**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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We thank J. Vila for his comments and will address each point in turn below.

1. How accurate are the LIDAR observations to determine the mixing-layer height?

The vertical velocity variance data is what has been used here, as discussed by Tucker et al. (2009, J. Atmos. Ocean. Tech., 26, 673-688). The LIDAR vertical resolution was 30m. Using the Dopplar velocity measurements offers the ability to visualize the vertical transport directly, without the need to infer the dynamics from secondary measurements such as aerosol distributions or potential temperature gradients (Pearson et al., Remote sensing of the tropical rain forest boundary layer using pulsed Doppler

LIDAR, in prep.). Consequently, in their review of LIDAR mixing height determination methods, Tucker et al. (2009) state, "Profiles of vertical velocity variance are, by the definition of the mixing height, the most useful data for estimation of mixing height, especially during convective conditions." Therefore we feel that this direct measurement is most appropriate for our purposes. We discuss the LIDAR data in more detail below.

2. Is the value of 800 meter always found during the 8-day simulation or there are certain variations?

Two points should be made in answering this question. Firstly, the LIDAR measurement used to define the boundary layer height is the standard deviation of the vertical velocity, and we will make this explicit in the next version of the paper. Using the standard deviation of the vertical velocity allows us to define as the mixed layer only the part of the atmosphere in which active eddy mixing is taking place. An entrainment layer, as expected from boundary layer theory (e.g. Seinfeld and Pandis, 1998, Atmospheric Chemistry and Physics) is visible in the data, but cannot be captured by a box model, of course. LIDAR measurements show the onset of these eddies to be at 0800 LT. There is only a very small lag, typically <30 minutes, between a given velocity onset at 100m and at say, 500m. Having reached their maximum vertical propagation at 1000 LT the maximum height at which significant eddy velocities are recorded is remarkably consistent at around 800m. This 'square' trend is seen both in the campaign average daily cycle, and in the weekly average plots.

Secondly, the model is run for 8 days as this was the time required to produce a steady diurnal cycle in the concentrations of atmospheric species of interest. The intention of this study was not to reproduce any one day, or series of days, but rather the replicate the 'typical' chemical concentrations found in the rainforest boundary layer. Therefore the first 7 days may be regarded as model spin-up time.

3. Would it be more useful to reproduce simultaneously in their chemistry box model the boundary layer growth and therefore the exchange of reactants?

We are not completely sure what the issue is here. Is Dr Vila suggesting that we should included a mixing layer model within our chemistry model? If so we would be reliant upon the mixing layer model having the correct inputs and producing a realistic result for our scenario. We do not need to do this as the LIDAR data gives a direct measurement of the mixing height. In answer to the next question we will outline the way mixing is treated in the model.

4. How are the residual concentration introduced in the morning hours?

We make the simplifying assumption that the mixed layer depth increases linearly from 200m to 800m between 0800 LT and 1000 LT. At each model timestep between these times, the concentrations of species from the 'engulfed' section of the residual layer are mixed into the lower box following

$$C_{lower}(i,t) = C_{lower}(i,t-1) + \left((C_{upper}(i,t-1) - C_{lower}(i,t-1)) \times \frac{m(t)}{h(t)} \times T \right)$$

where C_{lower} and C_{upper} are the concentrations of species i at time t for the upper and lower box respectively, h is the mixing height (height of the lower box), m is the rate of mixing height rise and T is the model timestep. We will modify the next version of the paper to make this clearer.

5. How accurate is this method in terms of clouds onset and cloud optical depth?

Whilst cloud onset and cloud optical depth are important variables for calculating photolysis rates from cloud cover data, we have the advantage of measured photolysis rates directly at our measurement site, and it is photolysis rates that we are concerned with for the chemistry, of course. Therefore, the cloud cover variable in the photolysis scheme has been used as a fitting parameter to generate the measured diurnal $j(O^1D)$ profile. Fitting cloud using the $j(O^1D)$ measurements (applicable wavelength <330 nm) results in the photolysis scheme producing a $j(NO_2)$ profile (applicable wavelength <415 nm) almost identical to that measured. We therefore conclude that the photon fluxes

used are realistic. We will report this in the next version of the paper.

