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 Dr Vila, Dr Karl, Dr Ganzeveld, Prof. Cohen, Dr Browne and the anonymous reviewer for their constructive comments, which we believe have led to a much improved manuscript. As the issue of the measurement heights has been raised more than once, we will address this first, before dealing with each of the other comments individually. As we have already addressed the comments made by Dr Vila, we will not mention them again here. Where minor grammatical comments have been made, we accept these without reservation and will incorporate them into the revised manuscript.

1 Measurement heights

In our original manuscript we opted not to describe fully the measurement site, instead referring the reader to Hewitt et al. (2009a) but we now recognise that a lack of detail in the current paper may have led to the concerns Dr Karl, Dr Ganzeveld, Prof. Cohen and Dr Browne expressed regarding the use of the 5m measurement height at Bukit Atur. We have independent measurements from aircraft sorties directly above Bukit Atur, and from inside the canopy nearby. These measurements provide strong evidence that the 5m measurements at Bukit Atur are representative of the well-mixed boundary layer during daytime, and are not in-canopy measurements (see new manuscript text, below). For a thorough description of the Bukit Atur measurement site and the OP3 measurements conducted the reader will still be referred to the overview paper of Hewitt et al. (2009a). However we will replace lines 5-9 on page 19248 with the following measurement site description:

The Bukit Atur (BA) GAW site is situated at an altitude of 437 m a.m.s.l., on a small hill approximately 260 m above the surrounding valley floor. The top of the hill features a small grassy clearing approximately 150 m by 50 m surrounded by secondary rainforest, rising to ~10 m on three sides. The surrounding rainforest is either virgin or has not been logged since 1988 (Tangki and Chappell, 2008). A 100 m high steel-framed measurement tower has been erected in the centre of the clearing as part of the World Meteorological Organisation Global Atmospheric Watch site that has been established at BA. The measurements used in this report were made at ~5 m above ground level in this clearing, with the exception of PTR-MS measurements of BVOC concentrations and fluxes which were made at 75 m, and PAN measurements which were made at 30 m. References to measurement heights in this paper are always relative to the top of the hill.
It is possible that the 5 m measurements are effectively within the canopy. To ascertain whether this is indeed the case, NO\textsubscript{x} measurements made at a nearby under-canopy site (4° 58′ 50″ N, 117° 51′ 19″ E) are compared with those made in the boundary layer by an aircraft and those made at 5 m at BA. The in-canopy measurements (8 m above soil surface) display significantly higher levels of NO (316 pptv as opposed to 37 pptv in the median at midday). However, the aircraft and 5 m measurements of NO and NO\textsubscript{2} show good agreement (Hewitt et al., 2009b), suggesting that the 5 m measurements may indeed be regarded as representative of the well-mixed boundary layer during daytime. Unlike NO\textsubscript{x}, isoprene measurements during OP3-1 are on average 36% lower at 75 m than at 5 m, indicating that isoprene does show a gradient in the surface layer. This is because the ratio of emission rate to chemical loss rate is much greater for isoprene than for NO. No such gradient is discernible for monoterpenes which have a lower emission rate. Good agreement is seen for 75 m and boundary layer aircraft measurements of isoprene Hewitt et al. (2009b). Model calculations suggest that, at most, OH concentrations would increase by 30% between 5 m and 75 m as a result of the gradient. An increase of this magnitude is within the uncertainty of the measurements and, since it is an increase, would not adversely affect the analysis carried out in this study. As explained in §6, there is considerable uncertainty over whether isoprene is a significant net OH sink at all. 5 m and aircraft measurements of OH concentration show close agreement, supporting the assertion that for most species (i.e. those lacking strong surface emission) the 5 m measurement height on top of the hill is representative of, the daytime mixed layer. At nighttime, stratification within the clearing (Pugh et al., 2009) means that these measurements cannot be assumed to represent the nocturnal boundary layer. This paper concentrates on the daytime measurements, drawing only limited comparisons with measurements made during the night.

2 Individual comments

2.1 T. Karl

RC: 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.

AC: We did not mean to suggest that the present results of the box model could derive isoprene fluxes from concentration measurements in a different setting, such as the Amazon during the dry season. To apply this method for a region with much higher isoprene fluxes it would be necessary to account for the different boundary layer behaviour and for extra removal of isoprene, e.g. by more efficient OH recycling. We demonstrate the potential requirement for this extra removal of isoprene on pg. 19264, lines, 4-11. In the OP3 measurements, the relatively low isoprene concentrations, compared to those reported in e.g. Karl et al. (2007), mean that an unknown recycling of OH during isoprene oxidation would not dominate OH production in the same way that it would in the very high isoprene environment of Karl et al. (2007). We will modify the revised paper to include the caveat ‘assuming that we adequately understand the chemistry and mixing’, with regard to the method of flux estimation.

Note, however, that we are not fully applying our model to the Amazon regime observed by Karl et al. (2007), as we are just considering the different fluxes. For instance we do not consider the higher temperatures and likely higher boundary layer
that would be found in the Amazon.

RC: 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.

AC: The model features a parametrised entrainment of the residual layer into the growing boundary layer between 0800 and 1000 LT. This is a simple mixing between the two air-masses. No other entrainment processes, such as at the PBL-FT interface are considered in the model. Given the very low levels of tracers such as isoprene observed in the free troposphere, mixing across the PBL-FT boundary will decrease isoprene concentrations. We will ensure the model mixing processes are clearly explained in the revised manuscript.

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

AC: We note that the literature contains several cases where several tens of ppb of HONO have been observed over forests during the daytime (Trebs et al., 2004; Kleffmann et al., 2005; Kleffmann, 2007; Zhang et al., 2009), suggesting that as high as 56% of daytime OH production could be due to HONO photolysis (Kleffmann, 2007). Ren et al. (2006) failed to find a significant underestimation of [OH] in a relatively low isoprene (<1 ppbv) rural environment. However a notable feature of this analysis is that they had measurements of HONO against which to constrain their model and found it to be a major HOx source during the day. Measurements of HONO appear to be lacking in the studies of Tan et al. (2001), Carslaw et al. (2001), Butler et al. (2008), Lelieveld et al. (2008). Hence it appears possible that a large HONO source, such as that suggested by Kleffmann et al. (2005), could be responsible for the missing OH in these studies.

