Interactive comment on “The CO₂ inhibition of terrestrial isoprene emission significantly affects future ozone projections” by P. J. Young et al.

P. J. Young et al.

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We are grateful for the comments, corrections and suggestions provided by both referees, which will all contribute to improving our manuscript. Below we have made detailed responses to what their reviews and, where appropriate, we have revised our manuscript. Quotes from the reviews are in italics.

Response to Reviewer 1

General comments

1. Comments regarding comparing the emission algorithm used here with that of Wilkinson et al. (2008) and Fig. 1.

Fig. 1 has been revised as suggested and the different studies are now denoted by separate symbols.
The curve shown in Fig. 1 is not a fit to the data but follows the simple relationship \( C_{i-370}/C_i \) as described in Arneth et al. (2007a, 2007b). \( C_i \) is the internal CO\(_2\) concentration of non-stressed leaves (0.7 times the atmospheric CO\(_2\) concentration, \( C_a \)), and \( C_{i-370} \) is this value taken at ambient (see Figure caption). The data from the studies are plotted to demonstrate this simple \( C_i \)-based parameterisation holds, but also to draw attention to the scatter that exists with respect to this response. We have included the following paragraph into the text (after "...(Sharkey et al. 1991)."):

Recently, Wilkinson et al. (2009) proposed a sigmoidal, Hill-reaction type isoprene-CO\(_2\) response, that was based on isoprene measurements taken in parallel with short-term CO\(_2\)-response curves at young aspen trees grown in four different CO\(_2\) concentrations (between 400 and 1200 ppmv). The parameterisation of this algorithm differed between the CO\(_2\) treatments, as the sensitivity of the short-term CO\(_2\)-isoprene response varied between growth environments. By pooling the normalised isoprene aspen data, the authors proposed a common parameterisation to apply the observed short-term Hill-response also to the long-term isoprene-CO\(_2\) response. For above-ambient CO\(_2\) concentration this algorithm projects a mildly lower inhibitory effect compared to the empirical fit and \( C_i \)-dependent relationship as used by Possell et al. (2005) and Arneth et al. (2007a) respectively. This small difference is unlikely to change the results in our study substantially. However, the study draws attention to the uncertainty of the below-ambient isoprene-CO\(_2\) response. Wilkinson et al. (2009) found a large increase in leaf isoprene emissions for Eucalypt grown at 240 ppmv CO\(_2\), but not for Sweetgum (see also Figure 1).

2. Comment regarding mentioning further uncertainties in the work.

The reviewer is correct in that the overall story may become quite complicated if a number of modelling and laboratory results are brought together. We have highlighted this in our revised manuscript by including the following two paragraphs at the end of the conclusions, highlighting both the uncertainty in the atmospheric chemistry as well as the BVOC emissions:
Our results have demonstrated the different response of atmospheric chemical models to isoprene emissions, namely that the globally averaged response of UM_CAM to less isoprene emissions is an increase in ozone, rather than the decrease noted by some other studies (Sanderson et al., 2003; Hauglustaine et al., 2005). Whilst we have tried to rationalise the differences by appealing to differences in the model isoprene schemes, there is a need to better quantify the differences between atmospheric chemical models and their constituent parts. Initial work in this direction has been completed by studies such as Mallet and Sportisse (2006), who conducted an ensemble simulation of ozone by substituting different values for parameters such as turbulent closure and the model resolution, though further work is needed to expand this effort to different model systems. Clearly, the models are also limited in their ability to represent isoprene chemistry accurately and new mechanisms (e.g. Butler et al., 2008) need to interface with new laboratory measurements for evaluation.

