Response to Reviewers
ACP-2009-778

We thank our Reviewers for their helpful and constructive comments concerning our manuscript.

In response to the comments from Reviewer #3, we have significantly restructured the box model section of the paper. We have separated some of the material from the previous version of the manuscript to the Supplementary Materials, and included results from a more constrained version of the model in the manuscript.

Responses to each reviewer are listed in order below.

Sincerely,
Rachel

Response to Anonymous Reviewer #1

General comments:
In response to the comments regarding the NO budget, we have included a description of the equation and terms (coinciding with comments from Reviewer #3) in the introduction of the paper. In the Supplementary Materials, we have added plots of total NO_x and the $NO:NO_2$ ratio in order to describe the chemical mechanism's ability in more detail. We have also added a description of the full budget. We acknowledge that there may be unknown oxidants that contribute to uncertainty in our calculations, and have included this in the budget analysis section.

1. The pressure of 1013 hPa was misreported; a fix in which pressure is overwritten was overlooked. The pressure was actually run at 950 hPa, and this has been amended in the text. This is the same pressure that was used in Hewitt, et al., 2010 for back trajectory calculations.

2. We recognize that an additional exploration of OH recycling in isoprene oxidation would be interesting. Considering the continued debate in the literature as to the mechanism and impact of OH recycling (e.g. Archibald, et al., 2010), we think that this is best left for future work. We have added a sentence in the Summary section acknowledging that the potential impact of OH recycling is an uncertainty in our work.

There is currently no monoterpene emission and therefore no terpene chemistry represented in the box model. We are using the chemical mechanism that matches the global model mechanism, which is why we do not include monoterpenes. We have added a line to indicate that monoterpenes may play a roll (2^{nd} paragraph of the box model description section).

To address Reviewer #1's point about monoterpene chemistry, we point to the budget analysis in the final section of the paper. For ozone concentrations, we find that deposition is a more important factor than chemistry. This is shown both in the chemical budget (Table 3), and in the sensitivity studies described in the Supplementary Materials, in which deposition makes a small difference, and chemical parameters make almost no difference to the results. A simple back of the envelope calculation looking at the recycling of NO by various peroxy radicals (Tables 3 and 4) shows that an increase in isoprene of 20% only results in a 7.3% increase in recycling of NO. Although this is a crude estimation, in which the difference in rates of reaction between terpene and isoprene degradation is ignored, we think it illustrates that monoterpenes do not have the largest role in determining the ozone or NO_x budgets.

3. A sentence describing the vertical structure of p-TOMCAT has been added to the global model description. The global model comparisons are with the surface box which is over the measurement site, as indicated in the caption of Fig. 3.

4. The emission and diurnal profiles of isoprene will be discussed in an upcoming paper on the subject by Langford, et al., ("Fluxes of volatile organic compounds from a south-east Asian tropical rainforest"), which is due to be submitted to the same special issue. We also refer the reviewer to the diurnal cycle shown in Figure 9a of Hewitt, et al. (2010). We have used the same measurements as input into our box model, albeit for the first intensive observation period, which occurred in April. The diurnal profile of isoprene looks similar in the box model, with a peak of approximately 2.6 ppbv around 3 pm.

As per request of both Reviewer #1 and #3, we have included a table of dry deposition velocities (Table 1).

5. In response to the comments by Reviewers #1 and #3, we have added a "constrained" box model, in which photolysis is unchanged, and we have moved the "fixed" model studies that have an altered jNO2 to the Supplementary Materials. In this additional document, we have included a more in depth explanation of our changes to jNO_2 in the model description, including plots of the correlation between reducing only jNO_2 and reducing all the photolysis rates. We found that the slopes of the correlation plots were very close to 1.0, with values of 0.99, 0.93, and 1.22 for ozone, NO_2, and NO, respectively.

Reviewer #1 asked for a comparison of jNO_2 with measurements. We have not done so because the results have not yet been made available to the OP3 community.

6. The initial concentrations of CH_4 and H_2 have been included in the initial data table. With regards to the diurnal concentration profile of isoprene, we have mentioned above that the measurements presented in Hewitt, et al., 2010 are identical to our box model input, and that they will be presented in more depth in a forthcoming paper (Ben Langford, et al., "Fluxes of volatile organic compounds from a south-east Asian tropical rainforest").

The impact of VOC concentrations on the ozone budget is now discussed in the budget analysis section at the end of the paper.

7. We have clarified the explanation of the venting parameter, and changed its name to "dilution parameter" in order to make its purpose in the model more obvious. We have assumed zero concentrations in the free troposphere of all constituent species except for ozone, which is discussed in the introduction of the dilution parameter and in the text explaining Figure 5. Our reasoning is informed by the measurements provided in Pearson, et al., 2010, which indicate that the ground site may be in the free troposphere during the latter part of the night. This is now described in the second paragraph of the dilution section.