The CiTTyCAT model suggests very low nighttime HONO concentrations of around

0.1 pptv using OH + NO reaction, although it does not incorporate the heterogeneous formation mechanisms for HONO outlined in e.g. Kleffmann (2007). GRAEGOR measurements of HONO at ∼8-m at the Bukit Atur site record peak HONO mixing ratios less than 10 pptv, with a median of 6 pptv. The detection limit of this instrument for HONO is around 10 pptv, hence any analysis of trends in data below this limit must be treated with caution. Analysis of the difference between speciated and total NOx measurements (Aruffo et al., 2009) supports [HONO] measurements of this magnitude. At a midday HONO photolysis rate of $8.7 \times 10^{-4}$ s$^{-1}$, as calculated by CiTTyCAT, 6pptv of HONO would generate $1.2 \times 10^5$ molecules OH cm$^{-3}$ s$^{-1}$. This is <2% of the modelled OH source at that time, therefore we conclude that HONO photolysis most likely had a minimal effect on OH production and hence the HOx budget during OP3. However, as these HONO measurements were only made during OP3-3 there is a possibility that HONO concentrations were higher during the OP3-1 period upon which our model analysis is based. This will be investigated further by Whalley et al. (2009a).

RC: 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).

AC: We thank Dr Karl for providing us with these numbers, and we will include them within the revised manuscript (we assume the AMAZE Va is a personal communication as we cannot find mention of it within Karl et al. (2009)). We will also add some recently processed results from the measurement campaign over oil palm (OP3-2), which show MACR/MVK deposition velocities of 1-2 cm s⁻¹, commenting that it is not possible to explain these high deposition velocities using current theory.

RC: 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?

AC: We would not go so far as to say that 50% recycling ‘has to be assumed’. We simply show that, for the OP3 measurements, the optimal way to reconcile measured concentrations and fluxes with the model is to assume a 50% reduction in the isoprene/monoterpene + OH rate constant. The segregation hypothesis is the best rationale for such a step as far as we are aware. However, by the very nature of the processes which cause segregation (e.g. heterogeneous spatial and temporal emission from the canopy), it is impossible to impose a blanket figure which meets every scenario. Whilst it is certainly interesting that our optimised value of 50%

agrees with the figure proposed by Butler et al. (2008) over another tropical rainforest, this may be to some extent fortuitous and we would expect a different figure over a substantially different forest landscape, for instance one with a less varied distribution of VOC emitting species or different turbulent mixing characteristics. As we mentioned in our reply to Dr Vila, whilst these reductions of 50% are certainly high, they are not unreasonable when compared to the 30% reduction calculated by Krol et al. (2000) and the 40.5% reduction recommended by Vinuesa and Vilà-Guerau de Arellano (2005), and when the stated 20% error in the isoprene + OH rate constant (IUPAC, 2009) is taken into account.

The question of whether HOx recycling might be linked to other processes than the ones proposed in previous work is an interesting one. Detailed investigation of the various OH recycling processes is beyond the scope of this work, and as regards OP3, will be considered further by Whalley et al. (2009b) and other forthcoming papers in the special issue. However the mainstay of our VOC:OH analysis in this paper is that we cannot reconcile measured isoprene and OH concentrations. Whichever process we use to increase OH (e.g. reduction of OH sink to oxidation products, OH recycling, formation by ozonolysis of an unknown sesquiterpene-like compound), an increase in [OH] brings about a decrease in isoprene concentration. A subsequent increase in isoprene emission into the model (which we note would go above the measured fluxes), can correct the underestimation in isoprene concentration, but [OH] is once again depressed, almost to the extent of the original underestimation. Based upon this analysis, we cannot envisage any scenario of OH recycling alone which would correct the deficiencies in the model estimates.

RC: 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 HO$_x$ 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.

AC: We thank Dr Karl for these helpful comments. In our discussion of the Peeters et al. (2009) OH recycling mechanism, we will refer to the results of Karl et al. (2009), which were not available when we submitted our manuscript.

RC: 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.

AC: The discussion in section 6.4 aims to demonstrate that we cannot rule out a role for OH recycling. It is not necessarily the case that OH recycling would have to be of the same magnitude over different regions. For instance, the hypothesis of Hofzumahaus et al. (2009) postulates an unknown compound with a reduction capacity similar to NO is responsible for cycling peroxy radicals back into OH more rapidly. If this is the case then it is quite likely that the concentration of such a compound would vary from location to location. Given the current state of the knowledge in this field, we present our results in good faith, in the hope that they can provide a useful contribution to the debate.

As we have mentioned above, by ignoring differences in temperature, boundary layer height, etc between the Amazon and OP3, we have not tried to accurately model the chemistry for the Amazonian studies. Whilst no doubt interesting, application of our model to the results of other field campaigns is beyond the scope of this study.

2.2 L. Ganzeveld.

RC: However, it does not address according to me very novel issues; it is basically considering the previously identified issues on tropical forest photochemistry but then for this particular, interesting location. For example, the discussion on the issue of the overestimation of the VOC oxidation products possibly due to a misrepresentation of dry and wet deposition has been already been discussed previously, first of all by von Kuhlmann et al. (Sensitivities in global scale modeling of isoprene, von Kuhlmann et al., Atmos. Chem. Phys., 4, 1-17, 2004). We also discussed this extensively in the evaluation of the Guyana Gabriel campaign observations. (Ganzeveld et al., ACP, 2008) but also indicated that making assumptions on a more efficient removal of these products only reduced the surface/canopy layer concentrations and not the concentrations aloft.

