Author response

This document comprises three parts:

1. Point-by-point responses to the reviewer comments
2. A list of all relevant changes made in the manuscript
3. A marked-up version of the manuscript

Part 1: Responses to the reviewer comments

Anonymous Referee #1
Received and published: 29 January 2015

This is a useful paper that presents the changes in tropospheric ozone and its precursors through the 21st century for one widely-used emissions/concentration scenario. It clearly demonstrates in a quantitative manner that changes in ozone precursor emissions dominate these changes, and that increased methane concentrations make a substantial contribution to this. It also highlights that climate changes under this scenario have little net impact on mid-tropospheric ozone, but that this masks increased ozone influx from the stratosphere and from lightning along with increased ozone destruction from humidity/temperature changes. These competing factors are not quantified, which is disappointing, and this constitutes one of my main concerns the manuscript, as outlined below. However, the paper is worthy of publication once the points below have been addressed suitably.

General Comments:
The model used has a number of weaknesses, and the authors appear to avoid discussion of surface ozone or its changes wherever they can. On the positive side, the authors have justified their choices and have demonstrated that although there are some large biases in the mid troposphere compared with current observations, these are generally self-consistent and can be rationalized if not fully explained. However, the biases may be heavily influenced by what is happening at the surface, and so it would be very helpful for the reader if a few sentences were included in the evaluation section (3.1) on model performance at the surface.
First of all, we would like to thank Reviewer 1 for their helpful comments on both the initially submitted and ACPD versions of this manuscript. As suggested here, we have added some discussion on surface ozone to the evaluation section in Section 3.1:

Surface ozone in SOCOL is biased on a similar order of magnitude in the Northern Hemisphere compared with the mid-troposphere, with ozone over Europe, the US and Asia up to 20 ppb higher in 2000 compared with the ACCMIP ensemble mean (Young et al., 2013).

The least satisfying part of the paper is the final paragraph before the conclusions, which highlights the potential impact on ozone of changes in lightning, but is unable to quantify this. While the paper demonstrates that this term together with the change in stratospheric influx (which is quantified) balance the increased destruction from humidity and temperature (which is not quantified), it is not clear if the two unknown terms are negligible (sub-ppb level) or substantial (4-5 ppb or more, but counteracting each other). Some attempt to establish this, or at

least to speculate in a semi-quantitative manner, would add substantial value to the paper. A short model run with scaled lightning NOx emissions would be sufficient to estimate this, and hence quantify both terms. What have other studies found?

Indeed, since increased ozone destruction from humidity and temperature, and increased ozone production from lightning NO$_x$ emissions are both linked to climate change, we cannot separate the two terms in our simulations. However previous studies with scaled lightning NO$_x$ emissions provide an estimate of the impact of lightning NO$_x$ on ozone, and so we have incorporated these results into this section of the paper:

As discussed in Section 3.2, methane leads to ozone production in the presence of NO$_x$. Along with humidity and STE, lightning NO$_x$ emissions may increase in a warmer climate, either due to increased frequency of thunderclouds (and therefore lightning), or more intense thunderstorms (Schumann and Huntrieser 2007; Price 2013). Figure 9a shows lightning NO$_x$ emissions from SOCOL averaged over the 1960s, and shows that most lightning is produced over Africa and South America. Lightning NO$_x$ emissions increase over the continents by 61% between 1960-2100 (Fig. 9b), and by 48% between 2000-2100. Smyshlyaev et al. (2010) found that ozone increased between 10-20% when lightning NO$_x$ emissions increased by 2 Tg(N) year^{-1} (depending on latitude and season), and up to 90% with a 20 Tg(N) year^{-1} increase in lightning NO$_x$. Banerjee et al. (2014) calculated increases in lightning NO$_x$ emissions of 33% (2 Tg(N) year^{-1}) and 78% (4.7 Tg(N) year^{-1}) between 2000-2100 in simulations using RCP 4.5 and RCP 8.5, respectively. 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. Banerjee et al. (2014)~~.~~ also showed that under RCP 8.5, the increase in lightning NO$_x$ emissions of 78% caused ozone increases of up to 30% in the troposphere (maximizing between the equator and 30 °S). Although we cannot quantify ozone increases induced by lightning NO$_x$ emissions in our simulations, the studies referred to here indicate the likely magnitude of increase (20-30%). 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. ~~However,~~ Finally, we note that the results also depend on the chosen lightning parameterization, which is coupled to the cloud top heights;~~.~~ Grewe (2009) showed that lightning NO$_x$ emissions might also slightly decrease, when stronger but fewer convective events occur in a future climate.