8. We have moved the discussion of the fixed model cost function to the Supplementary Materials.

The difference in modeled and measured NO_2 for the "best fit" run in the Supplementary Materials has been described in stronger language. The use of further physical parameters (afternoon convection) is postulated as a possible cause for the model-measurement discrepancy. Although the contours in the cost function analysis are varied, we were able to locate a low point in the results for all three. This provided the basis for the "best fit" run. We disagree that the requirements for each species are entirely incongruous with one another; for example, both NO and NO_2 needed to be vented in order to achieve a low value for the cost function. An additional discussion of budget terms has been added to the final section of the paper.

9. We have added a section to the box modelling section of the paper describing a full budget analysis. We were able to pull out individual fluxes, identify sources and sinks of ozone and their relative importance, and show the variation of key fluxes in the final Figure of the paper. We found that there is a net production of ozone during the day and net loss at night, while NO remains in steady state throughout the diurnal period.

10. In the last paragraph of the Final global model simulation section of the Supplementary Materials, there is a description of the behaviour of the boundary layer in the global model compared with the measurements. As we state in that section, a global model is not able to resolve the orography specific to the measurement site. We think a direct comparison of the two would be misleading, which is why we chose to describe the behaviour in text (rather than a figure).

11. The aircraft data are indeed from July; the aircraft was not part of the campaign during April, as indicated in the caption of Figure 2. We have changed the language in the final paragraph from "vertical mixing down" to "mixing and dilution up" to clarify our meaning.

12. Rainfall at the Bukit Atur site was discussed in depth in Hewitt, et al. (2010), in their section 2.2.; we refer the Reviewer to that paper. In our figures, the measurements shown include all available data from the first intensive measurement period (between April 8th and May 3rd). The shape of the diurnal profile is consistent throughout (the pattern of the 25 and 75 quartiles closely resemble the shape of the median data) and therefore we conclude that rainfall data is not impacting the observations strongly, which is why all data points have been included in the final version of the Figures.

Figures:
We have included an updated, higher resolution version of Figure 1.

Response to Anonymous Reviewer #2

1. We have changed the paper title from "Can a global model chemical mechanism reproduce NO, NO_2, and O_3 measurements above a tropical rainforest?" to "NO_x and O_3 above a tropical rainforest: an analysis with a global and box model."

2. We have changed the language regarding ozone production to clarify the point as the Reviewer requested.

3. We have amended the range of the ozone lifetime.

4 & 5. We have included and changed the text from "zero air" to "NO_x free air" and replaced "zeros" with "interference determinations" to be more clear.

6. The right-hand side of Figure 2 is also medians, to be consistent with the left hand side.

7. The language "ozone shows little vertical structure" has been changed to "[t]he values of ozone aloft show little difference, and therefore vertical structure, when compared to values of the ground-based measurements."

8. The references for the global model emissions of anthropogenic, biomass burning, and lightning emissions have been included in the manuscript. As our goal is to ascertain if a global model mechanism is enough to capture the measurements, we think including these datasets is appropriate. A study of the emissions datasets would be extremely useful, but we believe it is outside the remit of our work here.

9. The global model gridbox was 100% land; there are no split gridboxes in the p-TOMCAT model. The measurement site was approximately 55 km from the coast. For further information regarding the location of the ground based measurement site, we refer the reviewer to Hewitt, et al., 2010.

10. We have removed "24 hour" from the sentence.

11. We have changed "observations" to "results".

12. As mentioned above, we have updated the resolution of Figure 1.

13. Thank you for catching the typo; we have updated the affiliation.

Response to Reviewer #3, Mat Evans

1. Introduction

In response to Reviewer #3's comments, we have reorganized the Introduction section and added two paragraphs which outline the budgets of O_x and NO. We agree that this adds to the introduction and the structure of the paper. We have also created a section dedicated to budget analysis of a more constrained version of the box model. Two references to inorganic chemistry above forests have been added: Ganzeveld, et al., 2008 and Trainer, et al., 2001.

2. Model Set Up

We have created a distinction between a "constrained" version of the box model and the "fixed" version (with adjusted jNO_2) of the model, which is now only included in the Supplementary Materials. There, we describe the basis for the reduction in jNO2 was to correct for a photolysis scheme which was optimized for Europe, and to match the global model output. One of the reasons we want to keep the global model results in the paper (a point brought up below) is that this also provides context for the methodology of the box modelling work. Our goal is to assess the ability of the global model mechanism, which is usually employed alongside a different photolysis scheme, which is able to successfully reproduce the correct NO:NO_2 ratio. In order to evaluate the other components of the mechanism, we applied the simple adjustment to jNO_2.

As described in our response to Reviewer #1, above, we also performed a sensitivity in which all photolysis rates were reduced. We found that the slope of the correlation between the two runs were very near to 1.0 (0.99, 0.93, and 1.22 for ozone, NO_2, and NO, respectively).

