NO_x and O_3 above a tropical rainforest: an analysis with a global and box model

Supplementary Materials

This supplementary material describes a series of sensitivity tests performed with the box model in a 'test' setup. This model is different from the 'constrained' model, the results of which are included in the main body of the paper.

In the Section 1, we described the differences in the box model setup between the 'constrained' and 'test' models. Section 2 details six chemical sensitivity studies used to assess the variability of the model response to various changes in the model chemistry. Finally, Section 3 describes a cost function analysis performed on three variables: the boundary layer height during the day, the boundary layer height at night, and the strength of the nighttime mixing due to the dilution parameter.

1 Test box model setup

The test box model differs from the 'constrained' box model in three key ways. First, the emission of NO is not constant in the model. Instead, it is set to 12 pptv hour^{-1}, which implies a varied flux given the change in boundary layer height between day and night.

Secondly, the photolysis rate of NO_2 was altered. The box model uses the photolysis mechanism of the MCM which has not been optimized for the region in which the measurements were made. The MCM photolysis rate constants are for clear sky conditions in July and were not able to produce the correct NO:NO_2 ratio. The rate

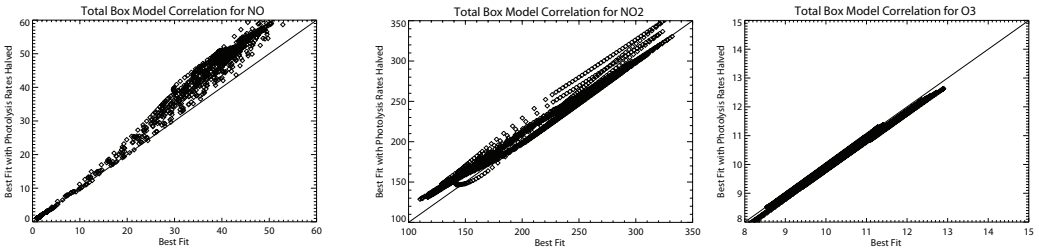

Figure 1. Correlation between runs with all J values reduced by 50%, and only J_{NO2} reduced.

constant for j_{NO_2} was thus pragmatically reduced by 50% to account for clouds and aerosol. To ensure that targetting a single photolysis rate was an effective technique for capturing cloud variability, a sensitivity experiment was run in which all photolysis rates were reduced (as opposed to just j_{NO_2}) by 50%. Figure 1 shows the correlation plots of NO, NO_2, and O_3 concentrations between the runs with only j_{NO_2} reduced, versus the photolysis rates of all three species being reduced. The slopes are 1.22, 0.93, and 0.99, for NO, NO_2, and O_3 respectively, showing that this method was an appropriate estimation.

Finally, in the physical sensitivities section of the Supplementary Materials (Section 3), the boundary layer height was altered as an input parameter for the box model. In the constrained version of the model, this never changes.

In all other respects, the box model described here is identical to that used in the main part of the paper.

2 Chemical sensitivities

A range of experiments was performed to explore the sensitivity of the model O_3 and NO_x budgets to various parameters. First, a series of emissions sensitivities was carried out (not shown.) In order to determine if the nighttime NO concentration could be captured if emissions were altered, a sensitivity study was performed in which emis-

Table 1. Summary of chemical sensitivity tests

Short name	Fig. Colour	Description
Base	Light Blue	The base case
O3 phot	Aqua	j_{O_3} divided by 3
Vd O3	Orange	Ozone deposition velocities reduced by 75%
Horowitz	Green	NO_x recycling rates as [Horowitz et al., 2007]
ISON dep	Yellow	ISON tracer deposition velocities set equal to those of PAN
Reinit	Red	Reinitialized the model each day at midnight
Init O3=9	Purple	Reinitialized at midnight with 9 ppbv O_3

sions of NO were tripled to 1.8 ppbv day^{-1}[1]. This did not improve the agreement between the modelled and measured values at night. Nonzero nighttime NO could arise from emission taking place very near to the measurement inlet, which would not be reproduced by the box model as NO quickly reacts with O_3 to form NO_2 in a zero dimensional model.

The sensitivity of the model to changing isoprene emissions was also examined (not shown). The emissions were adjusted to be unvarying during the diurnal cycle (i.e. constant), but this only produced a limited response in the box model. Doubling the isoprene emission flux into the model reduced NO and NO_2 by approximately 12 pptv during the day, due to sequestration into organic NO_y species such as ISON. However, the ozone concentration was relatively unaffected. Overall, the diurnal patterns were very similar between the two runs, and between these two studies it was determined that the shape of the diurnal profile was not likely to be emissions controlled. Although it has been proposed that some chemistry in high-VOC environments might be explained by the presence of unknown reactive hydrocarbons [see Di Carlo et al., 2004, and references therein], it seems that a VOC with similar reactivity to that of isoprene is unable to explain the divergence in the model-measurement comparison.