Specific Comments:

Abstract l.12: add "compared to 1960" somewhere in this sentence.

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.

p.483, l.12: visibility doesn't just affect traffic.

True, but disruption of traffic is one of the more disruptive effects on human activities. We have modified by adding "for example":

tropospheric ozone has harmful effects because it is an air pollutant, with adverse effects on crop yields (and therefore food security), visibility (affecting, for example, all forms of traffic) and human health (West et al., 2007).

p.484, l.2: the distribution and abundance of ozone may also be affected by changes in transport and convection.

We have noted this and added to the manuscript:

Depending on the sensitivity of ozone budget reactions to humidity and temperature, the distribution and abundance of tropospheric ozone may also be affected by climate change and changes in transport and convection through the 21st century.

p.486, l.18: What are the implications of adding NMVOC as CO? This method captures some of the increase in O3 and decrease in OH that might be expected from NMVOC, but over much longer timescales and hence in different locations.

Considering NMVOCs as an additional source of CO by directly adding a certain fraction of emitted NMVOCs to CO led to a substantial improvement of the simulated CO and OH levels. Before that modification SOCOL showed a severe low bias in near-surface CO mixing ratios and a pronounced high bias in OH. We agree that this rather simple approach neglects the different timescales of the involved chemical conversions, but nevertheless it leads to an improved model performance all over the globe.

p.489, l.10: "constant removal value": a clear explanation is needed here. Is HNO3 given a simple first-order loss globally throughout the troposphere, or only where there are clouds or rainfall? What lifetime is assumed?

2.5% of HNO3 in the gas phase is removed everywhere up to 160 hPa, in every time step, independent of clouds or rainfall. The lifetime of HNO_3 is not taken into account. We have added some details here to the manuscript:

In the model setup for the present study, a constant removal value was applied to the HNO_3 gas phase at each time step (2.5% of gas-phase HNO_3 was removed everywhere up to 160 hPa, independent of clouds or rainfall).

p.489, l.16: how might inclusion of anthropogenic NMVOC affect these biases? Nitrate formation and RO2 could increase NOx removal and ozone formation may be localized where lifetimes are much shorter, reducing O3?

As mentioned by Young et al. (2013) a high bias in NH tropospheric ozone and a low bias in the SH are widespread features in current chemistry-climate models, irrespective of the complexity of the applied chemical mechanism. That means that the inclusion of additional NMVOC species into SOCOL does not necessarily lead to an improved representation of tropospheric ozone in both hemispheres. Recently, the HNO_3 washout routine in SOCOL has been modified from a constant removal rate to a cloud cover- and precipitation-based approach. While this change indeed led to an enhanced NO_x removal throughout the NH, the signal in tropospheric ozone was less homogeneous.

p.490, l.22: emissions are a source of uncertainty, but are the same as those used in other model studies, e.g., ACCMIP. How do the NO2 biases compare with those from other models?

To the best of our knowledge, none of the ACCMIP studies analyse NO_2 biases. We are unable to find a multi-model study (with the models using the same emissions we did) which compares model-simulated NO_2 with observations.

p.493, l.25: the mid-tropospheric signal is clearly not representative of the surface, but it is broadly consistent with it. How does the surface ozone compare with that seen in recent model studies, e.g., ACCMIP?

We have changed “representative” to “broadly consistent,” and addressed how surface ozone compares with ACCMIP as above.

p.497, l.14: "on atmosphere": word missing here.

We have corrected this:

Although the fEmis simulation was designed to assess the impacts of climate change on the atmosphere (Eyring et al., 2013a),

p.497, l.26: "... up to 6 ppb almost everywhere" is unclear; 6 ppb is a maximum, and not everywhere. Either present this as a range (2-6 ppb?) or drop "almost everywhere".

We have deleted “almost everywhere”:

Here, with NO_x, NMVOCs and CO fixed in the fEmis simulation, ozone increases up to 6 ppb ~~almost everywhere~~ (a global-mean increase of 6%).

