Anonymous Referee #3

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GENERAL COMMENTS:

The manuscript by Revell et al. investigates the behaviour of the SOCOL CCM when it comes to capturing tropospheric ozone and related species from the mid-20th century to the late 21st century. Following a brief evaluation for present-day conditions, analysis of a control and two sensitivity simulations provides insight into the role of emissions and climate change in driving ozone changes. The role of NOx is found to be dominant, with methane being the second most important factor and climate changes only having a minor contribution.

Given that the study is based on a single model and a single scenario, its value as a prediction of future ozone is relatively limited. However, through the sensitivity experiments and the diagnostic analysis performed, it manages to provide some mechanistic understanding of the behaviour of this model, and to therefore add to the body of literature that aims to understand the contribution of different processes to past and future tropospheric ozone changes. Since the latter is quite an uncertain area of study, contributions of this kind are useful. Also, the manuscript is well written, and suitable for publication in ACP. However, there are several - mostly minor - amendments that I believe would need to be made before publication (see below).

GENERAL COMMENTS:

- It would have been useful to discuss the results in the context of the performance of the model, using what was found in Sect. 3.1, but also in previous evaluation efforts of SOCOL. The reader is not getting an idea of what are the main implications of those biases for the main features of the evolution of ozone, NOx, and CO+VOCs. Also, it is not clearly discussed what are the implications of model structural deficiencies, e.g. the crude handling of wet removal of HNO3. Maybe all those can be discussed in a "Discussion" session before the conclusions.

First of all, we would like to thank Reviewer 3 for a very thorough review of our manuscript. This is the first paper to use SOCOL with the isoprene oxidation mechanism and to focus on tropospheric chemistry, therefore we cannot refer to previous evaluation efforts of SOCOL. However we have added the following to Section 3.1:

Furthermore, given that the changes in ozone, NO_x, NMVOCs and CO over the period 2010-2100 are on the same order magnitude as past changes between 1960-2010 (shown later in Fig. 5), we do not expect non-linear feedbacks caused by the processes contributing to the biases to severely compromise our results for the future.

Concerning the HNO_3 parameterisation, we do see differences in tropospheric column ozone between the old and new parameterisation, although these are not systematic differences. We have noted this in Section 3.1.

- There is very little discussion on how well the model represents OH, which is key for several processes discussed here. It would be useful to give a sense to the reader of how well the model does in capturing present-day OH and/or methane lifetime, and how OH evolves with time in the simulations.

While OH evolution is an important and interesting topic, we feel that discussing the future evolution of OH and the performance of SOCOL in this respect is beyond the scope of this paper. To understand how well SOCOL performs, one would need data from the other CCMI models (which are not yet available), and this would constitute a paper on its own.

We have however compared the global OH concentration with that of the ACCMIP models in Section 3.1:

The OH abundance is also in agreement with the multi-model mean of the ACCMIP models; in the year 2000, the global tropospheric airmass-weighted OH concentration is 11.5×10^5 molecules cm^{-3}, compared with the multi-model mean of 11.7 ± 1.0 molecules cm^{-3} in the ACCMIP models (Voulgarakis et al., 2013).

- There is almost no mention of aerosols. I know this is not a central aspect, but there are some things for which the reader is left in the dark: Does the model include any aerosol tracers? I presume not, but Table 1 mentions "Ozone and aerosol precursor emissions", which is confusing.

The model does not include aerosol tracers. Table 1 contained the label "Ozone and aerosol precursor emissions" as that is how it is referred to in Eyring et al., 2013a. But we have changed this to "Ozone precursor emissions" for clarity.

There is also a mention of "16 heterogeneous reactions", and it is not clear whether that refers to the troposphere or the stratosphere, and what fields are used to drive those reactions (e.g. tropospheric aerosol fields).

These are stratospheric heterogeneous reactions, and we have clarified this in the text.

It would be good to clarify those aspects in the model description section, and to discuss any implications of the lack (?) of aerosols for the ozone/chemistry results (via e.g. photolysis, or heterogeneous processes).

We have added a paragraph to Section 2.1 describing the treatment of tropospheric aerosols in SOCOL:

The treatment of stratospheric aerosols in SOCOL is described by Stenke et al. (2013). Tropospheric aerosols in SOCOL include sulfate, dust, sea salt, black carbon, organic carbon and methane sulfonate. For the simulations presented here, we used a tropospheric aerosol dataset, as described by Anet et al. (2013). Tropospheric aerosols are used to calculate local heating rates and shortwave backscatter, however aerosol-cloud interactions and tropospheric heterogeneous chemistry are not considered.