[1]Further discussion of the nighttime NO concentrations can be found in Pugh, T., Ryder, J., MacKenzie, A.R., et al., "Modelling chemistry in the nocturnal boundary layer above tropical rainforest: enhanced box-modelling using an effective deposition velocity", this special issue, in prep., hereafter refered to as Pugh, et al., in prep.

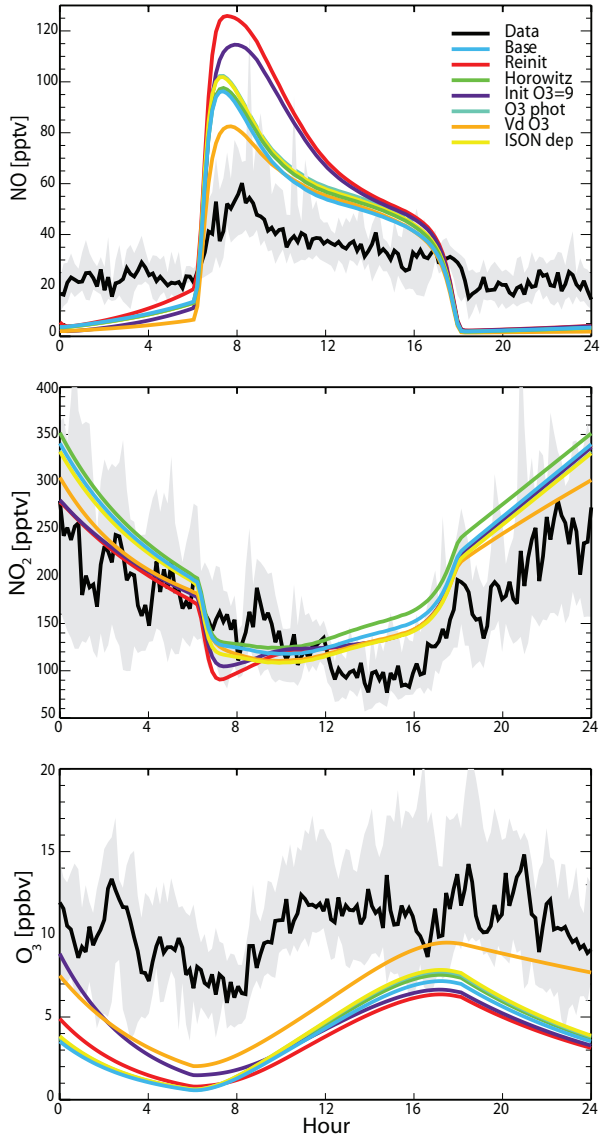

Figure 2. 15 day average diurnal (a) NO [pptv], (b) NO_2 [pptv], (c) and O_3 [ppbv] from measurements (black) with 75% confidence intervals shown in the shaded grey. Seven model experiments are overlaid in various colours: the base run is shown in light blue, reduction of ozone photolysis rate is shown in dark blue, reduction of ozone deposition velocities is shown in orange, adjustment of NO_xrecycling rates is shown in green, ISON deposition change is shown in yellow, reinitialisation at midnight is shown in red, and reinitialisation with high ozone is shown in purple.

Table 1 provides a summary of the various chemical sensitivity runs, with corresponding results plotted in Fig. 2. Generally, the budget was largely unchanged and the diurnal cycle was relatively insensitive to chemical changes. The overall diurnal structure for NO is well captured, with the maxima at 8:00 h. With the inclusion of the dilution parameter, the NO_2 diurnal structure is also always well simulated. All the chemical sensitivity runs capture the cycle of ozone but not the magnitude.

In the first chemical sensitivity test (Fig. 2, aqua line), the photolysis rate of O_3 was reduced by a factor of three. The chemical mechanism shows very little sensitivity to $jO(^1D)$, barely changing from the base case run. In the second test, ozone deposition velocities (both daytime and nighttime values) were reduced by 75% (Fig. 2, orange line). For ozone, this simulation has the most impact of any of the chemical sensitivity studies, but still does not increase the concentration enough to match measured values. The change in deposition velocities also alters the shape of the diurnal cycle, as nighttime deposition drops to 0.075 cm s^{-1}.