In this experiment, we only highlight one of the many uncertainties in the overall response of future BVOC emissions, atmospheric chemistry and climate. A number of additional factors will also affect future BVOC emissions. Firstly, future land use and land cover change is likely to alter emissions substantially, particularly in tropical ecosystems where conversion of rainforest, woodlands and savannahs into agricultural ecosystems will decrease isoprene and monoterpene emissions (Lathière et al., 2006). Furthermore, the net effect of interactions between BVOC emissions, tropospheric ozone and plant productivity are as yet unresolved. Ozone is phototoxic and reduces photosynthesis and net carbon uptake (Sitch et al., 2007). However, some studies have shown that isoprene and monoterpene emissions may help plants to withstand the phytotoxic effects (Loreto and Velikova, 2001; Fares et al. 2008). How these additional interactions affect biogenic emission projections and atmospheric chemistry remains to be tested.

**Specific comments**

1. *What is the rate constant for the ISO2 + NO reaction?*
The rate coefficient for this reaction used in this experiment was $2.5 \times 10^{-12} \exp(360/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$. This is the same as recommended by Pöschl et al. (2000), itself from the MCM (see the MCM kRO2NO rate coefficient). To the best of our knowledge, there has been no direct determination of this rate constant for any of the ISO$_2$ isomers, and most mechanisms use values inferred from similar reactions (e.g. MIM/MCM). So, whilst the rate of this reaction is important in determining the efficiency of ozone production in the presence of isoprene and NO$_x$, most model mechanisms use similar values for the rate constant and we decided not to highlight our value in the text. However, when the properties have been reported, the yield and subsequent chemical behaviour of isoprene nitrates can be seen to be quite different between model mechanisms. Considering their importance, we made sure to clarify their treatment in UM_CAM.

2. How long were the simulations?

We have revised the text to include this information for the UM_CAM model integrations, at the end of Sect. 3. The simulation for the present day climate (BASE) was 2.5 years and we reported the average of the final 2 years. For the future climate simulations (noCO2 and wCO2), the run length was 5.5 years and we reported the average of the final 5 years.

We used a shorter run time for BASE as the climate was forced with climatological sea-surface temperatures (SSTs); i.e. the annual cycle was constant and the only difference between model year 1 and model year 2 is due intrinsic model variability, which is very much smaller than the difference between BASE and the future climate runs. For wCO2 and noCO2, we forced the climate with sea-surface temperatures (SSTs) and sea-ice fields from 2096-2100, calculated from a run of the fully coupled (ocean-atmosphere) UM with doubled CO$_2$ concentrations. To account for the interannual variability of SSTs/sea-ice, we used a longer run than for BASE, although the interannual variability was significantly smaller than the difference between wCO2 and noCO2 in many locations (see also revised Fig. 3 in response to Referee 2).
3. Young et al. is cited several times, yet it is not a published paper.

This paper is currently in draft form and will contain a detailed discussion of the impact of isoprene on the tropospheric ozone budget in UM_CAM that is beyond the scope of this paper. Although we have only cited this paper twice (and once was just to introduce the fact that further discussion on isoprene and UM_CAM was forthcoming), we have replaced this citation with a different example of where these factors are discussed, as well as for P. J. Young’s thesis (soon to be available on-line), which discusses isoprene-ozone links for UM_CAM.

4. Is it possible to attribute the change in ozone concentrations/burden to climate versus chemistry? Based on the wide variety of chemistry options and climate forcing, what does this tell us?

The signal of climate versus that of chemistry is generally diagnosed by taking the difference between 2 runs where all is constant, except for the climate; see, e.g. Johnson et al. (1999), Hauglustaine et al. (2005) and Zeng et al. (2008), as referenced in our discussion paper. These model studies all report that climate change tends to decrease the tropospheric ozone burden overall, due to higher water vapour concentrations increasing ozone loss (O¹D+H₂O). However, we have re-emphasized the diverse nature of climate-chemistry impacts by including the following sentence at the end of Sect. 5:

Of course, the result of climate change is regionally heterogeneous and influences many other reaction rates and meteorological parameters relevant to atmospheric chemistry.

5. Comment regarding 13% increase in tropical tropopause OH and Fig. 4.

This value is calculated from the average OH concentrations in the tropical UT (30S-30N, 500-250hPa), which can themselves be calculated from the values in figure: e.g. 5.3 x 1.181 gives the average OH concentration for noCO2 between 30S-EQ and 500-
250hPa. The 13% value quoted in the text was intended to give more information than was immediately available from the figure, to save repetition.