And we discuss in Section 3.1 the potential implications of not considering tropospheric aerosols in SOCOL's photolysis and heterogeneous chemistry schemes:

As discussed in Section 2.1, tropospheric aerosols are considered in SOCOL's radiation scheme but not in the photolysis or heterogeneous chemistry schemes, which may be a further reason for the tropospheric ozone biases. Dentener and Crutzen (1993) showed that N_2O_5 hydrolysis on tropospheric aerosols reduces the tropospheric ozone burden by 10-25%, although the reaction probabilities they used were likely too large. Recent sensitivity simulations with the SOCOL model show that tropospheric ozone is reduced by a maximum of 10% when N_2O_5 hydrolysis is included in the model (following the parameterization of Evans and Jacob (2005)), although some regions show a slight increase in tropospheric ozone. Improving the treatment of tropospheric aerosols in SOCOL is the subject of ongoing research, and is not further addressed here.

SPECIFIC COMMENTS:

Page 482, Line 9: Later on it appears that climate change includes methane affecting chemistry. You may want to rephrase to ". . .climate change (including methane effects)", as otherwise the reader gets the first impression that methane changes are ignored.

Done – changed to:

We examine the influences of ozone precursor emissions (nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs)), climate change (including methane effects) and stratospheric ozone recovery on the tropospheric ozone budget, in a simulation following the climate scenario Representative Concentration Pathway (RCP)

Page 482, Lines 10-11: In this part of the abstract, it would be useful to make a brief statement on the nature of the RCP6.0 scenario (i.e. optimistic, pessimistic, moderate), and on why it was chosen. I know this is discussed later on, but it would be nice to clarify it to the reader up front (i.e. that it is a "medium-high" scenario, and therefore fairly realistic).

Changed to:

in a simulation following the climate scenario Representative Concentration Pathway (RCP) 6.0 (a medium-high, and reasonably realistic climate scenario).

Page 482, Line 13: Please rephrase to ". . . at 23% compared to 1960", for clarity.

Done – changed to:

Changes in ozone precursor emissions have the largest effect, leading to a global-mean increase in tropospheric ozone which maximises in the early 21st century at 23% compared to 1960.

Page 482, Lines 18-19: Not clear what is meant in this context by ". . .together with the longevity of ozone in the troposphere" - please rephrase.

Here we refer to ozone's long tropospheric lifetime. We have rephrased as:

together with the long lifetime~~evity~~ of ozone in the troposphere.

Page 482, Lines 19-20: "A simulation. . ." – by when?

By the end of the 21st century – we have clarified this in the text:

A simulation with fixed anthropogenic ozone precursor emissions of NO_x, CO and non-methane VOCs at 1960 conditions shows a 6% increase in global-mean tropospheric ozone by the end of the 21st century, with~~and~~ an 11% increase at northern midlatitudes.

Page 482, Line 27: I would suggest rephrasing to "Overall, the results show that, in this scenario, ozone in the future. . .".

Done – changed to;

Overall, the results show that, under this climate scenario, ozone in the future is governed largely by changes in methane and NO_x;

Page 483, Line 17: Better to use the most recent IPCC forcing chapter citation (Myhre, Shindell et al., 2013).

Done – changed to:

it has the third-highest pre-industrial to present day radiative forcing after carbon dioxide (CO_2) and methane (CH_4) (Myhre~~Forster~~ et al., 2013~~07~~; Stevenson et al., 2013).

Page 483, Line 21: Worth mentioning CO as well.

Done – changed to:

In addition to its roles in air pollution and climate change, tropospheric ozone is important in determining the oxidation capacity of the troposphere; the hydroxyl (OH) radical is principally produced from ozone, and controls the lifetime of many atmospheric species such as CH_4, CO and NMVOCs (non-methane volatile organic compounds), including some halocarbons (Thompson, 1992).

Page 484, Line 12: Worth also citing Kawase et al. (2011), who examined this effect.

Done – changed to:

(2) stratosphere-to-troposphere transport of air will accelerate due to a strengthening of the Brewer-Dobson circulation as projected by climate models, resulting from enhanced tropospheric warming and convection, and subsequent wave activity (Butchart et al., 2010; Kawase et al., 2011).

Page 484, Lines 13-15: Clarify that this effect is due to photolysis.

Done – changed to:

Stratospheric ozone recovery may further affect the evolution of tropospheric ozone through decreased solar actinic flux to the troposphere, which slows photolysis rates in the troposphere (Zhang et al., 2014).

Page 484, Line 28: It would be better to replace "projections" with "changes", as much of the ACCMIP work that you mention looks at historical changes too, not just future projections.