In an attempt to keep ozone production values high by increasing the concentration of NO_x in the system, an additional simulation was carried out. Recycling of NO_x from the reaction of ISON with OH was modified by increasing the ISON + OH rate constant from 1.3 x 10^{-11} cm^3 s^{-1} Chen et al. [1998]; Pöschl et al. [2000] to 4.5 x 10^{-11} cm^3 s^{-1} Horowitz et al. [2007] (Fig. 2, green line). An experiment was also performed in which NO_x concentrations would decrease. In this sensitivity study, ISON deposition velocity was increased to match that of nitric acid (Fig. 2, yellow line), an increase to 3.20 (a factor of $\sim$4) and 1.40 (a factor of $\sim$25) cm s^{-1} during the day and night, respectively. Neither experiment has a notable impact on the modelled values of O_3.

Two computational tests were also performed. In the first, the model species concentrations were reinitialized each day at midnight, rather than using the values calculated by the model the previous day (Fig. 2, red line). This introduced a stronger bias in NO and NO_2 around 6:00 h, the first time photochemistry turns on after reinitialization. A second study reinitializes the model at an artificially high value of ozone, and this too displays a similar model bias at sunrise (Fig. 2, purple line). These two experiments give confidence that the model sensitivity to initial conditions is eliminated by reusing the concentrations calculated from the previous day.

The six studies discussed emphasize that the budgets from the chemical mechanism are relatively robust to chemical, photolytic, and deposition rate changes. From our analysis, it appears likely that the regime is more sensitive to physical processes and parameterizations than chemical ones. In order to assess the impact of these chemistry factors in relation to physical parameters controlling the processes of emission, mixing and deposition, we conducted a further series of experiments based on physical variables.

3 Physical sensitivities

Three variables were used to further test the physical boundaries of the box model: the exact quantity of material lost at night (the dilution parameter), the height of the boundary layer during the day, and the height of the boundary layer at night. In order to obtain the best value for these three parameters, a cost function analysis was used:

$$\mathrm{CF_x} = \frac{1}{\mathrm{t}} \sum_{\mathrm{t}} \frac{(|\mathrm{model_x} - \mathrm{measured_x}|)}{\mathrm{measured_x}} \tag{1}$$

where for each species (denoted by x) and at each timestep (t), the difference between modelled and measured values of NO, NO_2, O_3 are evaluated and averaged over 24 hours and 15 experiment days. The cost function gives the average devation of the model from the measurements expressed as a fraction, where zero is a perfect match. The NO cost function is only evaluated between 6:00 and 18:00 h due to the mechanism's inability to capture nighttime NO concentrations, so that results are not skewed because of nighttime values. The results of the three cost functions are shown in Fig. 3, where a lower value of the cost function represents better agreement between measured and modelled concentrations.

The NO cost function shows a dependence on the dilution fraction until the value reaches 2% per timestep, at which point model and measured data converge to a reasonable agreement of less than 30% difference in value. At the zero value for dilution, NO shows almost no dependence on the nighttime boundary layer height, reflecting the fact that the cost function is only evaluated during daytime hours. NO matches

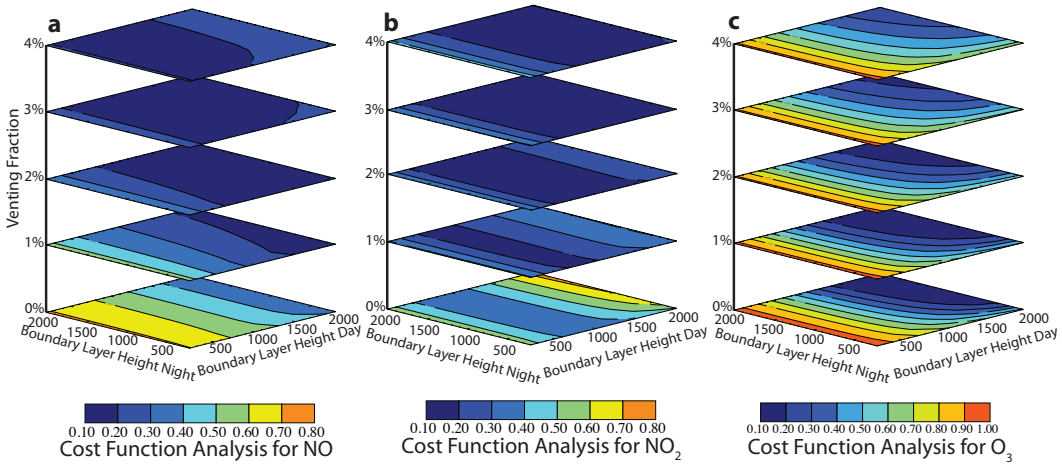

Figure 3. Cost function [|%| difference] of model-measurement comparison to diurnal average a) NO, b) NO_2, and c) O_3. See text for a description of the cost function.

the measurements best (values less than 0.20) for high values of the daytime boundary layer height, though the gradient of dependence on daytime boundary layer height decreases with increasing dilution fraction.