We understand the Reviewer's apprehension about this adjustment, and now the version of the model now described in the main manuscript has no change to jNO_2. This model version also has an emission rate of NO of 6×10^9 molec cm^2, which is in between the rates reported in Bakwin, et al., 1990, and Pugh, et al., 2010.

Isoprene emissions were constrained to measured fluxes, which are described in brief in the measurement "methods" section as well as in the box model set up. We have included a reference to Hewitt, et al., (2010) in which the diurnal cycle of isoprene is shown for July using the same technique. The isoprene measurements will also be reviewed in Langford, et al., Fluxes of volatile organic compounds from a south-east Asian tropical rainforest, 2009, which is in preparation for the same special issue.

Deposition velocities have been added in Table 1.

Nitric acid is not deposited in the model. As described above, it acts as a stable reservoir species since its photolysis and reaction with OH is extremely slow.

The constant temperature was misreported. In the same location where pressure was set but later over written, so was temperature. We have fixed this error and included reference to the correct temperature data, which was recorded in connection with the PTR-MS isoprene data.

We have changed the name of the "venting parameter" to "dilution parameter" in order to clarify its role. Regarding the venting of ozone, we agree with the Reviewer. In the discussion of the fixed version of the box model (Supplementary Materials), we reach the same conclusion and do not dilute ozone.

3. Night Time Chemistry

We point the Reviewer to the beginning of the chemical sensitivities section in the Supplementary Materials, in which NO emissions were tripled in order to attempt to capture night time concentrations of NO. We were not successful in this endeavour.

A set of collaborators in OP3, lead by Tom Pugh (Lancaster) are circulating a draft regarding nighttime NO concentrations. They examine NO using both a box model and a single column model. We refer the Reviewer to this upcoming work for discussion concerning nighttime chemistry.

We do not include heterogeneous nighttime chemistry in the box model. Although we agree that N_2O_5 and NO_2 uptake onto aerosol could play a role at night, for the first half of the night total NO_x values increase in the measurements. While a simple first order loss rate could parameterize the uptake process, the impact on modeled NO_x would be the opposite to the observed trend. We have included a sentence in the Summary section which points out this uncertainty.

4. Comparison with Observations

We have added a plot of total NO_x and NO:NO_2 ratio to the "best fit" discussion in the Supplementary Materials in order to pull apart the skill of the model on both long and short time scales, and a discussion of this has been added as well. As mentioned before, jNO_2 values were not measured during this campaign period, and the data has not been made available to us, so we are unable to compare the model to data in this regard.

The recycling and reactions of NO and NO_2 are now quantitatively discussed in the budget analysis section.

5. Diagnostics

In response to the request by Reviewer #3 for more diagnostics, we have included a budget analysis of ozone for the box model.

6. Venting parameter

We have added a sentence to page the section describing the dilution parameter which explains the units on a number of time scales. The dilution parameter is similar to the work of Biesenthal, et al., 1998, and a reference to this paper has been added to the Dilution section.

7. Qualitative language

Where appropriate, we have made every effort to change the language and add quantitative descriptions to the text of the paper. In particular, the budget analysis and the correlation between photolysis rate reduction experiments (now in the Supplementary Materials section) are both quantitative.

8. Global model simulations

We disagree with the Reviewer on this point. We think that the global model simulations provide both context and background for the box model work. We think they show that the box model can indeed be used to approximate the global model output in the first instance (as shown in Figures 3 and 4), and that this is helpful is justifying the use and setup of the box model. To clarify our intentions, we have changed the language in the abstract to indicate that the global model is used to set the context of the box model experiments.

9. Role of isoprene

We performed a number of studies in conjunction with the isoprene emissions sensitivity tests, including no isoprene, and flat isoprene emissions. We found that isoprene was needed but that within physically representative changes to the emissions, the effects were limited. We have added a sentence to the chemical sensitivities section of the Supplementary Materials to indicate this.

10. Specific comments

We have amended the text in each place where indicated:

- Figure 1 has been updated.
- The description of sub-grid scale processes has been updated.
- "Troposphere" has been added to the sentence describing NO_2 photolysis.
- "Emissions" has been added to the sentence.
- The difference between these paragraphs is the number of data points included in the sample and the month, both of which are included in the caption. We have added additional text to make this difference more clear to the reader.
- The value of the ozone deposition has been included in the budget section.

- As the chemical sensitivity section is now in the Supplementary Materials, the reference to Emmerson and Evans (2009) has been removed.
- We have added a full budget analysis in the final section of the paper, in which we quantitatively compare the contributions of dilution and deposition.
- We do not state that the diurnal structure of NO_2 is entirely controlled by physical processes, but that our results indicate that physical processes dominate the structure. We hope that by adding a plot of total NO_x and a budget analysis that our conclusion is clearer.

Works Cited

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