

2<sup>nd</sup> April 2015

Dear Professor Wennberg,

Firstly, thank you for your feedback and comments on our ACPD manuscript and allowing us the extra time to reply.

We have uploaded a new version of the manuscript and a document detailing the changes we have made. We are very grateful for your suggestions of performing more evaluation of the reduced isoprene chemistry schemes in the box model and, as a result, have made major modifications to the structure of section 3. We have performed analysis of the NO<sub>x</sub> lifetime (as defined in Equation 1 of Browne and Cohen [ACP, 2012]) and included a discussion of the biases relative to the MCM. Briefly, we find that changes in the NO<sub>x</sub> lifetime, and hence abundance of NO<sub>x</sub>, can explain much, **but not all**, of the structure of the biases in O<sub>3</sub> that the reduced mechanisms simulate, compared with the MCM. Whilst we agree with your suggestion that complex/expensive mechanisms should be used to generate simplified parameterisations, we consider this is beyond the aims and scope of our paper.

Our motivation for this study was to investigate the sensitivity of the results from our previous simulations of the effects of changing land use, climate and anthropogenic emissions (Squire et al., ACP 2014), and to quantify the effect of the chemical mechanism in our global chemistry-climate model. To this end, this paper documents the impact of changing chemical mechanism on these emission change experiments and, we hope determines the level of uncertainty introduced by the use of different chemical mechanisms in multi-model experiments. While we did not aim in this study to develop new reduced mechanisms, we agree that the box model set up we have used will provide a nice tool for performing this type of work in follow up studies.

In the light of the supportive comments from the reviewers, and our modifications to the manuscript in line with your suggestions, we hope that we have now met the requirements for this manuscript to be published. Please see below for a list of the changes made.

With best wishes,  
Alex



### List of changes made (01/04/2015)

All of the small grammatical changes (purple) proposed by the Editor, have been undertaken and are not listed specifically here. The following more major changes (the blue changes proposed by the Editor, as well as the changes made in response to the Editor's general comments), are listed below.

#### Title page

Added author D. Smith

Changed affiliation of P. T. Griffiths to only be (1) rather than (1) and (2).

#### Abstract

p2, l19-20 changed from:

"The wide ranging response is due to differences in the types of peroxy radicals produced by isoprene oxidation, and their relative rates..."

to:

"The wide ranging response is due to differences in the model descriptions of the peroxy radical chemistry, particularly their relative rates..."

p3, l7: after "More measurements" added "and laboratory studies"

#### Introduction

p3, l10: "the atmosphere under the presence of..."

changed to: "the atmosphere in the presence of..."

p3, l25: "...reactions are known fundamentally."

changed to "...reactions are known in depth."

p6, l14: removed reference Lee et al. 2014

#### Methods

p7, l13: "The overall CheT mechanism also forms the basis of all the schemes studied, with only the parts pertaining to isoprene being different."

changed to:

"The overall CheT mechanism also forms the base case against which all the schemes studied, are compared."

p8, l1: Added a bracketed note:

"(it should be noted, however, that Lee et al. (2014) found that Lockwood et al. (2010) substantially overestimated the rate of this reaction)".

#### Box model experiments

p9, l10: Added sentence:

"Furthermore, many of the recent discoveries such as the isomerization chemistry of ISO2 and methacrolein are not included."

p9, l25: updated incorrect H2O percent from 0.01% to 50%.

#### Global perturbation experiments

p10, l19. Added sentence: "It should also be noted that with the change in land use, we assume no change in NOx emissions."



### **Section 3: Mechanism intercomparison with a box model**

This section has undergone a significant re-write, so it's worth re-reading the whole thing. Mainly, the text has been split into 5 subsections (one for each reduced mechanism 3.1-3.4, and one summarising our findings (3.5)). We have extended the discussion to include examination of differences in the NO<sub>x</sub> lifetime as per the Editor's request. We have added two new Figures (fig 2 and 4), which show the NO<sub>x</sub> lifetime in the MCM (fig 2) and differences between this and the four reduced mechanisms (fig 4).

### **Present day mechanism intercomparison with a global model**

p17, l9: Changed "whereas AQUM and LLSF show much greater increases in NO<sub>3</sub> - up to 7 times more. This has implications..."

to:

"whereas AQUM and LLSF show much greater increases in NO<sub>3</sub> - up to 7 times more. This is a consequence of the lower formation rates of nitrate reservoirs in these schemes, thus NO<sub>3</sub> formed from the base non-isoprene chemistry, by reactions such as N<sub>2</sub>O<sub>5</sub> photolysis, is removed more slowly. These differences in NO<sub>3</sub> levels have implications..."

p17, l14 and l17: Added in Paulot et al. (2009) reference.

### **Climate change**

p18, l19: local isoprene levels do increase slightly, so changed:

"The flux through this reaction under climate change decreases by ~20 % in all schemes, leading to associated increases in OH."

to:

The flux through this reaction under climate change decreases by ~20 % in all schemes, leading to associated increases in OH and isoprene export".

### **Conclusion**

p25, l15-19. Changed to:

"Using the CheT scheme, Squire et al. (2014) found that the calculated increases in O<sub>3</sub> due to cropland expansion (LC) were too small to cause a significant increase in O<sub>3</sub> - induced vegetation damage. As the three additional mechanisms examined here simulate similar or negative changes in O<sub>3</sub> with cropland expansion, this conclusion would not change with the use of these schemes, and further calculations (not shown) demonstrate this to be the case."

### **Figures**

Added fig (2) and (4) shows NO<sub>x</sub> lifetimes from the box model studies (see Sect. 3 changes for more details).