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Comment

Interactive comment on “Influence of isoprene chemical mechanism on modelled changes in tropospheric ozone due to climate and land use over the 21st century” by O. J. Squire et al.

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Comments from Referees

1. 22393, 15: how did you calculate photolysis rates and how can you ensure that differences in your oxidation chemistry are not due to differences in photolysis between the mechanisms?
2. 22393, 19-20: rephrase - without removal but including emissions your box model will never reach steady state. You will accumulate oxidation end products.
3. 22393, 25ff: The editor suggested to do additional simulations with potential

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changes in NO_x in the tropics (referring you to Paulot et al., *acp*, 12, 1307-1325, 2012, figure S12). Why did you not do this? Or is 22401, lines 20 ff meant to discuss this? Please clarify.

4. 22395: you should discuss the overall significance of the exact numbers you give here - as your box model is not in equilibrium, what do those numbers tell us? They are picked at an arbitrary point in time.

5. 22400, 3ff: it should be made more prominent that differences in the isoprene oxidation mechanisms do not only influence O₃, but also key radicals like OH (what about NO₃?). They are of prime importance also for other parameterisations like e.g. secondary organic aerosol formation.

6. 22406, Conclusions: what is the way forward? How do we tackle these discrepancies? Is MCM 'right'?

Author's response

We would like to thank both referees for their constructive comments and for their support of our paper. We would like to thank reviewer two for their endorsement of our work and our replies to reviewer one can be found below.

1. Most global models use, to a first order, very similar approaches to calculate photolysis coefficients and so we would expect that there would be little impact by our harmonization of photolysis coefficients in this study. However, we do acknowledge the importance that uncertainty in photolysis coefficients can have. Most recently Muller et al. (2014) have shown that there can be considerable impacts to the photolysis of carbonyl nitrates when considering enhanced absorption cross sections. Whilst we agree that uncertainty in photolysis coefficients can have an impact on modelled composition, we feel that it is outside the scope of the paper to include much more discussion on this topic but that further work in this area would be useful.

2. We thank the reviewer for their comment. We intend on modifying the text to reflect

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the reviewers point.

3. We would like to thank both the reviewer and the editor for raising this issue. We are very interested to assess the impacts that changes in NO_x emissions would have on the results derived from the different isoprene mechanisms. Unfortunately we were not in a position to perform these runs but we hope to in a future publication. We do however want to add to the text to emphasise this point.

4. The reviewer makes an important point here. We have not run our box model simulations to equilibrium but have opted to compare the results of the box model runs after a fixed period of time (constant for all mechanisms). Whilst this may produce slightly different results to the comparison of an equilibrium simulation we feel that these results are still instructive, and can be considered quantitative. The arbitrary time was in fact chosen to emphasise the effect of primary and secondary chemical processes, while avoiding possible artefacts introduced by e.g. not including advection or deposition. Text will be added to the manuscript to emphasise the point.

5. We thank the reviewer for their comment. We propose some additions to the manuscript to help emphasise the point.

6. We thank the reviewer for raising this issue. This really is an important issue but one that is very much beyond the scope of this paper. In this paper we have specifically highlighted that significant variability in secondary compounds is caused by the mechanistic assumptions used in models. We have tried, where possible, to highlight that erroneous assumptions (e.g. missing products which are known to be formed) can lead to significant deviations from our best understanding of the secondary chemistry. The reviewer asks the question “is the MCM right?” This is an excellent question. What is right? One can argue that all models are, inherently, wrong. However, we have argued in the manuscript that the MCM is “right” in that it contains a more complete description of the chemistry that we know to be occurring than the simplified chemistry schemes employed in 3D models. The MCM clearly is not completely “right” as there are, un-

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doubtedly, aspects of the chemistry of isoprene that remain to be elucidated (one only needs to look through the literature over the last decade to see that significant insight into isoprene chemistry occurs every few years). In this paper we don't wish to make any profound recommendations as to the way forward, in fact we think that it falls out of the scope of the paper. However, we have stated in our conclusions that the box model framework can be used as a computationally cheap but accurate tool for assessing mechanistic performance in complex global models. We would therefore encourage global modellers to evaluate the sensitivity of their simple mechanisms over the wide ranges of VOC and NO_x emissions found throughout the atmosphere by using box model simulations in the way we have.