Done – changed to:

Furthermore, several studies examining tropospheric ozone budgets and ~~projections~~ changes over time from the ACCMIP (Atmospheric Chemistry and Climate Model Intercomparison Project) ensemble of models have been published recently (e.g. Bowman et al., (2013); Stevenson et al., (2013); Young et al. (2013)).

Page 485, Line 22: Suggest rephrasing "obtaining grades in the midrange" to "obtaining performance grades in the midrange".

Done – changed to:

Both compared reasonably with other CCMs, obtaining performance grades in the midrange.

Page 485, Line 26: Please delete space between "." and "2".

Done – changed to:

rather than the hybrid scheme of Zubov et al. (1999), which was used in SOCOL v. 2).

Page 486, Lines 1-2: Here it is worth summarising the major features of performance in a couple of sentences. They will be helpful later on in the discussion.

We have added the following text:

As a result, SOCOL v.3 shows more realistic distributions of chemical trace species compared with its predecessors (both in the mean state and also with respect to annual and interannual variability), and slower tropical upwelling in the lower stratosphere

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Page 486, Lines 18-20: Where do those conversion factors come from? Are they totally arbitrary (I presume not), have they been shown to lead to better performance, do they come from the literature? Worth stating in the text.

The conversion factors are derived from CO emissions (Tg/year) in the IPCC's Third Assessment Report; we have included a citation in the manuscript:

For anthropogenic NMVOC emissions, the conversion factor to CO is 1.0, for biomass burning it is 0.31, and for biogenic NMVOC emissions it is 0.83; these conversion factors were derived from Ehhalt et al. (2001).

Page 486, Lines 28-29: Would the scaling prevent future convective activity changes from modifying the magnitude of lightning NOx production (as well as the areas of occurrence, which is already discussed)? Please discuss.

Indeed, the scaling approach is uncertain in the future. Observations show where the model overestimates or underestimates lightning, according to the model's convection representation, and according to the cloud-top height parameterization that we use. We use the scaling factors to ensure that historical lightning in the model is consistent with observations, however for the future the scaling factors lead to many uncertainties. We have noted this in the manuscript:

Although the scaling approach is widely used to improve the representation of the global distribution of lightning, it carries some uncertainty as the future regions of lightning occurrence may differ from those currently observed (Murray et al., 2012). Furthermore, the scaling approach may prevent future changes in convective activity from modifying the magnitude of lightning NO_x production.

Table 1: For the ozone and aerosol precursors, pre-2000 emissions are not exactly "observations" (second column) – especially for those short-lived species there has not been that detailed observational information with global coverage. Perhaps it could be rephrased to "Historical emissions until 2000. . .".

Done.

Also, for ODSs, until when are observations used?

Until 2009 – we have clarified this in Table 1.

Page 487, Line 24: I would suggest adding a word so that it reads "These transient simulations. . .", to emphasise on the fact that the simulations are not timeslice/equilibrium.

Done – changed to:

These transient simulations are described in depth by Eyring et al. (2013a), but salient details are reproduced in Table 1.

Figure 1: Please mention in caption that emissions shown are global total.

Done – changed to:

Figure 1. Boundary conditions used in the REF-C2 simulation (global-mean concentrations/emission fluxes).

Also, for NMVOCs, mention that they are non-biogenic.

In Figure 1, the NMVOC emission fluxes shown include CH_2O, CH_3OOH, isoprene and anthropogenic, biomass burning and biogenic emissions. Therefore we have not made this change.

Page 488, Lines 18-20: I presume the fixing of methane will directly impact both the radiation and the chemistry? Please clarify in the text.

Done – changed to:

The fCH_4 simulation used identical boundary conditions to the fEmis simulation, except methane concentrations were held constant at 1960 levels (thus impacting both chemistry and radiation directly).

Sect. 3.1, beginning: Some further details are needed here for the model-observation comparison. E.g. why was 2005-09 chosen (I presume because it is representative of the present-day and because of good data availability).

Correct – we have added these details to the text:

We chose the period 2005-2009 over which to compare data as it is representative of the present day and because of good data availability for this period.

Also, was the model output processed with satellite operators (averaging kernels and a prioris) for TES, to account for observational sensitivity? If not, implications need to be discussed.

No, satellite operators were not used; we have discussed implications in the manuscript:

And with what tropopause definition was the model tropospheric NO2 column calculated?

The WMO-defined tropopause – we have added this to the text:

The WMO-defined tropopause was used to calculate SOCOL NO_2 columns.

