Review of Pike et al., ‘Can a global model chemical mechanism reproduce NO, NO_2 and O_3 measurements above a tropical rainforest?’

This paper describes efforts to investigate the suitability of a relatively simple chemistry scheme to simulate the chemistry occurring within a rainforest boundary layer. The chemistry scheme has been taken from a chemistry transport model and this helps to motivate the exercise. Observations of NO, NO_2 and O_3 made as part of the UK OP3 programme in Borneo are used.

I have significant reservations about this paper. I believe studies of this kind are essential if we are to have confidence in the chemistry schemes used in global composition transport models. However, I do not think that this paper in its current form provides significant insight into the model chemistry scheme performance.

Thus my recommendation is that the authors re-write much of the paper with a tighter focus on a detailed understanding of the processes they describe and re-submit.

Introduction

The premise of the paper is an assessment of the ‘simple’ chemistry used in the global model pTOMCAT. The implication is that a more ‘complex’ chemistry would do a better job of simulating the NO, NO_2 and O_3 in the forested boundary layer. However, it is not clear why you would think this was the case. What aspects of the chemistry are likely to be well simulated by the simple chemistry? What aspects might be expected to be badly simulated?

This lack of detail in the basic premise is reflected in the complete lack of description of the fundamental chemistry occurring in the forested boundary layer. There is a large body of work in the literature which described the photochemical production of O_3 and the partitioning of NO and NO_2. There are papers in the literature which describe the cycling of NO_x within the forested area. None of this is mentioned in the introduction. There is little context for this study from previous work.

The introduction should provide a context to place the subsequent analysis of the paper into. As I understand it the modelled O_3 could be described by something along the lines of

$$\frac{d[O_3]}{dt} = -k_{dep}[O_3] + k_{mixing}([O_3]_{freetrop} - [O_3]) - kJ_{O1D}[H_2O][O_3] + k[NO][HO_2] + k[NO][RO_2]$$

The first 2 terms are essentially physical and the last 3 terms are essentially chemical. The whole paper is based on an assessment of these terms, their sensitivity and their change over the day. Describing this context in the introduction would be extremely useful to the reader. Similarly, NO_x can be described as

$$\frac{d[NO_x]}{dt} = k_{emiss} - k_{dep}[NOx] + k_{mixing}([NOx]_{freetrop} - [NOx]) + k[NOy] - k_{loss}[NOx]$$

And the NO to NO_2 ratio can be described as

$$\frac{[NO]}{[NO_2]}=\frac{J_{NO2}}{k[O_3]+k[HO_2]+k[RO_2]}$$

Thus by providing this framework in the introduction the rest of the paper can be placed into a context. I would imagine that even a simple chemistry scheme should be able to simulate the NO to NO_2 ratio correctly with increased levels of difficult for NO_x and O_3. However unless the introduction to the paper creates the context the rest of the paper seems a little confusing.

Model set up and description

In general I find the description of the model confusing with often apparently arbitary decisions made about the choice of parameters.

What is the basis for the 50% reduction in JNO_2? Why 50% and why JNO_2 alone and not $J(O^1D)$, JCH_2O etc? This appears un-physical. JNO_2 plays a central and linear role in determining the NO to NO_2 ratio. Failures to simulate NO may reflect uncertainties in JNO_2 however this is not described in any detail.

Similarly, how was the NO emission of 600 pptv day-1 calculate? How were the concentrations in Table 1 chosen?

What were the isoprene emissions? Their rates are not discussed

What were the deposition velocities used? Was nitric acid deposited? A lack on nitric acid deposition to have significant impact for the NO_y budget.

A 5^oC temperature change at 25^oC leads to a ~10% change in the [NO] to $[NO_2]$ ratio through the NO + O_3 reaction. Although small compared to the model to measurement failure it is not obvious that the model should be completely insensitive to the temperature.

The venting parameter is not well explained. As I understand it this is a relaxation of the model back to a zero concentration. Although for NO_x (which is log normally distributed and much lower away from the boundary layer) this may be a somewhat justifiable methodology, for O_3 this appears completely inconsistent with what is know for the profile of O_3 in the atmosphere. Forcing the O_3 to tend to 0 ppbv appears to be un-physical.

Night time chemistry

The observations of night time NO are extremely difficult to reconcile with current understanding of photochemistry. However, they need to be dealt with in a more coherent manner than they are in the paper where they are mainly ignored. If the observations are too be believed they constitute a significant finding. It is presumably possible to get the model to agree with the observations by introducing a new ‘magic’ reaction which would convert NO_2 into NO and $O(^3P)$. The forest is a chemically complex environment. The conversion of NO_2 into HONO at the surface has been seen before. Is it a possibility that NO_2 coverts into NO? It would be interesting to know how fast would this reaction have to be to reconcile the night time observations with the measurements? If this continues through the day what impact does this have for the NO to NO_2 ratio? Does it improve the daytime simulation? An alternative approach would be consider the night time NO as an artefact and remove it from the signal. Does that improve the simulation of the daytime NO to NO_2 ratio?