Author's changes in the manuscript

1. Change 22393 I14 to: Atmospheric pressure (1×10^5 Pa) and temperature (298 K) were kept constant, and the amount of light varied through the day as in a gridcell at 14° latitude on Julian day 172 (solar declination angle = 23.44°). To ensure that differences in the oxidation chemistry were not due to differences in photolysis between the mechanisms, the MCM photolysis parameterization was used in all cases. Details of how photolysis coefficients are calculated using this parameterization are given in Jenkin (1997).

Get rid of "The MCM photolysis scheme was used for all schemes." on 22393 I22.

2. Change 22393 I18 to end-of-paragraph to: The box model does not include any advection or deposition processes, and as such O₃ values are likely to be higher than those measured in the field or calculated in UM-UKCA. Other consequences of including emissions but not removal pathways are that steady state will never be reached and long lived reservoir species will accumulate. For example, OH could be modified by accumulation of H₂O₂ via OH + H₂O₂. To minimize such effects on oxidant fields, a relatively short run length of three days for the runs was chosen. In all runs, to provide a consistent point of comparison between mechanisms, the maximum O₃ value on the

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third day was compared.

3. 22401 I26: ADD: If instead the scenario had included large NO_x changes in the tropics where isoprene emissions are high, it is likely that the schemes would respond differently. It has previously been shown that changes in tropical NO_x associated with increased anthropogenic activity can lead to large changes in O₃, e.g. Paulot (2012) where NO_x emissions everywhere were set to those of the USA in terms of GDP per capita. Conducting a similar experiment with different isoprene chemical mechanisms would be a worthwhile extension to our work but is beyond the scope of this paper where the primary focus is on climate and isoprene emission changes.

4. 22395 I8: ADD: Considering that the box model never reaches equilibrium, the precise numbers reported here (e.g. 140-160 ppb) are not of much significance to the real world where removal processes exist. However, what is significant, is the overall pattern and relative differences in ozone between the isoprene chemical schemes (Fig. 2). These differences give us useful information about variations in chemical oxidation between the schemes, which may be used to help diagnose their differences in the more complex context of a global model (Sect. 4).

5. 22400 I11 - Add new paragraphs about NO₃ and epoxides:

Levels of the main night-time oxidant, NO₃, are higher in CheT2, AQUM and LLSF than in CheT (not shown). By percentage, the largest increases are calculated in the main isoprene emitting regions (tropics). Here CheT2 shows increases in NO₃ compared to CheT of around 30%, whereas AQUM and LLSF show much greater increases in NO₃ - up to 7 times more. This has implications for the rate of oxidation at night. As key oxidants, differences in both OH and NO₃ are important for secondary organic aerosol (SOA) formation, which requires the formation of oxidised organic products.

Another mechanistic difference between CheT2 and CheT that has the potential to affect SOA production, is the inclusion of epoxide formation in CheT2, based on the work of Paulot et al. (2009). In the tropics high levels of epoxides (50 ppt to 70 ppt)

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reach an altitude of nearly 5 km, and similar mixing ratios are present even in the lower Tropical Tropopause Layer (TTL) (10 km to 13 km). Isoprene-derived epoxides are known to be precursors of organic aerosol formation (Surratt et al., 2010), and as such, the presence of epoxides at high tropical altitudes could have important implications for cloud formation. In fact, Froyd et al. (2010) made measurements that showed large contributions to free-tropospheric organo-sulfate aerosol from isoprene-derived epoxides.

Add to abstract line 24: We also note changes other key oxidants such as NO₃ and OH (due to the inclusion of additional isoprene-derived HO_x recycling pathways). These have implications for SOA formation, as does the inclusion of an epoxide formation pathway in one of the mechanisms.

6. 22408 I19 (before "Here we have...") ADD: The findings reported here should help to guide mechanistic development strategies. For example, we found that the LLSF scheme tended to produce much higher O₃ near isoprene source regions than the other three schemes. This was the only scheme where only simple peroxy radicals were produced, and crucially there was no PAN production from isoprene chemistry. Adding in some simple parameterisation of PAN formation would likely improve the distribution of O₃ to be more in line with the other schemes, and as such we would recommend the inclusion of PAN as a basic isoprene mechanism requirement.

References

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