6. Page 19903, lines 14;15: The authors may want to reword to state it’s caused by reduced reactions of isoprene and OH.

We thank the reviewer for highlighting this ambiguity, which has now been corrected.

7. Page 19903: "Globally, the average tropospheric OH concentration was 7.2 percent higher in wCO2 which extended the tropospheric chemical lifetime of methane by 7 months (Table 1), illustrating the indirect radiative forcing attributable to isoprene (Collins et al., 2002)." If OH concentrations are higher, then wouldn’t that mean that there is more OH to react with methane, and the methane lifetime would be reduced? It looks like in Table 1, the sentence should read that the CH4 lifetime was reduced by 7 months? (and from which simulation?) Also, this would reduce the indirect radiative forcing of isoprene, wouldn’t it?

Yes, this is an error and the text has been corrected to read something similar to what the reviewer suggests. With regard to the comment on radiative forcing: regardless of whether isoprene increases or reduces RF, it still has a role in determining it, which is the point of the last clause in the paragraph.

8. Page 19904: So it’s a wash between the climate influence on OH and the isoprene emission change on OH? The authors state that the climate influence on OH is the same magnitude (but opposite direction) of the change in OH from the wCO2-noCO2 simulations. However, don’t those two also take into account the climate? I find it difficult to pull out the significance of this evaluation explanation, and suggest a rewrite of this section would be helpful.

To make these statements, we involve a further model run in the discussion: a repeat of wCO2, but with the climate as per BASE (wCO2_p). We estimate the impact of climate change by taking the difference between wCO2 and wCO2_p (see com-
ments above) and we find that the impact of climate on OH concentrations (wCO2-wCO2\textsubscript{p}) is similar in magnitude, but opposite in sign to the impact of the isoprene emissions changes (wCO2-noCO2). The purpose of this was to compare the impact of the isoprene change to other changes in the atmosphere. As suggested, our revised manuscript includes a partial re-write of the final paragraph of Sect. 5 to ensure that the meaning is clear.

9. *Page 19904: The last sentence of the Conclusions section could be reworded. The impact on future \(O_3\) concentrations is important not only for climate forcing, but also for future air quality impacts. The authors may want to consider mentioning this, too.*

The second sentence of our conclusion already mentions future AQ, so we are unsure to what the reviewer is referring to.

**Technical corrections**

We are grateful to the reviewer for pointing out some corrections that will improve the readability of the manuscript.

**Response to Reviewer 2**

**General comments**

1. Comment regarding uncertainty of isoprene-CO\textsubscript{2} effect.

The reviewer is correct about the uncertainty in the overall isoprene-CO\textsubscript{2} response (and also the response of other atmospherically important BVOCs like the monoterpenes). As mentioned in the response to reviewer 1, we have included a paragraph that highlights some of the uncertainties.

**Specific comments**

1. *Page 19892, L20: ‘lifetime by 7 months’ Is it possible to describe this using percentage change instead of absolute lifetime (or adding it in parentheses)?*
This change has been made.

2. Page 19892, L21: ‘and emphasize the problems of using globally averaged climate metrics...‘. The meaning of this part appears to be unclear to those who reads this paper from the first. The authors should explain more.

We have clarified in the abstract the potential difficulties of using metrics like global radiative forcing for climate change effects of reactive substances.

3. Pages 19894-19895: ’LPJ-GUESS and isoprene emission‘: This section discusses the mechanism of isoprene emission response to atmospheric CO₂ changes with showing the previous experimental studies, briefly mentioning their used vegetation models. However, their adopted methodology of isoprene emission simulation was not so clear to me. Please clarify in the text if you use the parameterization like Arneth et al (2007a), or simulate explicitly isoprene emission response with a process-based calculation.