The reduction over the night of NO_2 concentrations is discussed in the paper. There is however, no mention of the modelled night time chemistry. NO_3 and N_2O_5 uptake onto aerosol can play a role in determining the loss of NO_x during the night-time. There is however no discussion of this at all. Is the heterogeneous uptake of N_2O_5 and NO_3 considered in the model?

Comparison with observations.

This section should provide a more sophisticated evaluation of the model than it does. The modelled response can be investigated in terms of fast processes (photochemical steady state) and slow processes (emissions, deposition etc). This can be achieved by looking at the variation of NO_x (rather than NO and NO_2) which should respond slowly and then the ratio of NO to NO_2 which should respond quickly. This should allow various different factors to be tested. NO and NO_2 should be in a photochemical steady state. Given the low O_3 concentrations are they? Are measurements of JNO_2 available for comparison with the modelled values? This is of central importance for the NO and NO_2 comparisons. It is hard to make any quantitative statements about NO and NO_2 concentration if the photolysis rates are uncertain to ~50%. Is the diurnal variation in NO_x (which is less subject to fast photochemistry) better understood than NO and NO_2 individually?

Diagnostics

The advantage of a model over observations is that it can be fully diagnosed. This paper takes very little advantage of this capability. There is no description of why there is O_3 production during the middle of the day? Given the remoteness of the area it is surprising that there is net O_3 production. Is the O_3 being produced from HO_2 from O_3 photolysis or CH_2O photolysis, RO_2 from the degradation of the hydrocarbons, which hydrocarbons contributed? What are the relative importance of O_3 deposition, mixing to the background, O_3 chemical loss and production. The model is capable of producing all of these diagnostics but none of them are described. An evaluation of which of the terms are physical and which are chemical would allow the implications of a simple chemistry to be evaluated. Although these diagnostics are not needed for every simulation performed, they should be provided for the final simulation which is considered the ‘best case’ in describing the processes controlling the atmosphere at the site. Otherwise it is very hard to know what has been learnt from the study.

Increased use of diagnostics would also remove the need for statements such as can be found on line 15 of page 27629. We can diagnose the model and thus understand its response. There needs to be no ‘presumption’ about the reasons why the model responds in the way that it does.

Venting parameter

The venting parameter is described in terms of % per timestep. This is not a very useful unit. The timestep is not described in that paragraph (although it is described earlier in the document). Does the description on page 27628 of 2% per timestep (10 mins?) imply a relaxation timescale to a concentration of 0 pptv on an 8 hours timescale? Is this reasonable? Are there any literature papers to help back this up?

Qualitative language

There is much use of qualitative language in this paper. ‘decently captured’, ‘good agreement’, ‘relatively small’, ‘little sensitivity’, ‘barely changes’ etc. This is not useful language. If these terms are to be used they must be backed up by a quantitative statement of what is meant - ‘reducing $J(O^1D)$ by 10% leads to a change in noon time O_3 concentrations of 3%’ etc. The model can be diagnosed very easily and thus qualitative statements about the model are not needed. These qualitative statements of model success or failure should be removed.

The Global Model simulations

It is not obvious to me what we have learnt from the global model simulations. There is some rough suggestions that the higher resolution version of the model performs better but this is not diagnosed to show whether that is local, regional or global in scope thus making any useful interpretation difficult. My suggestion would be to remove the global model studies as I don’t think they add anything.

Role of isoprene

No comment is made in the paper on the impact of the isoprene chemistry and presumably the suppression in OH that is associated with it. This is extremely topical but is not mentioned. Does it matter? Do you need isoprene in the model at all?

Specific comments

Figure 1. The concentrations here are shown in ppbv whereas through the rest of the paper they are shown in pptv.

Page 27614
Line 1 Unless there is a specific sub-grid scale parameterization included in the model, all models have no ability to model sub-grid scale.
Line 28. Photolysis of NO_2 is the only mechanism to produce O_3 in the *troposphere*. In the stratosphere photolysis of O_2 produces O_3.

Page 27615
Line 15. It is not clear how why NO_x species influence local chemistry significantly. NO_x species are responsible for defining the local chemistry. Do the authors mean that local NO_x *emissions* can influence local chemistry?

Page 27618

The initial paragraph on this page describes a diurnal variability in O_3. Two paragraphs later the diurnal appears to be unclear. What is the difference between these two paragraphs.

Page 27620
The description of the differences between the model and measurements is often qualitative and it is not obvious what has been learnt. O_3 deposition being an important term in the budget of O_3 should be referenced by previous work or shown from a model diagnostic rather than just stated.

Page 27627
Emmerson and Evans make almost the opposite conclusion to the one stated in the paper. It concludes that for all situations, other than for high biogenic loadings, models perform similarly. Under the conditions being investigated here the model simulations using differing chemistry schemes show a large degree of difference.

Page 27629
You can demonstrate that venting is a less important process than deposition by looking at the budget of NO_2. You don't need to infer it from the value of the cost function.

Page 27630
I think it is hard to argue that the diurnal structure of NO and NO_2 is entirely determined by the physical processes. The NO to NO_2 ratio is determined by the photolysis rate and O_3 concentration. The variation in slower changing components like NO_x and O_3 may be impacted by transport but without budgets it is hard to be convincing of this.