AC: We think that the new location, the breadth of measurements in that location, and the approach to modelling those measurements, make our manuscript novel. Without doubt, the principle issue in our current understanding of atmospheric chemistry over tropical rainforests is the underestimation of [OH] by current models in regions of high isoprene concentration. Without a good understanding of the basic oxidation process of BVOCs such as isoprene, drawing conclusions about other aspects of the chemistry is much more challenging. As such we are forced to devote considerable time to this, admittedly not new, problem in our study. Where this work particularly adds value to the current literature on this subject is firstly, in the availability of on-site measurements of BVOC fluxes which constrain our isoprene and monoterpane input into the model. Given that OH recycling regimes such as Lelieveld et al. (2008), Hofzumahaus et al. (2009), Peeters et al. (2009) increase the OH concentration, they simultaneously increase the BVOC loss rate, as found by Butler et al. (2008), and Ganzeveld et al. (2008). This measured constraint on the BVOC emissions substantially reduces the model response-space within which a good
model fit must be found. Secondly, Butler et al. (2008) find that their model cannot maintain the measured isoprene and OH concentrations without reducing the effective rate constant for the reaction between them. Our analysis comes independently, for an entirely different regions of the tropics, to the same conclusions, showing that this effect is likely to be a global phenomenon. Thirdly, we find that the segregation effect alone (i.e. without significant OH recycling), is sufficient to bring OH and isoprene concentrations within the bounds of the measurements. To our knowledge, the lack of an improved fit by OH recycling in forest scenarios has not been reported before.

In answer to the points raised regarding deposition, we have read the paper by von Kuhlmann et al. (2004), but note that, in their purely modelling based study, the discussion of the effects of varying the deposition of isoprene oxidation products (in this case peroxides only were considered) was limited to the effects on ozone and PAN, along with the changes in upper tropospheric HOx wrought by a change in PAN abundance and the photolysis of peroxides at high altitudes. Unlike von Kuhlmann et al. (2004), we are in the fortunate position of having measurements of several BVOC oxidation products with which to compare our model output. In the case of MACR/MVK in particular, this allows us to make a suggestion for an appropriate deposition velocity, a value for which there is some uncertainty in the literature. As mentioned in the response to Dr Karl, what we did not report in our original submission, because the analysis was not yet completed, is that MACR+MVK deposition over the oil palm plantation during OP3 was calculated to be between 1 and 2 cm s$^{-1}$, an excellent agreement with our modelling result.

Ganzeveld et al. (2008) also found that their model overestimated MACR+MVK concentrations in the Amazon boundary layer. When they applied an increased deposition rate for MACR and MVK they find the effects were confined to the nocturnal canopy/surface layer concentrations. We observed the same effect in our model during the night, where deposition effects were limited to the lower box. As such, the true effect of this deposition is not felt until the resumption of turbulent mixing the following day, and it is mitigated by the lack of deposition in the upper box or 'residual' layer. During the day however, enhanced deposition in both our model and that used by Ganzeveld et al. (2008) will decrease MACR+MVK throughout the BL. We find this daytime deposition substantial enough to yield most of the required decrease for the model to approach the measurement.

In addition to the estimation of deposition velocity we reflect upon the effect of increased deposition of intermediate products upon the OH sink and hence emphasise its importance when considering the problems in modelling boundary layer OH over the rainforest. This is an aspect of the problem that is not discussed in the papers above.

RC: I recall that having met the first author on a workshop beginning of October that we have extensively discussed the issue on the possible importance of the residual layer chemistry for this misrepresentation of the MVK and MACR concentrations (as we also hypothesized in the Gabriel modeling paper). Having the 75m observations (still in the inversion layer?) of OP3 it would be interesting to shortly discuss in this manuscript what these observations show on nocturnal MVK/MACR mixing ratios.

AC: We agree that this is an interesting issue, and although this manuscript does not focus on nighttime chemistry we will include a short discussion:

Our model also observes a small increase in the residual layer MACR and MVK during the night. The small magnitude is likely due to the lower concentrations of ozone and isoprene during our study. It is possible, although we are unable to confirm it, that the 75-m observations are within the residual layer during the night. If this is the case, the decrease observed during the night in average total MACR
MVK mixing ratios from 335 pptv at 1800 LT to 91 pptv at 0600 LT, suggests the model is incorrectly modelling production and/or loss during the night. Nighttime measurements of isoprene concentration at 75-m are around 50% of those modelled in the residual layer. Therefore, if these measurements really are in the residual layer, it is clear that we are modelling ~50% too much nighttime production of MACR and MVK (note this does little to affect the model overestimation of [MACR+MVK] as most of the modelled increase takes place during the day). However, the model overestimation of [MACR+MVK] also means we are overestimating the loss rate to its reaction with ozone many more times than we are overestimating its production. This is demonstrated in Fig. 6 of our paper, when MACR and MVK concentrations overall are reduced by deposition, the net nighttime production in the residual layer is increased as gross production is virtually unchanged, but loss to ozone is reduced.

This lends support to the hypothesis of Ganzeveld et al. (2008) that intermittent nocturnal transport events may be connecting the residual layer with the surface, allowing some deposition from the residual layer. In our model such effects are implicitly accounted for in that by defining the NBL height (which controls deposition rates) by a sensitivity study optimised to daytime concentrations, we have actually defined an effective NBL height with the aim of producing the correct concentrations at the end of the night. The idea of an optimised NBL height implicitly incorporating mixing with the residual layer has been suggested before by Strong et al. (2009). Indeed, the net change in [MACR+MVK] over both boxes during the night is negative when we apply $V_{d(MACR+MVK)}=1.5 \text{ cm s}^{-1}$. As a box model cannot reproduce the chemical gradients caused by limited mixing in a stable boundary layer, this solution is adequate for our purposes as we cannot hope to provide valid comparisons with observations during the night. However, assuming our 75-m nighttime measurements are in the residual layer, it would appear any model attempting to accurately recreate residual layer concentrations will need to account for such nocturnal transport events.