Yes, in the paper we use the parameterisation from Arneth et al. As described on page 19895 of the discussion paper, these calculations build on a process-based calculation of isoprene production in response to light and temperature (since production is linked to photosynthesis which delivers the isoprene precursors) and empirical parameterisations for processes that are not yet fully understood (like the direct CO₂-isoprene inhibition, for instance). We have added clarifying statements into the manuscript in section 2.1, 2nd paragraph:

Vegetation isoprene emission calculations combine a mechanistic representation in response to light and temperature that arises from the metabolic pathway of isoprene being linked leaf photosynthesis, while the long-term CO₂ inhibition follows an empirical parameterisation reflecting the as-yet not fully understood cellular process. Connecting photosynthesis and isoprene production ensures that global vegetation carbon cycle and total isoprene calculations and isoprene emissions are performed in a coherent modelling framework that also accounts for effects of vegetation productivity to
increasing CO₂ (Hickler et al., 2008).

The two paragraphs following these added lines briefly summarise how the leaf isoprene calculations were done in the emissions model.

4. Page 19895, L16: 'successfully reproduced the leaf isoprene response observed in most experimental studies in which plants were grown in a range of CO₂ environments (Possell et al., 2005).‘ What kind of plants are considered in those experimental studies? I presume that most important plant type for global isoprene emission is the tropical rain (evergreen) forest. Such is included in those studies?

That is true, and we highlight this already in section 2.1, end of paragraph 2. We add to this section the following text:

Studies on isoprene-CO₂ interactions have been performed on a limited number of species, mostly from temperate growth environments. Initial experimental evidence obtained on Acacia indicates that the overall trend between three CO₂ treatments (sub-ambient, ambient and elevated) observed by Possell et al. (2005) may also hold for tropical tree species; but as the experiment is still ongoing these observations must be considered to be preliminary (M. Possell, pers. comm.).

5. Page 19895, L26: Does your model include temperature and CO₂ fertilization effects on isoprene emissions? If so, you should mention the simulated sensitivities to temperature and CO₂ fertilization, apart from CO₂ inhibition effect. At least, the authors should describe their treatment of these two effects in the model.

Yes, the model includes CO₂ fertilisation on vegetation productivity. These arise from the mechanistic treatment of photosynthesis in LPJ-GUESS, which is adopted from the widely-used Farquhar et al equations. A tabular overview over the T and CO₂ response of vegetation productivity is provided in Arneth et al. (2007b) and we have clarified the text in Sect. 3, middle of paragraph 1, as follows:

In the former, emissions respond to warmer temperature (an effect of stimulating pho-
tosynthesis in many environments and of the high temperature optimum of isoprene production) and enhanced vegetation productivity (an effect of CO$_2$ fertilisation of photosynthesis). In the latter the long-term leaf CO$_2$ isoprene inhibition is included in addition. The indirect effects of temperature and CO$_2$ concentration on vegetation productivity were the same in both cases (see Sect. 2.1 and Arneth et al., 2007b).

6. **Page 19896:** Could you add a description of your adopted lightning NO$_x$ emissions with its global amount (Tg N yr$^{-1}$)?

We have added this information to the experiment description section, though we re-emphasise that a complete model description has been provided by Zeng et al. (2008), which also discusses lightning NO$_x$ emissions.

7. **Page 19896:** Does CO$_2$ inhibition cause any impacts on dry deposition process in your model?

In UM_CAM, dry deposition velocities are prescribed for particular land types and times of year; see Zeng et al. (2008) and refs. therein. As for the isoprene emissions, so far no direct interaction of O$_3$ deposition and stomata conductance and photosynthesis is included in LPJ-GUESS (e.g., as proposed by Sitch et al., 2007).

8. **Page 19897-19898:** Are meteorological fields in noCO2 and wCO2 runs identical completely? If your model includes feedback from chemistry to climate, meteorology should differ between these two runs. In that case, it might be difficult to extract the impacts of CO$_2$ inhibition only.

UM_CAM was not run interactively with the radiation code and, as such, the impact of isoprene changes on concentrations of radiatively active reactive gases (e.g. ozone) was not included in the radiation code. We have clarified the description of UM_CAM to make this fact plain.