Figure 3: Panels c and d showing the ratio would be clearer with a dichromatic color scale centered at 1 (perhaps red/blue like Fig 6). Is this figure (and Fig 4) a multi-annual average?

Yes, as noted in the caption, the figures are multi-annual averages from 1960-1969. The colour scales on panels c and d have been changed as suggested:

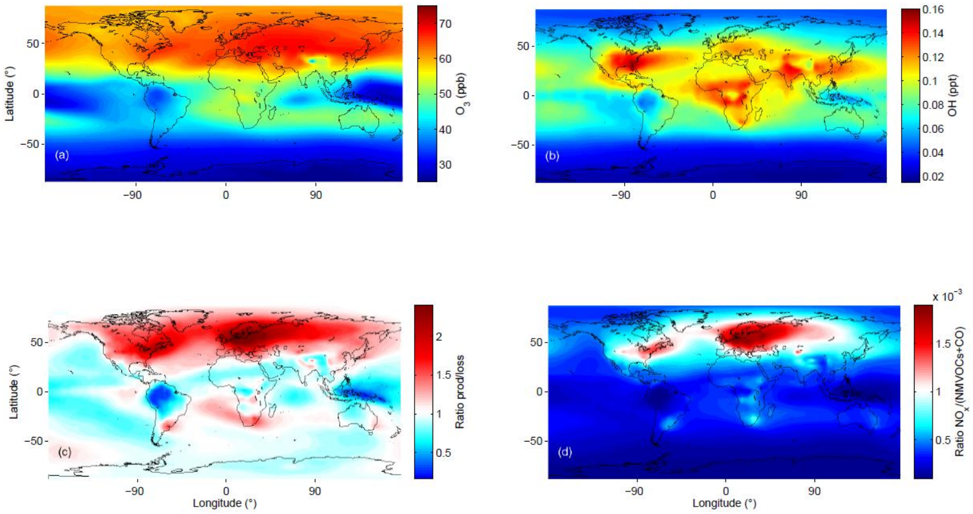

Figure 3. Results from the REF-C2 simulation, 1960-1969 average, 500 hPa. (a) Ozone; (b) OH; (c) Ratio of ozone production over loss; (d) Ratio of NO_x: NMVOCs+CO.

Anonymous Referee #3

Received and published: 3 March 2015

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~~vity~~ 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:

SOCOL data were not processed with satellite operators (such as averaging kernels). While this results in a less meaningful comparison, it has been shown that only minor differences result from the application of satellite operators (Huijnen et al., 2010).

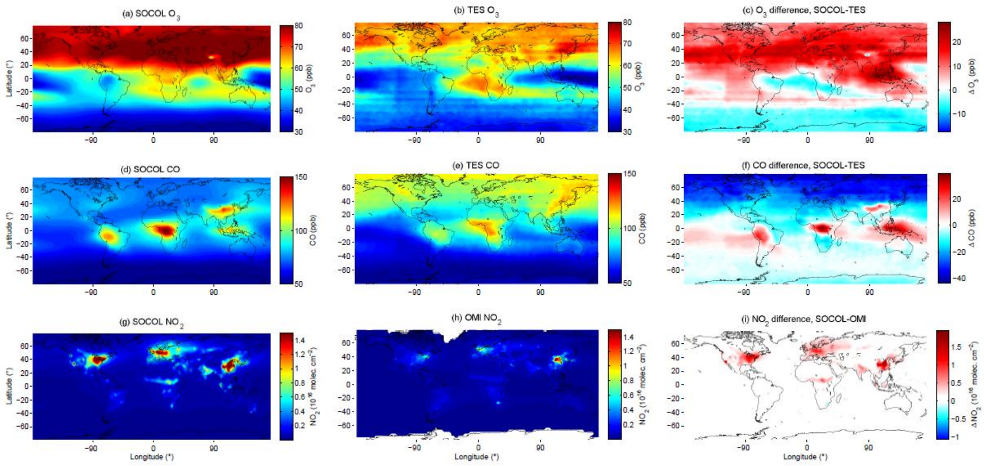
And with what tropopause definition was the model tropospheric NO2 column calculated?

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.