Figure 2: The title TES/OMI in the second column is a bit misleading, as nowadays there are combined satellite products (e.g. MLS/TES) and the reader may think that is the case here (without reading the text). I suggest labelling every panel with the species being looked at and the instrument/model. There is no need to increase the size of the figure, as there is already enough space between the panels. Also: The panels are not labelled with the letters mentioned in the caption.

Done, as suggested:
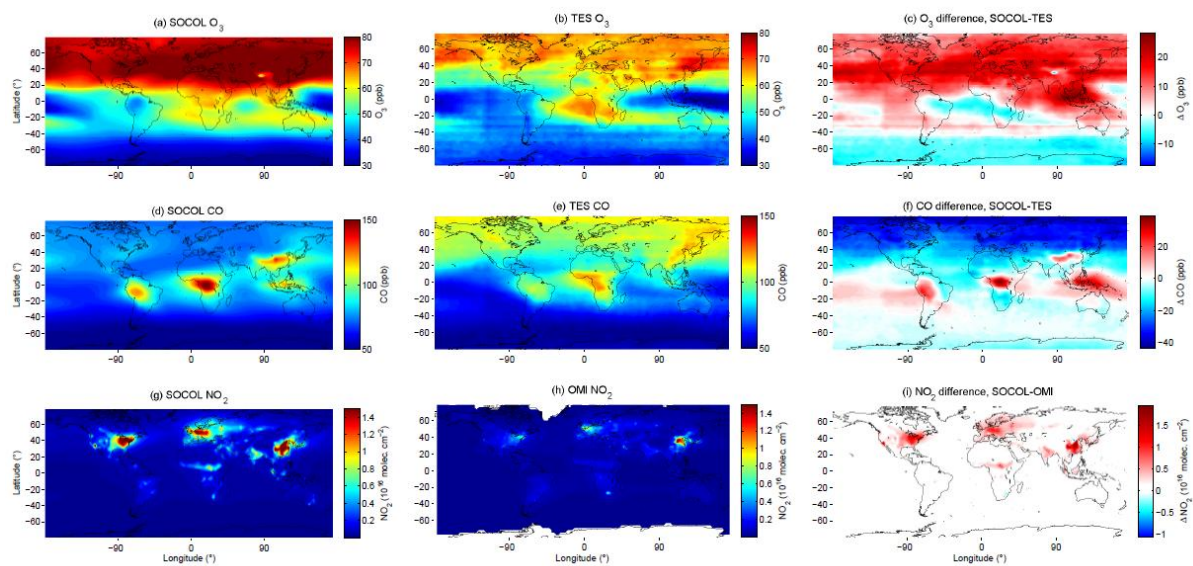
Page 489, Line 14: Please change "large burden" to "large ozone burden" for clarity.

Done – changed to:

Because HNO_3 can lead to ozone production when it is photolysed to form NO_2, recently obtained results suggest that a more realistic removal process for HNO_3 (based on in-cloud and below-cloud precipitation, and aerosol interaction (Chang, 1984; Seinfeld and Pandis, 2006)) indeed reduces SOCOL's overly large ozone burden in the Northern Hemisphere.

Page 490, Line 3: Perhaps use "low" instead of "depleted", as the latter may imply that there was ozone there that was depleted.

Done – changed to:

ozone concentrations are elevated in the Northern Hemisphere and over Africa compared with the Southern Hemisphere, and ~~depleted~~ low ozone concentrations are seen over the tropical Pacific Ocean (discussed further in Section 3.2).

Page 490, Lines 8-10: It would be useful to give the reader a sense of how high OH is in the model. Either the global mass-weighted mean OH concentration, or the methane lifetime would give some good general picture. And it would also be useful to compare against recent multi-model (Voulgarakis et al., 2013) and observational (Prather et al., 2012) estimates.

We have compared the global airmass-weighted OH concentration in SOCOL with the multi-model mean in the Voulgarakis et al. (2013) study:

The OH abundance is also in agreement with the multi-model mean of the ACCMIP models; in the year 2000, the global tropospheric airmass-weighted OH concentration is 11.5×10^5 molecules cm^{-3}, compared with the multi-model mean of 11.7 ± 1.0 molecules cm^{-3} in the ACCMIP models (Voulgarakis et al., 2013).

Page 490, Lines 18-19: Please change "and also to the general high ozone bias" to "and also leads to the general high ozone bias".

Done – changed to:

and also leads to the general high ozone bias in SOCOL throughout the Northern Hemisphere

Page 490, Lines 25-28: How does this performance compare to the earlier evaluation by Stenke et al. (2013)? Discussing this here will strengthen the conclusions of the evaluation.

The evaluation by Stenke et al. (2013) focussed on stratospheric rather than tropospheric species distributions, so we are unable to compare performance.

