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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Can a global model chemical mechanism reproduce NO, NO<sub>2</sub>, and O<sub>3</sub> measurements above a tropical rainforest?" *by* R. C. Pike et al.

**Anonymous Referee #1**

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Pike et al. report their global and box model studies about the observations of NO, $NO_2$, and $O_3$ in a high isoprene and low NOx condition which is of growing importance as highlighted by the works from Lelieveld et al., (2008), Ren et al., (2008) and Hofzumahaus et al., (2009). The major scientific question answered by this paper is "What are the dominant uncertainty sources of the global model for the simulations of NOx and $O_3$: chemical mechanism or the atmospheric dynamics?" This is indeed a very interesting issue which needs to be explored. In case of the air quality models, when they under-perform, problems are usually attributed to emissions (including their



quantity and the speciation of organic compounds); to meteorology and to sub-grid scale effects. While in many cases, the atmospheric chemical mechanisms are not questioned.

In this manuscript, the discussion is initiated by the discrepancies between the modeled and measured $O_3$ concentrations; then a question is naturally raised up as "why the model can reproduce the daytime NOx concentration but not $O_3$?" ; afterwards a number of sensitivity studies on the chemical mechanism modifications with a box model, however none of these chemical improvements are able to improve the simulation results; furthermore, the physics parameter adjustments (venting parameter and boundary layer height) are tried and finally can reach a reasonable $O_3$ simulation results. From that point of view, the authors conclude that the major uncertainty source should be come from the physical parameters setup (boundary height) in the global model. This is a interesting story and materials are good which is valuable to be published by ACP. However, I have some considerations especially on the chemical part which needs to be addressed before publication.

Let's think about the NO budget:

$$\frac{d[\mathrm{NO}]}{dt} = \mathrm{jNO_2} \times [\mathrm{NO_2}] - k[\mathrm{NO}][\mathrm{O_3}] - k'[\mathrm{NO}][\mathrm{ROx}] + E - k''[\mathrm{NO}][\mathrm{XO}] \quad (1)$$

Normally NO would reach steady state (d[NO]/dt=0) during daytime, the observed daytime concentration profile of NO also provide clues on that. Thus we can rearrange equation (1) to be:

$$\frac{[\mathrm{NO_2}]}{[\mathrm{NO}]} = \frac{k[\mathrm{O_3}] + k'[\mathrm{ROx}] + k''[\mathrm{XO}] - E/[\mathrm{NO}]}{\mathrm{jNO_2}} \quad (2)$$

For the environment the authors are discussed, I think the emission term of NO (as denoted by E in these two equations) could be neglected.

According to Fig. 3, actually I see very nice match between both global model runs with the measurements of NO and $NO_2$, this means that in the model the $[NO_2]/[NO]$ ratio is correctly reproduced. At this step if you want to improve the $O_3$ simulation without degrade that of the NOx, you should check if your model have correctly simulated $jNO_2$, ROx and possibly there are some unknown oxidations of NO (denoted by XO in these two above equations) which has not been incorporated into all the current chemical mechanism (In your conditions, the halogen chemistry might be a candidate for this extra oxidation). The later two factors are obviously point to the problems of the chemical mechanism. Detailed comments or suggestions about how to check $jNO_2$ and ROx issues are given by specific comments 2, 5 and 6 et al.

**Specific Comments**

1. Page 27616 line 9 The text describe the site is 426m high. However, later on the box model use 1013mbar which seems to be not suitable.

2. Page 27620 line 7 The text mentioned that the MIM is used, that is good, but could be better if you can try the proposed generic reaction mechanism proposed by Kubistin et al., (2009) and Hofzumahaus et al., (2009):

$$ISO_2 + HO_2 \rightarrow ISOOH + n \times OH \quad (3)$$

$$HO_2 + X \rightarrow OH || RO_2 + X \rightarrow HO_2 \quad (4)$$

since these two reactions could probably improve the ROx simulation results and thus help the $O_3$ simualtion. Besides, halogen chemical mechanism is also valuable to try. Nevertheless, this comment is only for the authors consideration. The major point is that I would like to see some argument about the quality and uncertainties of the ROx simulation. There were already relatively detailed discussions have been provided by a companion paper-Pugh et al.(2010) and probably



more detailed discussions would be given further by Whalley et al.(in preparation). Nevertheless, either a relatively detailed discussions about the ROx radical simulation should be included in this paper or the author should provide reasonable arguments that the uncertainty of the ROx simulation is not critical for the $O_3$ simulation herein.

Besides, only isoprene emissions has been considered by both the global and the box model, while terpene emissions could be of significance for forest region as well. Especially, some terpene chemistry has been discussed by Pugh et al.(2010). Therefore, it would be useful to account terpene chemistry in this case. And hopefully ROx radical concentration would grow up and the $O_3$ concentration may drop down then in the model system.