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Part 2: List of relevant changes made to the manuscript

Abstract and Introduction:

- Minor amendments made to the text following the reviewers' suggestions.

Section 2.1, The SOCOL chemistry-climate model:

- Added a description of how the SOCOL v.3 model has better performance compared with v.2.
- Added a paragraph describing how tropospheric aerosols are treated in SOCOL.
- Minor amendments made to the text following the reviewers' suggestions.

Section 2.2, Emissions scenarios:

- In the ACPD version of the manuscript, the fCH_4 simulation ran from 2080-2100. Since then we have had time to run a full simulation from 1960-2100. This section has been updated to reflect that change.

Section 3.1, Evaluation of model performance:

- Added details of how tropospheric NO_2 columns were calculated, how we selected the period 2005-2009 over which to compare observations, and discussed the implications of not applying satellite operators to model data.
- Added discussion on how well the model simulates surface ozone.
- Added details regarding the HNO_3 washout parameterisation.
- Added details regarding the model-simulated OH abundance.
- Discussed the implications of how the model treats tropospheric aerosols.
- Discussed the implications of biases (with respect to observations) for our results.

Section 3.2, Tropospheric ozone chemistry:

- Minor amendments made to the text following the reviewers' suggestions.

Section 3.3, Projections for the 21st century:

- Added a paragraph discussing the effects of decadal variability on future tropospheric ozone evolution.
- Minor amendments made to the text following the reviewers' suggestions.

Section 3.4, Ozone change with fixed precursor emissions

- Discussed the effect that fixed methane concentrations have on NO_x abundances.

Section 3.5, Impacts of climate change and stratospheric ozone recovery

- Expanded the discussion of lightning NO_x emissions and the role they are expected to play for tropospheric ozone evolution.
- Minor amendments made to the text following the reviewers' suggestions.

Conclusions:

- Minor amendments made to the text.

Table 1:

- Some details changed/clarified following the reviewers' suggestions.

Figure 1:

- Clarification added to caption following the reviewers' suggestions.

Figure 2:

- Labels on sub-panels changed for clarity following the reviewers' suggestions.

Figure 3:

- Panels (c) and (d) changed to a dichromatic colour scale following the reviewer’s suggestions.

Figure 5:

- Updated with results for the fCH_4 simulation from 1960-2100 (compared with 2080-2100 in the ACPD paper). Caption also updated.

Figures 4 and 6-9:

- No changes made.

Part 3: Marked-up version of the manuscript

Drivers of the tropospheric ozone budget throughout the 21st century under the medium-high climate scenario RCP 6.0

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Abstract

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Because tropospheric ozone is both a greenhouse gas and harmful air pollutant, it is important to understand how anthropogenic activities may influence its abundance and distribution through the 21st century. Here, we present model simulations performed with the chemistry-climate model SOCOL, in which spatially disaggregated chemistry and transport tracers have been implemented in order to better understand the distribution and projected changes in tropospheric ozone. 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) 6.0 (a medium-high, and reasonably realistic climate scenario). 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. The increase is

most pronounced at northern midlatitudes, due to regional emission patterns: between 1990 and 2060, northern midlatitude tropospheric ozone remains at constantly large abundances: 31% larger than in 1960. Over this 70 year period, attempts to reduce emissions in Europe and North America do not have an effect on zonally-averaged northern midlatitude ozone because of increasing emissions from Asia, together with the long lifetime~~vity~~ of ozone in the troposphere. 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. This increase maximises in the 2080s, and is mostly caused by methane, which maximises in the 2080s following RCP 6.0, and plays an important role in controlling ozone directly, and indirectly through its influence on other VOCs and CO. Enhanced flux of ozone from the stratosphere to the troposphere as well as climate change-induced enhancements in lightning NO_x emissions also increase the tropospheric ozone burden, although their impacts are relatively small. Overall, the results show that under this climate scenario, ozone in the future is governed largely by changes in methane and NO_x; methane induces an increase in tropospheric ozone that is approximately one-third of that caused by NO_x. Climate impacts on ozone through changes in tropospheric temperature, humidity and lightning NO_x remain secondary compared with emission strategies relating to anthropogenic emissions of NO_x, such as fossil fuel burning. Therefore, emission policies globally have a critical role to play in determining tropospheric ozone evolution through the 21st century.