At a 0% value for the dilution parameter, the NO_2 cost function shows values of 0.30 to 0.80. With dilution, the levels are lower (values less than or equal to 0.30), which suggests that the best fit requires at least some constituent species to be transported from the boundary layer at night. At values between 1% and 4% for the dilution parameter, however, NO_2 displays little variation in the cost function, and the entire cost function 'space' has a value less than 0.30. NO_2 also shows very little dependence on the nighttime boundary layer height, demonstrating that dilution is a more important loss process than deposition. The height of the boundary layer during the day is important only at heights less than approximately 700 m.

Ozone was not diluted in these experiments, so the cost function for ozone is relatively stable in relation to dilution parameter. Ozone is very sensitive to daytime boundary layer height (with cost function values ranging between 0.10 and 1.0) due to deposition. Ozone shows almost no sensitivity night except when it is below values of 500 m.

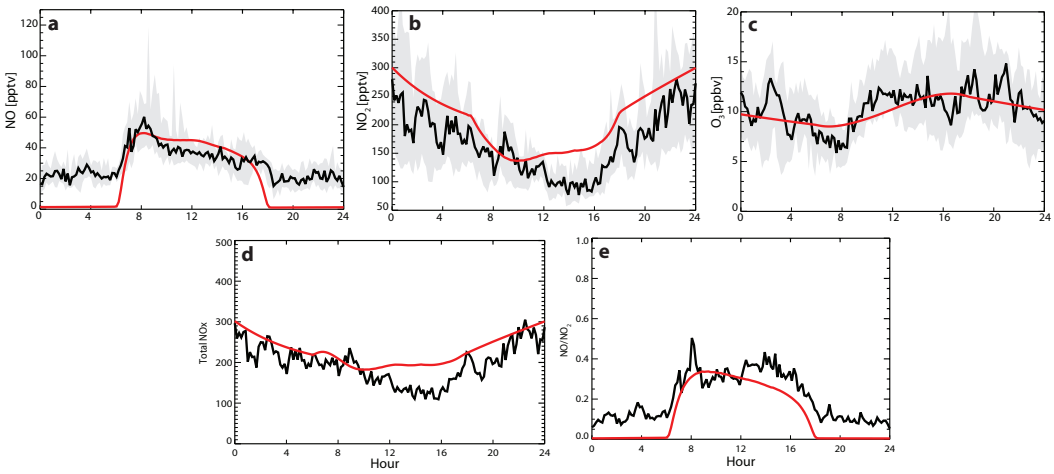

Figure 4. Red: Best fit box model comparison to diurnal average medians of a) NO, b) NO_2, and c) O_3 after adjustments to the dilution parameter and boundary layer heights. d) shows the total NO_x, and e) shows the NO to NO_2 ratio.

4 Test model best fit

Fig. 4 shows the best fit to the measurements obtained using the 'test' box model. The values for the dilution parameter (2%, as used in the more constrained version of the model in the main manuscript), boundary layer height during the day (1200 m) and night (750 m) were taken from the cost function analysis minima. The results show good agreement between measured and modelled values, capturing the majority of structure and diurnal variation for all three measured species. NO matches particularly well, though the model is still not able to simulate the residual concentrations at night. These could arise from a highly stratified boundary layer, or rapid mixing times up from the soil to the measurement inlet before chemical reaction[2]. In either case, these processes are very small scale, and beyond the capability of a global model (with a resolution of tens to hundreds of kilometres) to capture physically.

Modelled NO_2 is higher than the measured values but captures the structure of the measurements effectively. In particular, the nighttime structure of NO_2 is well

[2]The presence of nighttime NO concentrations will be the subject of a forthcoming paper by Pugh, et al., in prep. A discussion of nighttime NO can also be found in Pugh et al. [2010]

simulated once dilution was included in the box model. Afternoon NO_2 concentrations are higher (approximately 90%) in the model than measurements. Since our analysis shows that transport and physical processes dominate the diurnal structure, perhaps this afternoon discrepancy arises from afternoon convection or wet deposition. Ozone looks very similar to measurements, though the rapid rise in the morning is not entirely captured. Nonetheless, the magnitude and basic form of the diurnal cycle are simulated well.

Fig. 4 also shows the comparison of measured and modelled total $NO_x$and $NO{:}NO_2$ ratio. The afternoon shows an overestimate in the total NO_x calculation. As mentioned above, one possible explanation for this is afternoon convection. The $NO{:}NO_2$ ratio is also well captured. We acknowledge that the reduction in j_{NO_2} contributes to this, though the photolysis mechanism in the global model is also able to capture the daytime $NO{:}NO_2$ ratio well.

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