RC: By the way, more a minor comment; In the discussion on the MVK/MACR deposition process referring to the sensitivity analysis we conducted for the Gabriel campaign there are some misunderstandings. The numbers mentioned for the dry deposition velocities, 1 and 0.1 cm s$^{-1}$, refer to those explicitly simulated with the multi-layer canopy exchange model for $O_3$ and $SO_2$. Those for MVK and MACR end up being smaller based on the Wesely approach and we actually conducted an analysis modifying the dry deposition calculations using in one simulation (near) zero surface uptake resistances.

AC: We thank Dr Ganzeveld for pointing out this misunderstanding and will correct it in a revised manuscript.

RC: In the introduction of the model system it is indicated that the box model uses a maximum volume up to 800m altitude also based on the LIDAR observations. In some of the other reviews/comments this feature of the analysis has also been raised and want to add to this that it would be useful to shortly discuss this rather shallow tropical forest boundary layer depth by comparison with previously reported BL depths on the order of 1500m over the Amazonian rainforest (e.g. Fish et al., Eerdekens et al. ACP, 2009). According to me such a substantially shallower boundary layer could point at less efficient turbulent mixing (smaller presence of strong down- and updrafts?) compared to the conditions seen for GABRIEL with an inferred BL depth of about 1500 m topped by a shallow cumulus layer with enhanced transport. For these conditions a very/unrealistically large intensity of segregation between OH and isoprene of 50% was proposed whereas the numbers for the required Is in this manuscript are comparable or even larger.

AC: We agree that the above comparison makes an 800-m mixed layer look quite shallow, and will put this into context by replacing the sentence starting pp.
The box height is defined during the day by the height of the well-mixed PBL, which vertical velocity variance measurements from a pulsed Doppler LIDAR (light detection and ranging) indicate to be 800-m between 10:00–18:00 LT (Pearson et al., 2009). As measurements of vertical velocity variance are a direct measurement of the turbulent mixing process, they are the most useful data for the estimation of mixing height during convective conditions (Tucker et al., 2009). This estimation of mixing height also agrees closely with that derived from aerosol backscatter, which may be considered an indicator of the vertical extent of mixing. Aircraft profiles over the rainforest during OP3-3 indicated that the region of \( \frac{d\theta}{dh}=0 \) rarely extended above 1000-m above ground-level, whilst \( \text{NO}_x \) mixing ratios dropped off rapidly above \( \sim 800\)-m. A mixing layer height of 800-m is significantly less than the 1200–1500-m indicated in some studies of the Amazon (Martin et al., 1988; Krejci et al., 2005; Eerdekens et al., 2009). However it is comparable with the measurements of Fisch et al. (2004) who measured a mean maximum convective boundary layer height of 1002-m (standard deviation 195-m) during the wet season, measured using sonde profiles. The specification of wet season is important as the 1200–1500-m measurements were all made in the dry season when boundary layer heights have been observed to be higher than in the wet season (Fisch et al., 2004). As OP3 typically experienced daily rainfall episodes, a comparison against measurements made during the Amazonian wet season is most appropriate.

We also note that Fisch and dos Santos (2008) and dos Santos and Fisch (2007) find the parcel method used by Eerdekens et al. (2009) to overestimate maximum boundary layer heights in Amazonia by 30% compared to SODAR and sounding methods.

Regarding the hypothesis of a smaller boundary layer experiencing less efficient turbulent mixing, we agree that this is certainly possible. If it is the case then a large intensity of segregation might be more likely to exist during OP3 than during e.g. GABRIEL. However we have only limited information to discern whether this is the case. Eerdekens et al. (2009) report a maximum vertical velocity scale, \( w^* = 2.0 \text{ m s}^{-1} \), notably larger than that which we report of \( w^* = 1.4 \text{ m s}^{-1} \), but this is calculated using typical values from the TROFFEE campaign and therefore a direct comparison is not appropriate in this case. We note however, that Fisch et al. (2004) report a \( w^* = 1.2 \text{ m s}^{-1} \) for a broadly similar boundary layer depth under Amazonian wet season conditions.

With respect to the discussion in our manuscript of the reduction in the effective rate of isoprene + OH, we recognise that the most dramatic number tends to be the one which grabs the headlines, and with this in mind will remove the part of the discussion in section 6.3 which pertains to reducing the rate constant without first having applied our earlier findings regarding deposition of intermediates. The 70% value mentioned here is only intended as a stepping stone to the eventual conclusion of 50% when the other processes discussed are also included. Hence we feel removing this step will reduce any confusion as to the conclusions of the revised manuscript.

RC: Finally, I especially disagree with the opening statement of the Summary and conclusions section; “This is the first modelling study of the chemistry occurring in the tropical rainforest PBL to utilise such a wide suite of ground-based measurements, particularly VOC fluxes, to inform the modelling”. It were actually already the colleagues involved in the ABLE campaigns in the 80’s (recall the Jacob and Wofsy, J. Geophys. Res., 95, 16737-16754, 1990 paper) that were already doing this pioneering work on interpreting the observations of chemical composition and exchange over tropical forest.
AC: We do not suggest that we are the first study to use ground based measurements in the tropical PBL to inform the modelling. However we believe we are the first to have eddy covariance fluxes of NMHCs, combined with OH concentration measurements, and a wide suite of other tracers. For instance Butler et al. (2008) were one of the first studies to have access to OH concentration measurements in the tropical boundary layer, but lacked ground-based fluxes; the flux measurements of e.g. Karl et al. (2007) do not have available OH measurements, etc.

RC: Pp 19247; line 4, It is not only a challenge to test photochemical models; the challenge is to understand the role of photochemistry in relation to the role of surface exchanges and boundary transport processes.