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1 Introduction

Ozone is a key trace gas in the atmosphere, with approximately 90% residing in the stratosphere and 10% in the troposphere. While stratospheric ozone is essential for shielding life on Earth from harmful ultraviolet (UV-B) radiation, tropospheric ozone has harmful effects because it is an air pollutant, with adverse effects on crop yields (and therefore food security), visibility (affecting, for example, all forms of traffic) and human health (West et al., 2007). Indeed, a recent study by Silva et al. (2013) found that anthropogenic ozone contributes towards 470,000 respiratory deaths globally each year. Simultaneously, tropospheric ozone is a greenhouse gas that has contributed significantly to climate change; 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). 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).

Ozone exists in the troposphere as a result of in situ chemical production and transport from the stratosphere. Approximately 90% is produced via chemical reactions between nitrogen oxides ($NO_x = NO + NO_2$), hydrocarbons and carbon monoxide (CO) during daylight hours (Denman et al., 2007); therefore air pollution policy can be expected to play a significant role in the evolution of tropospheric ozone through the 21st century and beyond. Depending on the sensitivity of ozone budget reactions to humidity and temperature, the distribution and abundance of tropospheric ozone may also be affected by climate change and changes in transport and convection through the 21st century. Ozone can also be transported, either from the stratosphere (stratosphere-troposphere exchange, abbreviated to STE), or within the troposphere on long-range scales. Long-range ozone transport within the troposphere is modulated by decadal climate variability (Lin et al., 2014). Transport of ozone from the stratosphere is expected to increase through the 21st century as: (1) stratospheric ozone abundances will increase, due to the phase-out of ozone-depleting halogenated substances under the Montreal Protocol, and due to stratospheric cooling slowing the ozone destruction cycles (Bekki et al., 2011); (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). Both effects will lead to enhanced down-welling of ozone at mid- and polar latitudes. 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).

In recent years as computational cost has declined, models which couple chemistry and climate (chemistry-climate models, or CCMs) have become increasingly complex, with many now including detailed tropospheric chemistry and other tropospheric processes. Morgenstern et al. (2013) used the UM-UKCA CCM to look at how climate change, stratospheric ozone recovery and methane affect ozone, although they did not consider future changes in non-methane ozone precursors. They found that climate change and stratospheric ozone recovery have approximately equal and opposite effects on surface ozone by 2050, resulting in an increase in tropospheric ozone driven by methane. Doherty et al. (2013) also investigated climate change-related effects on tropospheric ozone with an ensemble of three CCMs, and found that increased temperature and water vapour influenced surface ozone more strongly than climate change-induced enhancements in STE. 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)). The ensemble mean of results obtained from ACCMIP provides a useful point of reference for the results obtained in this study, and as such we refer to ACCMIP results later on.

To gain a clear insight into projected tropospheric ozone changes through the 21st century, we have implemented a suite of chemistry and transport tracers into the SOCOL (Solar Climate Ozone Links) CCM, and used them to disentangle the various factors influencing the ozone budget in the free troposphere. Here we compare projected ozone changes in a future reference simulation, which assumes emissions of NO_x, CO, CH_4 and NMVOCs according to Representative Concentration Pathway (RCP) 6.0, with those in simulations with ozone precursor emissions fixed at 1960 levels. Climate change and stratospheric ozone recovery are fully simulated in both scenarios, and the chemistry and transport tracers allow us to analyse their effects, for example by quantifying STE fluxes and tracking reaction rates for key ozone budget reactions.

2 Computational methods

2.1 The SOCOL chemistry-climate model

In order to understand the influences of ozone precursor emissions and climate change on the free tropospheric ozone budget (we focus mostly on the 500 hPa level), simulations were performed with the SOCOL v.3 CCM. Its forerunner, SOCOL v.2, was extensively evaluated in the SPARC CCMVal-2 activity (SPARC CCMVal, 2010) in two variants; SOCOL operated by the ETH-Zurich group and NIWA-SOCOL operated by NIWA (National Institute of Water and Atmospheric Research, New Zealand). Both compared reasonably with other CCMs, obtaining performance grades in the midrange. Since then SOCOL has undergone some significant improvements from version 2 to 3 (notably, the core general circulation model has been updated, and the transport of chemical trace species is calculated with the advection scheme of Lin and Rood (1996), rather than the hybrid scheme of Zubov et al. (1999), which was used in SOCOL v.–2). 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; these changes, along with their effect on model performance, have been documented in detail by Stenke et al. (2013).