Page 492, Line 23: "are located in different places" – I would add the word "slightly" (different places), as the broader region is the same. Note that in Voulgarakis et al. (2013), multi-model mean surface OH was also lowest over Indonesia and not over the Western Pacific (Fig. 6a).

Done – we have also included a citation to the Voulgarakis et al. (2013) paper:

Results obtained from SOCOL largely support this hypothesis, except that the OH and ozone minima are located in slightly different places (over Indonesia and over the Western Pacific Ocean, respectively, which was also found by Voulgarakis et al. (2013)).

Page 492, Line 27: Not clear how R5 could be a result of low NOx and high CO+VOCs.

True – this was not worded clearly. We have changed this to:

The combination of high CO+VOCs and low NO_x drives ozone loss via R3 and R5, and suppresses ozone production via R1. In addition, ozone loss by R5 is fast because of high humidity and solar actinic fluxes in this region.

Figure 3: Again, letters that indicate the order of panels (a, b, c. . .) are missing.

These are shown on the panels themselves, bottom left corner.

Page 493, Lines 1-3: Wouldn't R1 also be partly responsible for this feature (less NOx so less OH recycling).

Yes, very likely so. We have amended the text to:

Because ozone and NO_x abundances are so low over Indonesia, the HO_x partitioning from HO_2 into OH (via reaction of HO_2 with ozone in R3, and via reaction of HO_2 with NO in R1) in R3 becomes very slow, resulting in low modelled OH abundances (Fig. 3b).

Page 493, Line 27: Please add "later" after "as shown".

Done – changed to:

Furthermore, most of the tropospheric ozone transport between low, middle and high latitudes happens in the mid-troposphere, as shown later in Fig. 7.

Page 494, Lines 1-2: Please explain why (I presume you mean that at this level the satellite instruments, e.g. TES, have a better sensitivity).

Yes – we have changed this sentence to read:

500 hPa is also high enough in the atmosphere to be able to compare model output with satellite observations, as here the satellite instruments have better sensitivity compared with closer to the surface (Fig. 2).

Page 494, Line 14: Please add "as seen here".

Done – changed to:

Projected accelerated tropical upwelling is also expected to lead to slight decreases in tropical stratospheric ozone through the 21st century, as seen here.

Page 495, Line 17: It seems completely offset rather than "partially", given the flat trends in Fig. 5c.

We have deleted "partially":

Page 496, Lines 21-28: Please clarify that this is an effect driven by OH differences. Here, it would actually be useful to show OH evolution plots.

Our understanding, as discussed in the manuscript, is that the effect is caused by methane, which is a large source of CO. Also, as noted above, while the evolution of OH is an interesting and important subject, it is outside the scope of this paper.

Also, relating to this subsection: The authors do not comment on the NOx response to fixing methane. It looks like NOx abundances are entirely driven by chemistry (short-lived emissions and methane) as 1960 and 2100 fCH4 levels look the same, so the meteorological changes (precipitation, lightning) do not play any role. Worth commenting here on how the model set-up (fixed wet removal rates, scaled lightning) could have affected this result.

We have inserted an extra paragraph discussing this point:

Figure 5a shows that fixing methane does not significantly impact NO_x concentrations. This demonstrates that modelled NO_x is driven by chemistry, rather than climate-induced changes in meteorology. As noted in Section 2.1, the scaling approach used to calculate lightning NO_x may not modify the magnitude of future lightning NO_x production which might be expected to result from changes in convective activity.

Page 497, Lines 1-2: Also, it is interesting that for the tropics the fCH4 simulation shows drastically different results for 2100 compared to REF-C2 and fEmis. Any ideas on why that is?

Yes, we understand that this is due to the behaviour of methane as an ozone precursor, as discussed later on in that paragraph.

Figure 8: What does the grey colour indicate in panel (b)?

It is actually white, but the hatching to indicate statistical significance makes it looks grey when viewed zoomed out.

Page 499, Line 10: You could add ", which is a scenario of intermediate severity compared to RCP4.5 and RCP8.5," after "RCP6.0".

Done – changed to:

In our fEmis simulation (~~Recalling that we~~which used RCP 6.0, a scenario of intermediate severity compared to RCP 4.5 and RCP 8.5), we calculate a 48% increase in lightning NO$_x$ emissions over the same period, which is broadly consistent with their findings.

Page 500, Lines 15-16: ". . .although their effects are relatively small." – this has not been demonstrated in the analysis.

True; we have modified the text to:

Together with STE, ozone increases induced by lightning NOx emissions are largely offset by the temperature-induced increased rates of ozone destruction in the troposphere.

REFERENCES:

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