AC: Indeed, but we are not suggesting just chemical schemes need to be tested. Rather the entire model, which must adequately account for all these processes in some manner.

RC: (Pp 19247) Line 9; as indicated in my comments above; it would be useful to give some background information on the particular features of the Borneo tropical forest site in terms of similarities and differences with other tropical forest sites subject of previous studies.

AC: We will insert here:

Forest in Borneo, including the Bukit Atur measurement site, is principally lowland evergreen broadleaf rainforest (Schmitt et al., 2008). Structurally and floristically, it is very different to the rainforest of Amazonia (Hewitt et al., 2009a). Seasonal cycles are weak, with dry periods of greater than 1 month absent or rare, cf. to Amazonia or Equatorial Africa where most of the rainforest experiences a significant dry season (Walsh, 1996). The average peak daytime temperature of 27°C is less than the 28-32°C observed by Karl et al. (2007) and the >30°C by Kuhn et al. (2007), in Amazonia.

RC: Pp 19249, line 2; what has been measured; the measured photolysis rates or the measured ozone/OH?

AC: The photolysis rate $j(\text{O}_1^\text{D})$ was measured directly using a filter radiometer. We will make this clearer in the revised version of the manuscript.

RC: (Pp 19249) Line 14-15; Apparently you assume that there is an nocturnal inversion layer 200m deep. Since you apply a box model system it implies that you assume that this is a well-mixed volume in direct contact with the surface. Do you calculations of deposition consider the limiting turbulent transport from the reference height of the 200m deep box (so 100m height) to the surface. And how do you consider to limited transport of the emitted species to this 100m reference height. What are your assumptions on the mixing in between the two different layers? no mixing at all?

AC: We assume no mixing between the two layers between 1800-0800 LT. This split in the boundary layer is of course very important for the concentrations of species which undergo dry deposition, as those in the upper layer are isolated from the surface. In the absence of measurements of nocturnal boundary layer height and mixing, we use a sensitivity study and optimisation procedure (using the method described in section 4 of our paper) to parametrise the height of the nocturnal boundary layer in our model. The aim of this procedure is to gain the best possible fit to the daytime concentrations, hence what really matters in this instance is that the measured con-
centrations are reproduced when the boundary layer once again becomes well mixed. Therefore in reality the nocturnal inversion layer may not be 200-m deep, and there may be some mixing across it, furthermore there may be a limited rate of transport throughout the inversion layer due to the lack of turbulence (we have investigated further the effect of mixing on nocturnal deposition rates using a 1-D model in a paper in preparation). However the net effect regarding the deposition flux to the surface should be representative of the deposition flux in the real atmosphere. For this reason comparison of the modelled nocturnal concentrations to the measurements should only be made with caution.

RC: Pp 19250; lines 1-2 and one ward; You just present the numbers on the NO and BVOC emissions without presenting any justification for the selection of these values (references). Later on some comparison of these numbers with the literature are presented but I propose to provide some short introduction of typical tropical forest NOx and BVOC emissions fluxes. In addition, with respect to the NO biogenic emissions it is essential to indicate if you refer to canopy-top emissions (of NOx) or to soil NO emissions. Since you apply one box it appears that you don’t treat the canopy interactions you apply the canopy reduction factor approach as proposed by Yienger and Levy. This feature of the model set-up is essential and should be explicitly mentioned. On the other hand, this issue about how to treat/ignore the canopy interactions comes also back to my comment about the reference height of the concentrations; 5m above the ground of the clearing.

AC: We mention on pp. 19250, line 3, that the selection of ranges for the sensitivity runs was informed by previous coarser resolution runs (we will change ‘runs’ on line 4 to ‘sensitivity studies’, to try and eliminate any confusion), which covered a very wide range of values (encompassing for instance the full range of isoprene emissions reported in Kuhn et al. (2007) and Guenther et al. (2008)). The optimisation clearly converged on a single minimum within the ranges we specify, but computational constraints meant we could not carry out these runs at a high enough resolution to identify the fluxes with sufficient accuracy. Hence the ranges reported were chosen to be able to pinpoint the fluxes with sufficient accuracy, whilst also demonstrating the uniqueness of the minimum.

As the optimised isoprene and monoterpene emissions were used as a cross-check on the optimisation process, by comparing to the measured emission fluxes, we do not feel it appropriate to spend time on a comparison here, which will be done much more thoroughly in the dedicated flux paper of Langford et al., which is due to be submitted to ACPD shortly. We will however add a sentence referring readers to the Langford et al. paper for more information on the BVOC fluxes. A much more detailed comparison of the NO fluxes to the literature and soil measurements is already included and we feel that it is most appropriate to the flow of the paper to keep it in its current place on pp. 19251-2.

Dr Ganzeveld is quite right in suggesting that we do not treat the canopy interactions here, and all mentions of the NO emission in this paper refer to the above-canopy (canopy-top) NO emission unless specified otherwise. We will ensure that this is explicitly stated in the introduction to the model in section 3. As we back-calculate the above canopy NO emission from the concentration data we do not apply any canopy reduction factor to the flux input to the model. The discussion of canopy reduction factors is restricted to comparing the modelled above canopy flux to measurements of the soil NOx flux made at the forest floor.

RC: Line 9-10; This estimate of 75% canopy reduction (expressed by a Canopy Reduction Factor of 0.25 according to Yienger and Levy, this always leads to confusion) of the soil-biogenic NOx source was based on a very simple first order estimate of the potential role of NO2 dry deposition. The LBA (Amazonia) observations and modeling work (Ganzeveld et al., JGR, 2002) resulted in an canopy reduction factor of 0.5 that does not only reflect NO2 dry deposition but also mixing and
in-canopy chemistry for tropical forest. Apparently, this doesn’t help you in explaining the difference between the canopy top flux soil NO emission flux of 93%.