SOCOL v.3 consists of the MEZON chemistry transport model (Egorova et al., 2003) and MA-ECHAM5, the middle atmosphere version of the ECHAM general circulation model (Roeckner et al., 2003), with 39 vertical levels between Earth's surface and 0.01 hPa (~80 km). For the present study, SOCOL was run with T42 horizontal resolution, which corresponds approximately to 2.8° × 2.8°. Dynamical processes in SOCOL are calculated every 15 minutes within the model, while radiative and chemical calculations are performed every two hours.

Chemical constituents are advected by a flux-form semi-Lagrangian scheme (Lin and Rood, 1996), and the chemical solver algorithm uses a Newton-Raphson iterative method taking into account 41 chemical species, 140 gas-phase reactions, 46 photolysis reactions, and 16 (stratospheric) heterogeneous reactions. Isoprene (C_5H_8) oxidation is accounted for with the inclusion of the Mainz Isoprene Mechanism (MIM-1), which comprises 16 organic species (degradation products of isoprene) and a further 44 chemical reactions (Poeschl et al., 2000). Aside from isoprene and formaldehyde, we consider only the contribution to CO from other NMVOCs; that is, a certain fraction of the NMVOC emission is directly added to CO. 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). Biogenic emissions are not interactive, but follow a climatology (described in Section 2.2).

Photolysis rates are calculated at every chemical time step using a look-up-table approach (Rozanov et al., 1999), including effects of the solar irradiance variability. The look-up tables provide photolysis rates as a function of O_2 and O_3 columns, meaning that the photolysis scheme sees interactive ozone. The impact of clouds on photolysis rates is accounted for by including a cloud modification factor, following Chang et al. (1987). Interactive lightning NO_x is calculated via a parameterization based on cloud top height (Price and Rind, 1992) with local scaling factors calculated from the Lightning Imaging Sensor (LIS) and Optical Transient Detector (OTD) satellite observations (Christian et al., 2003). 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.

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.

Key reaction rates for the ozone budget were saved in every model grid cell, enabling chemistry to be analysed as a function of latitude, longitude, pressure and time. This approach was successfully used by Revell et al. (2012) to study stratospheric ozone chemistry. To better understand ozone transport, ozone tracers were implemented into SOCOL, based on the work of Grewe (2006) and Garny et al. (2011). Following this approach, the global ozone mixing ratio is disaggregated into 21 separate fields, according to in which of 21 predefined regions (defined by latitude and pressure) of the atmosphere the ozone originated; this approach is discussed further in Section 3.3.

To evaluate how realistically SOCOL simulates the distribution of tropospheric species, we compared ozone, CO and NO_2 (three key components of the tropospheric ozone budget) with satellite measurements over the period 2005-2009. Level 3 ozone and CO profile data were taken from TES (Tropospheric Emission Spectrometer), a Fourier transform infrared spectrometer onboard NASA's Aura satellite (e.g. Ho et al., 2009; Richards et al., 2008). Tropospheric NO_2 columns were compared with those measured by OMI (Ozone Monitoring Instrument) (Boersma et al., 2007).

2.2 Emission scenarios

SOCOL simulations were performed in support of the IGAC/SPARC Chemistry-Climate Model Initiative (CCMI; Eyring et al., 2013a), and therefore the boundary conditions used here adhere to the specifications of CCMI simulations, namely the REF-C2 and SEN-C2-fEmis simulations (hereafter fEmis, for brevity). These transient simulations are described in depth by Eyring et al. (2013a), but salient details are reproduced in Table 1. The REF-C2 simulation (1960-2100) was developed as a future reference simulation, to understand how the atmosphere would evolve under "best guess" estimates of future greenhouse gas concentrations, ozone-depleting substances (ODSs), ozone precursor emissions and sea-surface temperatures (SSTs). REF-C2 is based on RCP 6.0, a medium-high climate change scenario. Prescribed mixing ratios of greenhouse gases and long-lived chlorine, as well as emission fluxes of surface NO_x, NMVOCs and CO for the REF-C2 simulation are shown in Fig. 1. For biogenic isoprene, formaldehyde and other NMVOC emissions we use a climatology for the year 2000 (based on a MEGAN (Model of Emissions of Gases and Aerosols from Nature; Guenther et al. (2006)) run), while the biomass burning emissions follow those described by Lamarque et al. (2010) until 2000, and RCP 6.0 thereafter. Similarly, anthropogenic emissions of formaldehyde and other anthropogenic NMVOCs follow Lamarque et al. (2010) until 2000, then RCP 6.0.