P27620 line 21: "Emissions of NOx, CO, ethane, propane and isoprene are included." Emissions of monoterpernes are not mentioned. The typical monoterpene to isoprene ration was between 0.2-0.25 at the Bukit Atur GAW station (Hewitt et al., 2010). Please clarify this as well.

3. P27621 line 26 Please give a brief description of vertical structure configuration of p-TOMCAT model. Are the modeled concentrations of $O_3$ and NOx in surface layer compared with ground observations?

4. Page 27620 line 27 It would be useful to present how are the diurnal profiles of the isoprene emissions look like since there are no reference given. (May be given as supplementary materials). The detailed number of the dry deposition velocity of NOx, $O_3$ and HCHO etc would be valuable to be presented for the reader to evaluate as well.

5. Page 27622 line 19, the rate constant for $jNO_2$ was reduced by 50% to account for clouds and aerosol. What is the detailed reason to reduce $jNO_2$ down by 50%? Obviously, two different mechanisms are used to generate $jNO_2$ in the box model and the global model. One is MCM approximations and the others are Cambridge

2-D model. It would be valuable to present the diurnal variations of $jNO_2$ along with the NOx and $O_3$ since that are critical for the reader to understand what was going on. Besides, according to Table 1 of Hewitt et al. (2010), there were in-situ photolysis frequency measurements in BA site, thus it would be valuable to perform intercomparsions of the calculated and measured $jNO_2$ since it is a critical parameter subjected to $O_3$ simulation.

6. Page 27622, How much are the $CH_4$ and $H_2$ concentrations set in your model?. Besides, since the authors had only include NO and Isoprene emissions, which indicate the dominant role of isoprene chemistry in the box model calculations. Could the author compare your calculated isoprene concentration profile with the that of the measurement show by a companion paper (Hewitt et al., 2010). It would be helpful to compare the simulated levels of individual VOCs or even total VOCs by the p-TOMCAT global model or the corresponding box model with observations, which might provide some insights to the deviation of modeled $O_3$ from the observed.

7. Page 27623 line 27 The authors stated:"A dilution parameter was introduced to simulate mixing with the free troposphere resulting from a collapse of the boundary layer at night. This Âą°venting parameterÂą± removes..." Could the authors provide a little more details? (i.e. what are the concentrations of $NO_x$ and $O_3$ you have assumed in the free troposphere?)

8. Page 27630 line 3 The author stated, "Modelled $NO_2$ is slightly higher than the measured values but captures the structure of the measurements effectively." Actually, this judgement is not true, the modeled $NO_2$ is about a factor of 2 higher than the corresponding measurement results during 12:00 - 16:00 (Fig.7). In fact, as the author discovered by the cost-function analysis(Fig. 6), the optimization results show that the requirements from $NO_2$ are very different with that of NO and $O_3$ which imply that only with adjustment of physical parameters is not enough.



9. As can be seen from the daytime concentration profile of $O_3$ (i.e. from fig. 2), the $O_3$ concentration profile is very flat. It looks like to be in kind of steady state. The behavior has been captured by both the global model and the final box model. It would then be useful to perform a budget analysis (a figure) to display how much is from transport and how much is from chemical production.

10. P27632 line 5 Based on the sensitivity tests of box model, the authors have reached that the physical parameters (especially those related to boundary layer structure) are important to the accuracy of modeled results. Although we cannot expect the boundary layer scheme of p-TOMCAT can capture the details of the boundary layer structure in the campaign area, the comparison of the diagnosed boundary layer height used in the global model (P27620 line 15) with the local observation-based boundary layer height (if available) would show a direct clue to the discrepancies between modeled results and observations.

11. P27632 line14-15 "The vertical gradient of $NO_2$, in both the model and the observations, suggests that transport down from the free troposphere is required to explain the observations." Two questions on this sentence. (1) Fig. 2 shows aircraft data in July, are the measurements aloft also available in April? (2) If based on the data in July, the right figure of Fig. 2 shows that the $NO_2$ levels in free troposphere aloft are much lower than those in boundary layer, which suggests a transport up to the free troposphere by the vertical gradient of $NO_2$. Please clarify this.

12. Rainfall and heavy cloud greatly decrease the role of photochemical process on the evolution of $O_3$ and NOx. How often wet precipitation happened during the April? Do the diurnal cycles of measured $O_3$ and NOx include the data during rainfall or only those in dry period?

**Technical comments**

1. P27642 Fig. 1: The data points are too dense, and it is not easy to distinguish the black dots and black line. A running average of half hour or one hour for smoothing is enough for the time interval used in later analysis. It will be clearer to use different colors to illustrate data dots and data lines.

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