AC: We find it very interesting that the OP3 measurements of the average soil NOx flux and the model estimated above-canopy NO flux differ so greatly, especially now that Dr Ganzeveld has made us aware that Ganzeveld et al. (2002) have revised down the Yienger and Levy (1995) canopy reduction factor of 75%. We discuss some possible reasons for this in our paper, however we think the most likely explanation is the heterogeneity of the soil NO emission (variations greater than an order of magnitude were recorded depending on the position of the soil chamber). Attempting to scale up such values is fraught with error as the heterogeneity of the source cannot be accurately determined. As a test we run the model with the measured soil NOx emissions, multiplied by a canopy reduction factor of 0.25 (to be conservative). This results in a 400% overestimation of midday [NO2] and 180% overestimation of [NO] compared to the measurements. Furthermore NOy mixing ratios are now hugely overestimated at greater than 2 ppbv. Such high emissions exiting the canopy are clearly not consistent with the measurements, unless some very large loss of NOy is not accounted for in the model. We test possible losses of NOy below.

Probably the most poorly understood NOy loss in this area is organic nitrates, particularly isoprene nitrates. However the 10% average alkyl nitrate yield in the MIM2 mechanism from the RO2 + NO reaction (Taraborrelli et al., 2009), is already at the high end of the spectrum suggested in the literature of 4-12% (Carter and Atkinson, 1996; Chen et al., 1998; Sprengnether et al., 2002; Paulot et al., 2009). Furthermore the dry deposition velocity (equal to nitric acid) which we apply to the isoprene nitrates is at the upper end of the range suggested in the literature (0.4–5 cm s\(^{-1}\)). Shepson et al., 1996; Rosen et al., 2004; Giacopelli et al., 2005; Horii et al., 2006). Hence the recycling of isoprene nitrates back into NOy is small. The NO2 + isoprene \(\rightarrow\) alkyl nitrate channel can be neglected due to the very low levels of NOy, and hence NO2 during OP3. Treves et al. (2000) have shown hydroxy alkyl nitrates, similar to those formed from isoprene, to be very soluble with Henry’s Law constants equal to 1.7 \times 10^4 at 298 K. Therefore the model is run with wet deposition enabled. Although the reduction in modelled afternoon [NOy] is striking, at its minimum value it is still more than twice the measured values. Furthermore, NOx concentrations are barely altered.

Another possibility is that increased PAN deposition, as observed by Turnipseed et al. (2006), could draw more NOx through PAN formation to maintain equilibrium as the PAN is deposited. To test this the model is run with \(V_{d(PAN)}=1.0\) cm s\(^{-1}\) and \(V_{d(higher\,PAN)}=1.5\) cm\(^{-1}\) following the average maximum observed by Turnipseed et al. (2006). NOx concentration is indeed reduced, however the reduction of 16% is nowhere near sufficient for the modelled concentrations to approach the measurements. In another test we increase \(V_{d(HNO2)}\) to 5.0 cm s\(^{-1}\), the very upper end of the literature range. This also results in a 16% reduction in [NOy], but virtually no change in [NOy]. As a final test we double the NO2 deposition velocity (from a max \(V_{d(NO2)}=0.5\) cm s\(^{-1}\) to max \(V_{d(NO2)}=1.0\) cm s\(^{-1}\)). Only a 7% decrease in [NOy] is achieved.

Even combining all these processes in a single run leaves the minimum in modelled [NOy] almost twice the measured value and concentrations in the morning, before substantial rainfall, are highly unrealistic. Therefore, excluding some hitherto unknown loss process for NOy, we conclude that the measured soil emissions, although interesting in their own right, are not appropriate as an input to our boundary layer atmospheric chemistry model.

RC: Pp 19256; In the discussion on the importance of wet deposition in removal of some of the products I wonder if you considered the fact that the convective precipitation might only over a smaller fraction of total area that your model somehow represents (e.g. the typical grid size of a large scale model).

AC: The wet deposition scheme incorporates a factor (f) defining the fraction of the grid box over which convective precipitation occurs. As standard this is set to f=0.3,
following Walton et al. (1988). However we also experimented with different values of this factor and some differences are observed. For $f=0.1$ midday concentrations of wet deposited species are in the range 11-100% higher than using $f=0.3$, whereas for $f=1.0$ they are 18-100% lower. However for the species of interest regarding affecting oxidation capacity (e.g. organic peroxides and aldehydes, due to their high model concentrations and fast reaction with OH) the difference between utilising and not-utilising wet deposition is much larger (we report a factor of 8 above). This is due to the very high solubility of these compounds, for which a large deposition rate facilitates a much earlier attainment of a steady diurnal cycle during the model run.

RC: Pp 19260, line 23; “Furthermore halving the daytime $z_{mix}$ from 800m to 400 m” Based on the previous comments it already seems that an 800m deep daytime BL seems to be substantially smaller compared to other tropical forest sites which would exclude the possibility of even having a shallower mixing volume.

AC: This is of course a reasonable argument. However considering the method we have taken using equation (2) to analyse the problem, we would argue it is sensible to explore any possibility which could reconcile the isoprene and OH concentrations. Hence we have analysed this, rather unlikely, possibility, and concluded it does not yield the result we require.

RC: Pp 19263; “Some care however, must be taken in using the modelled MACR/MVK concentrations as support for the rate constant reduction . . . reaction”, coming back to the previous comment about MVK/MACR deposition it should be added here that use of the concentrations of these isoprene oxidation products to interpret the OH-isoprene oxidation is limited due to potentially important and not well understood role of removal by deposition as well as diurnal boundary layer dynamics, e.g. entrainment of residual layer air masses.

AC: We agree and will add this to the revised manuscript.

