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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Simulating atmospheric composition over a South-East Asian tropical rainforest: Performance of a chemistry box model" *by* T. A. M. Pugh et al.

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Pugh et al. simulate the atmospheric composition of gasphase constituents in a South-east Asian tropical rainforest. A comprehensive new dataset is presented and, combined with a chemical box model, implications for atmospheric chemistry are discussed. The following comments should be addressed before publication.

(1) Abstract: "The excellent agreement between estimated values and measured fluxes of isoprene. . ...suggests that this method maybe applied where measured fluxes are not available." On page 19263 the authors find that the model would predict concentrations of 100 ppbv when isoprene fluxes, typically observed during the dry season in

the Amazon, are used instead. In these environments isoprene concentrations never really exceed ∼10 ppbv. This suggests that the box model can not be used to derive isoprene fluxes from concentration measurements. It seems that the sensitivity of the box model underestimates the removal of isoprene.

(2) Entrainment: It is not really clear whether entrainment is only treated as entrainment due to a growing PBL (=dilution) or if other entrainment processes at the PBL-FT interface are considered.

(3) Box model setup and comparison with concentration measurements: The daytime PBL consists of the surface layer (SL, surface layer scaling typically used) and the mixed layer (ML, mixed layer scaling) (e.g. Stull, An Introduction to Boundary Layer Meteorology). As a consequence reactive species such as isoprene exhibit a decrease throughout the surface layer. This can result in concentration differences of 20-40% between the surface and the mixed layer. Observations from the aircraft during OP3 could be used to assess this decrease, which seems to be an important factor when comparing ML box model simulations with SL concentration measurements for the presented optimization.

(4) Page 19254, line 7-18: Could the formation of HONO be important?

(5) Deposition: The discussion on dry deposition is intriguing. I would like to make a couple of comments on the issue of dry deposition. In our work in Costa Rica, dry deposition velocities (vd) of MVK+MAC during daytime inferred from a layered gradient technique were actually larger than 0.1 cm/s – these reported numbers referred to average vds across all layers per layer (unfortunately some of the labels were dropped during copyediting and we missed this typo during the galley proofs) – thus these velocities would have to be summed up over all layers to derive an ecosystem scale deposition flux (velocity) from our work. The study average daytime (noon) deposition velocity for MVK+MAC was 1.6 cm/s for Costa Rica. More recently we have revisited this issue during the AMAZE field study and consistently saw high deposition of

MVK+MAC and hydroxyacetone (see Karl et al., ACP, 2009, Figure 1). The corresponding deposition velocities were 2.4 cm/s. It is important to note that there is currently not a good explanation for these high rates. The Wesely scheme predicts significantly higher canopy resistances (e.g. 5-10 times). As another example the cited work by Zhang et al. (2002), which is largely based on Wesely (1989), predicts maximum deposition velocities of 0.4-0.5 cm/s for PAN type species – more recent measurements (Turnipseed et al., JGR, 2005) showed significantly higher deposition (e.g. up to 1.6 cm/s).

(6) HOx recycling: It appears that there is a fundamental problem in reconciling isoprene fluxes and concentrations with OH mixing ratios. The present work supports findings from previous studies. Similar to Butler et al. (2008) it is argued that a segregation of 50% for the OH+isoprene reaction has to be assumed in any scenario linking HOx recycling to isoprene chemistry. Results from LES have shown that this is most likely not a realistic assumption. Could this suggest that HOx recycling might be linked to other processes than the ones proposed in previous work?

Comment: It has been shown that the ISO2+HO2 (R1) as proposed by Lelieveld does not occur, but peroxyradicals originating from 2nd generation carbonyls can regenerate HOx. The effect of HOx recycling further down the oxidation chain however has likely a much smaller effect compared to direct recycling of ISO2. As mentioned a promising new chemical scheme for HOx recycling has been proposed by Peeters et al., (PCCP,2008), which postulates unimolecular decomposition of certain isoprene peroxy radicals. We have recently shown (Karl et al., ACP, 2009) however that the effective HOx recycling efficiency has to be much smaller than proposed (e.g. $\sim$70% lower) in order to bring the Peeters et al. mechanism in accordance with OVOC observations.

(7) Page 19265, line 10: The statement that the OH recycling rate is smaller than during previous field studies is somehow contradicted by the finding on Page 19263, line 10, where the authors show that their model would predict 100 ppbv of isoprene for higher isoprene fluxes.

(8) Minor comments: Page 19254, line3: change to “The reason for this is. . ..”

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 19243, 2009.