to the observed OH and HO₂ concentrations. They found an overestimation of the HCHO mixing ratio by the model, which they attribute to an underestimation of the entrainment and perhaps of the dry deposition velocity.

- Reference of Thornton et al.(2002):

Thornton et al.(2002) could explain their HO_x observations from the SOS campaign (Nashville) by including a decrease in the peroxide formation rate (RO₂ + HO₂ → ROOH) by about a factor of 10 in their box model.

In our studies we also modified the reaction





but in a more drastical way. We neglected the formation of ROOH completely, showing, that the omission of this reaction can also not explain our measured data. This modification should only be understood in a sense of a sensitivity study to give an upper limit. The reference of Thornton et al.(2002) will be included.

- Rate constants:

For our comparison we used the box model MECCA, which is described in Stickler et al.(2006) and Sander et al.(2005). We used this version of the model to be consistent with Stickler et al.(2007), who analysed the GABRIEL data with a different focus and for relatively long-lived reaction intermediates. Updated rate constants lead to 13 % less OH on average. The updated rate coefficients (Sander et al.(2006)) of $O(^1D) + H_2O$, $O(^1D) + O_2$, $O(^1D) + N_2$, account for a 12 % reduction of OH and a 5 % reduction for HO_2 . For our studies, this effect lies within our uncertainty and does not change our conclusions. In future studies, the updated rate constants should be used.

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