2.3 R. Cohen, and E.C. Browne

RC: In the discussion of these issues, the paper proceeds as if the tropics are on a different planet than mid-latitudes. Many of these issues have been discussed in detail in analyses of measurements at mid-latitudes and at conditions with under nearly identical NOx. We highlight some of our own work in this area but these are by no means the only literature ignored in the current manuscript. In our opinion these ideas provide an important context for the interpretation of the measurements described in this paper, a context that might lead to a different interpretation of the results and that is at least deserving of acknowledgment in the references.

AC: We recognise that the lack of a thorough discussion of mid-latitude work is a shortcoming of our original manuscript and will insert the following paragraphs on page 19257, line 17 to replace the current paragraph. However we note we were already aware of this literature and hence the results of our analysis are not affected.

The cause of [OH] underestimation over tropical rainforest is currently unknown, although such model underestimations of [OH] measurements have been observed before. Tan et al. (2001), measuring over a North American deciduous forest, found that observations of [OH] were on average 2.7 times greater than the modelled concentrations. However the modelled and measured HO$_2$ were in good agreement. Carslaw et al. (2001) similarly found that modelled OH concentrations over a forest in Northern Greece were on average, half the measured concentrations. For both these studies, observed concentrations of isoprene were >1 ppbv. More recently Ren et al. (2008) found observed [OH] was as much as 4 times larger than modelled
OH in the boundary layer over North America. They also found that higher model underestimation was clearly correlated to increased concentrations of isoprene. In the only other studies to date incorporating [OH] measurements over a tropical rainforest, Lelieveld et al. (2008) and Martinez et al. (2008) report very much higher observed concentrations of OH than predicted using their chemical model. A notable feature of all these studies is the low [NOx] observed at the sites, and that the model:measurement discrepancy is greater at lower NOx. In a different study Thornton et al. (2002) show that they are unable to close their HOx budgets at low [NOx] based upon current knowledge.

In contrast urban modelling studies have typically agreed well with, or overestimated [OH] compared to the measurements (e.g. George et al., 1999; Konrad et al., 2003; Emmerson et al., 2005, 2007), although Emmerson et al. (2005) did find some days when they significantly under-predicted OH concentrations. Ren et al. (2006) also modelled measured OH and HO2 concentrations well in a rural environment where isoprene concentrations were typically <1 ppbv. Similarly Kanaya et al. (2007) overestimate both OH and HO2 significantly in a model:measurement comparison for Japanese coniferous forests. Whilst Kanaya et al. (2007) measured 200–400 pptv of monoterpenes, they make no mention of isoprene concentrations, which are typically relatively low for coniferous forests (Guenther et al., 2006).

The above literature supports the hypothesis that the underestimation of [OH] is related to isoprene, or an unaccounted for compound that is emitted following the same pattern. It has been suggested (e.g. Tan et al., 2001; Karl et al., 2007) that the reaction of terpenes and ozone could produce sufficient OH to bridge the gap between models and measurements. However Ganzeveld et al. (2008) concluded that this pathway alone could not explain the model deficiencies. Modifying the model here such that each reaction of a terpene with O3 produces one OH molecule, can only generate [OH] within the bounds of measurements at terpene emission rates much greater than those of isoprene. This test was carried out utilising the rate constant of beta-caryophyllene, which, compared to most monoterpenes, has a very fast reaction with O3 and a relatively slow reaction with OH (Atkinson and Arey, 2003). Thornton et al. (2002) and Lelieveld et al. (2008) noted that errors in the photochemical rate constants could be responsible, particularly those for the dissociation of higher peroxides. However Kubistin et al. (2008) found no evidence for this.

A more explicit comparison of the VOC measurements made at 5 m and at 75 m should be able to provide some constraints on the gradients. If gradients do exist, then comparing the above canopy modeled concentrations to the in-canopy measurements is invalid because they represent different chemical environments. We believe a more thorough treatment and discussion of within canopy chemistry is necessary before conclusions about our understanding of tropical VOC chemistry vs. micromet can be made.

AC: There is clearly a misunderstanding here which we may have been precipitated due to an insufficient description of the measurement site in our original manuscript. The measurements made at 5-m in the clearing were not in-canopy measurements. Rather they were carried out in a clearing on the top of a hill, at the base of the 100-m high measurement tower. As stated in section 1, above, we can show that the measurements made here are representative of the boundary layer...
during the day, and they are distinct from the in-canopy measurements. At no point do we compare our box model to the in-canopy measurements.

Several studies of the effects of in-canopy chemistry on BVOC oxidation have been carried out (e.g. Fuentes et al., 2007; Farmer and Cohen, 2008). Whilst the effects reported are certainly not insubstantial, their relevance to our work is limited by two factors. Firstly, the emissions of isoprene and monoterpenes we compare the model against are above-canopy fluxes of these compounds. Hence the moderating effects of any in-canopy chemistry are implicitly included. It is possible that such chemistry may lead to the ‘emission’ of oxidation products from the canopy. For the purposes of our analysis of isoprene/monoterpenes and OH, such compounds would only serve to increase the OH sink and should not affect the OH:isoprene interaction we discuss. Although there could be some implications for our consideration of oxidation products as canopy ‘emission’ of these compounds would further increase the model overestimation. Ganzeveld et al. (2008) calculate that about 90% of their calculated isoprene flux exits the rainforest canopy. The missing 10% is not all reacted, with soil uptake also playing a role (Cleveland and Yavitt, 1997; Pegoraro et al., 2006). Given that oxidation products themselves may be deposited before exiting the canopy, the above canopy-flux of oxidation products will be a relatively small proportion of the whole.