6. Is the enhancement of vertical transport taken into account by their chemistry box model?

It is clear from the outset that we are interpreting the observed data in a box-modelling framework. We do this because box models are commonly used to compare with observations (e.g. Read et al., 2008, Nature, 453, 1232-1235; Hofzumahaus et al., 2009, Science, 324, 1702-1704; Emmerson and Carslaw, 2009, Atmos. Envi. 43(20), 3220-3226) and because box models usually carry much more chemistry than 1-D, 2-D, or 3-D models (cf. Vila et al., 2009 with the chemistry scheme reported in our paper). When we find that mixing is important we either (i) discuss how this might affect the results using scaling considerations, or (ii) leave these times out of the main part of our discussion. So, we optimise our model using daytime observations, and find that we fit other daytime measurements, not used in the optimisation, well.

7. Reactants introduced in the cloud layer during the day (higher than the 800 meter mentioned) remain in the upper boundary layer and therefore have an effect on the nocturnal chemistry of the residual layer.

We would assume that these reactants would undergo largely the same chemistry during the day as those in the mixed layer and hence their inclusion would not greatly modify the concentrations found in the nighttime residual layer. We do not explicitly consider heterogeneous chemistry in this study.

8. The large values discussed by Krol et al. (2000) were a consequence of the large segregation of species due to the non-uniform emission. In any case, they were less than 20 %.

Due to the heterogeneity of the natural rainforest the emissions of VOCs and NO_x are almost certainly non-uniform. Measurements of soil NO_x made at the forest floor varied greatly depending upon their location, even within a small area. Likewise, surveys of

tree species (both previous, e.g. Bebber et al., 2002, Forest Ecology and Management, 157, 65-75, and ones carried out as part of OP3) showed the species distribution to be highly heterogeneous. The emission spectra from different tree species can be very marked (Owen et al., Leaf level emissions of volatile isoprenoid and other organic compounds from forest tree species in SE Asia, in preparation).

In Table 4 of their work, Krol et al. (2000) report an intensity of segregation (and hence rate constant reduction) of -29.4% between RH and OH when the emission of RH is non-uniform. Moreover, they find an increase in the reaction rate of OH and RH also increases segregation. Given that the reaction rate of 0.6 $ppb^{-1}s^{-1}$ between OH and RH, utilised to yield the 29.4% segregation, is approximately one quarter of that between isoprene and OH at 298K (IUPAC, 2009), we find it reasonable that even stronger segregation may exist under the conditions in our study. We note that we have not discussed this thoroughly in the current version of the paper, and will include this discussion in the next version.

9. I think the used value of 70 % requires to be justified.

We think there is some misunderstanding here. We find a rate constant reduction of 70% alone, ignoring the other issues we highlight in our work, is capable of bringing OH and isoprene concentrations within the range of the measurements. However we then show in section 6.4 that only a 50% reduction is required once effects such as the deposition of oxidation products are considered. The intention is to show that (i) we cannot simultaneously make modelled OH and isoprene concentrations match observations by adjusting the chemistry alone, and (ii) that consideration of incomplete mixing is able to explain this conundrum. The availability of flux measurements of isoprene and monoterpenes for our work allows us to further corroborate the results of Butler et al. (2008) and emphasises the importance of further investigation, particularly measurements, within this field.

10. My suggestion is to use a less ad-hoc approach and represent the inefficient

mixing using a parameterization depending on boundary layer dynamics and chemistry conditions (Vinuesa et al. (2005), Atmospheric Environment 445-461).

We do not think that we are using an ad-hoc approach. We are simply approaching the problem from a different side. We are interested to learn of the Vinuesa et al. (2005) reference, which we had overlooked, and we will consider whether we can add a section using the theory developed in that paper to critique the value that arises objectively from the optimisation of the box model. In particular we note that Vinuesa et al. (2005), in Table 2, recommend a reduction in reaction rate between OH and RH, where RH + OH has a very similar rate constant to isoprene + OH, of 40.5%. This lends further support to our findings, particularly when the 10% stated error in the IUPAC (2009) rate constant is considered, and we will include this reference in the next version of the paper.

11. Finally, I found a small typo error on equation (5). The convective velocity scale should be with the power of 1/3.

We thank Dr Vila for pointing this out and will correct this in the final manuscript.

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