9. **Page 19897-19898:** I'm a bit concerned about year (ensemble) number of the three runs.
Please refer to our answer to referee 1 above.

10. Page 19897-19898, Fig 2: Does this result (wCO2) include CO2 fertilization as well as inhibition?

All isoprene emission simulations include CO2-fertilisation as well as inhibition. We have updated our experiment description section to make this clearer.

11. Page 19899, Fig 3(a): The figure displays a large reduction over the Indian Ocean in January. Please describe this and the reasons.

The first paragraph of Sect. 4 discusses the change over the oceans in general (mainly related to PAN chemistry), though we now mention this area specifically in this discussion.

12. Page 19899, Fig 3: These pictures depict differences between 2 distinct model runs. Did the authors check the statistical significance of these results? I recommend for the authors to check it with the t-test.

We have revised Fig 3a and b to include shading where the difference is significant at the 95% level (t-test). As Fig 3c is comparing 2 differences, we have left this as is. It was just meant to highlight how large the wCO2-noCO2 difference is (just changing isoprene emissions) compared to the noCO2-BASE difference (changing isoprene, climate and anthropogenic emissions). This latter difference is significant (>95%) over most areas of the globe.

13. Page 19899, L17: 'The ozone increase resulted from reduced sequestration of NOx by isoprene oxidation products (isoprene nitrates and PAN) (e.g. Roelofs and Leliveld, 2000), leading to increased NOx levels (10-30%) and increased ozone production in these regions, as well as reduced isoprene ozonolysis (as noted by Fiore et al., 2005; Wiedinmyer et al., 2006).' I think reduced ozonolysis is the dominant factor for the ozone increases rather than reduced NOx sequestration, since the NOx levels in Amazon Africa are not so high.
At least in UM_CAM, it is mainly the result of reduced NO\textsubscript{x} sequestration. Analysis of the ozone budget terms showed that the greatest impact was on production (increased in noCO2) rather than any changes in loss. It is precisely because levels of NO\textsubscript{x} are lower in these locations that this impact on production is felt so keenly; ozone production is NO\textsubscript{x} limited and removal/translocation of NO\textsubscript{x} results in a decrease in production. Furthermore, NO\textsubscript{x} carrying compounds such as isoprene nitrates are stabilised by the relatively low OH levels modelled in the less polluted regions; this is also mentioned in the text. Reduced ozonolysis is of some importance (and this is why it is mentioned in the text), but the relatively long lifetime of the isoprene-ozone reaction goes some way to reducing the impact. Often, model studies of the impact of isoprene will invoke the ozonolysis reaction to explain ozone decreases as a response to increases in isoprene without mentioning the ozone budget evidence to back it up. Fiore et al. (2005) is an exception to this, and hence comes up in the discussion in the text. A forthcoming paper, currently in draft form, will discuss the isoprene-tropospheric ozone budget links in UM_CAM in more detail than is relevant in this current manuscript.

14. Page 19902, line 23: How about the impacts of temperature increase (or decrease) on isoprene emissions and associated ozone distribution changes in your model? If your model includes temperature impacts on isoprene emissions, you should contrast them with impacts of CO\textsubscript{2} inhibition.

The isoprene emissions are not calculated online in UM_CAM, rather the pre-calculated LPJ-GUESS emissions are used. The changes in the ozone distribution between wCO2 and noCO2 are due to the impact of changed isoprene emissions, which are themselves a result of the changes in CO\textsubscript{2} concentration and temperature as seen by LPJ-GUESS. Isolating the individual atmospheric chemistry impact of the temperature effect and CO\textsubscript{2} effect on isoprene emission is not possible with this experiment and is beyond what we were aiming to achieve.

15. Page 19904: ‘Conclusions’: The authors should mention the model diversity of the response of ozone distribution to isoprene change as discussed in Sect. 4 with
suggesting possible reasons for it.

We have now updated and expanded our conclusions section to include a summary of this. Please see our response to the first reviewer’s general comments.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19891, 2008.