Secondly, these in-canopy studies show that the photolytic source of OH is substantially reduced within the canopy due to the reduced photolytic flux density. In the reported studies oxidation by ozone and/or NO$_3$ become important. For instance Farmer and Cohen (2008) infer very high levels of OH in the canopy of a pine forest, following work by Goldstein et al. (2004). They suggest these high levels of OH are due to the ozonolysis of very reactive organic compounds emitted within the canopy, such as those implied by Holzinger et al. (2005). However the forest in which these measurements were conducted experiences high levels of ozone, with Murphy et al. (2007) finding average 8 hour maximum ozone concentrations >60 ppbv. This is compared to the very low ozone (4–8 ppbv) concentrations measured within at the OP3 in-canopy site. Without a substantial O$_3$ concentration to initiate oxidation within the canopy, it is unlikely that such high in-canopy OH concentrations would be observed. The low in-canopy NO$_x$ mixing ratios during daytime (typically <0.5 ppbv) also suggests that NO$_3$ oxidation is likely to be of much lesser importance than in e.g. Fuentes et al. (2007). For these reasons we believe that in-canopy processes will be of much lesser importance for remote Borneo rainforest than for the reported studies, and hence we neglect them here. We will make this explicit within the revised manuscript.

RC: We also note the discussion of HO$_x$ chemistry is confounded by the multiple couplings that are misrepresented by the model. For example, correcting the model underestimate of NO would enhance OH. Also, any claim the HO$_2$ + RO$_2$ is correctly modeled without constraining OH to observations is at best misleading.

AC: It is true that increasing the modelled NO (either by greater NO emission or constraining to the observations) leads to a substantial increase in [OH]. However it also leads to a very large increase (~100%) in concentrations of NO$_2$ and NO$_y$, which in turn yields a 5 ppbv increase in ozone mixing ratio. This suggests that it is not the amount of NO per se that needs to be increased, but rather the NO:NO$_2$ partitioning, with perhaps a small increase in the emission of NO$_x$. As NO:NO$_2$ partitioning is controlled principally by the available peroxy radical concentration, we must reduce our overestimate of peroxy radicals to the observed value to see if this has the desired effect on the NO:NO$_2$ partitioning. As we cannot easily constrain our total peroxy radical concentration to observations, due to the many radical species involved and a lack of knowledge of their relative importance, we instead use wet deposition to reduce the number of peroxy radicals. This acts in two ways: by direct removal of HO$_2$, and by reducing the number of oxidants with which OH can react to generate peroxy radicals. Fortuitously this results in a daytime peroxy radical concentration which agrees well with that measured. The reduction in [HO$_2$+RO$_2$] results in less cycling of NO to
NO\textsubscript{2}, bringing about an increase in [NO] to within the bounds of the measurements and a small decrease in [NO\textsubscript{2}]. A small increase in NO emission (which we estimate using the model fit) would then be enough to bring both [NO] and [NO\textsubscript{2}] into close agreement with the model. As we state in section 5.2, turning on wet deposition brings about an increase in [OH] (although not enough to bring it within the bounds of the measurements) and also a concomitant decrease in isoprene and monoterpene concentration. We will include a synopsis of the above analysis in a revised version of the paper.

As an aside, we also constrain the model to measured daytime OH concentrations. The result is a strong increase peroxy radical concentrations to more than twice the measured values, whilst decreasing [NO] and [NO\textsubscript{2}]. We concede that this indicates problems in modelling the peroxy radical concentration. However it is interesting to note that the concentration of HO\textsubscript{2} is insensitive to the model being constrained to OH. Hence the increase in total peroxy radicals is due to RO\textsubscript{2} from the increased oxidation of VOC under the higher [OH] conditions. If, as we discuss in section 6, the rate of VOC oxidation is retarded by inefficient mixing, then this large increase in RO\textsubscript{2} will not occur. We will adjust the sentence starting on line 10 of page 19254 to reflect this discussion.

RC: We point the authors to Thornton et al. 2002 who present an alternative approach to assessing HO\textsubscript{x} chemistry and who to our knowledge were the first to point out the need for recycling in isoprene peroxy radical chemistry.

We thank Prof Cohen and Dr Browne for pointing us to the Thornton et al. (2002) paper, which is a very clever and interesting piece of work, and we agree that it would be very interesting to see the chemical coordinates method of Cohen (2000) and Thornton et al. (2002) applied to the OP3 dataset. However we do not feel that this method is any more valid than the model analysis which we have applied. Rather the existence of a range of methods to assess our understanding of the detailed processes at work is vital. As such our work is complementary to approaches such as Thornton et al. (2002). We will be sure to include the Thornton et al. (2002) paper in our discussion of this problem.

2.4 Anonymous referee 1

RC: Page 19265, line 13, it is worth mentioning here that the 200 ppt of NO\textsubscript{x} observed during OP3 (page 19249, line 22) is an order of magnitude more than was observed in the GABRIEL campaign (Lelieveld et al. 2008). This will tend to recycle more OH from HO\textsubscript{2} via reaction with NO, and require less OH recycling within the isoprene oxidation mechanism itself.

AC: We think there is some confusion here. Lelieveld et al. (2008) give an average daytime mixing ratio for NO of 20 ppt, this is very similar to the 30–40 pptv of NO we observe. However they do not report total NO\textsubscript{x} mixing ratios.

3 Other author comments

Since the submission of our original manuscript a small error in the model coding has come to light. This error led to the model losing NO\textsubscript{x}. We have corrected this problem and the vast majority of our results and analysis remain unchanged. The only notable changes are that our estimate of NO emission is revised down 36% and the model overestimation of peroxy radicals is increased in the first optimisation. This raises the question of whether the possibility of the Hofzumahaus et al. (2009) hypothesis of increased cycling of peroxy radicals into OH via an unknown compound with a similar reduction capacity to NO is behind our modelled [OH] underestimation. We test this in the model by adding such a compound with the same concentration and reaction
rate with peroxy radicals as NO, and find that it can bring about a >100% increase in OH concentration for a 10% decrease in peroxy radical concentration. However the problem of isoprene and OH concentrations not matching the measurements simultaneously is still observed. Hence this simply represents another possible method for OH recycling. We will include the description of this simulation in a revised manuscript.

References


Pugh, T. and et al.: Nocturnal profiles of NO\_x and O\_3 over a South-East Asian rainforest, in preparation, 2009.


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