The fEmis "fixed emissions" simulation (1960-2100) is identical to REF-C2, except that non-methane ozone precursor emissions are held constant at 1960 levels. For the present study, this simulation allowed us to explore the question of how global tropospheric ozone would evolve if air pollution remained at continuously low (1960) levels throughout the 21st century.

Because methane is also an air pollutant but not fixed at 1960 levels in the fEmis simulation (as we are interested in its climate impact), we ran a ~~short~~ fCH_4 "fixed methane" simulation for 1960~~2080~~-2100. ~~We chose this period of time because methane concentrations maximise under RCP 6.0 in the 2080s.~~ 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).

~~The REF-C2 and fEmis s~~Simulations were started in 1950~~, and the fCH_4 simulation was started in 2070,~~ to allow ten years for the model to reach a steady state; this spin-up period was subsequently discarded and not used in our analyses.

3 Results and discussion

3.1 Evaluation of model performance

Model simulated ozone, CO and NO_2 fields from the SOCOL REF-C2 simulation were compared to satellite observations over the period 2005-2009 (Fig. 2). Ozone and CO profiles were taken from TES and NO_2 columns from OMI. The WMO-defined tropopause was used to calculate SOCOL NO_2 columns. SOCOL data were not processed with satellite operators (such as averaging kernels). While this results in a less meaningful comparison, it has been shown that only minor differences result from the application of satellite operators (Huijnen et al., 2010). 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. Relative to TES, SOCOL has a large positive ozone bias at 500 hPa of up to 30 ppb in the Northern Hemisphere and tropics, and a smaller negative bias (~5-10 ppb) in the Southern Hemisphere (Figs. 2a-c). Surface ozone in SOCOL is biased on a similar order of magnitude in the Northern Hemisphere compared with the mid-troposphere, with ozone over Europe, the US and Asia up to 20 ppb higher in 2000 compared with the ACCMIP ensemble mean (Young et al., 2013).

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One possibility for the large Northern Hemisphere bias might be a too-weak removal of NO_x from the troposphere, which is described by the HNO_3 washout process. In the model setup for the present study, a constant removal value was applied to the HNO_3 gas phase at each time step (2.5% of gas-phase HNO_3 was removed everywhere up to 160 hPa, independent of clouds or rainfall). 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. However, the effect is not systematic, and this is not pursued in the present study.

We note also that SOCOL is not alone among the current generation of models in overestimating northern midlatitude ozone. Small systematic high biases in the Northern Hemisphere and low biases in the Southern Hemisphere were also observed in the ACCMIP models (Bowman et al., 2013, Young et al., 2013). ACCMIP included a range of models, from coupled CCMs with comprehensive tropospheric and stratospheric chemistry, to chemistry transport models (CTMs) which do not calculate meteorology online, and CCMs with very simple tropospheric chemistry (Lamarque et al., 2013). Because the models used the same emissions (as each other, and as in the present study), it was concluded that "the prevalence of this bias could suggest they [the emissions] are deficient in some way, in either their amount or distribution, or both." (Young et al., 2013). It is not clear whether SOCOL's high ozone bias is a source issue (that is, emissions), a sink issue (HNO_3 washout), or a combination of the two, and this requires further investigation. However, similar to the ACCMIP models, SOCOL correlates spatially very well with observations, despite biases in absolute ozone values; 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).

SOCOL simulates higher CO over regions where biomass burning is prevalent, namely South America, Africa and Indonesia, than observed by TES (Figs. 2d-f). Southern Hemisphere CO in SOCOL is in good agreement with TES, however in the Northern Hemisphere, CO is biased low by 20-40 ppb. The low Northern Hemisphere CO bias is linked with the high ozone bias in the same region, as ozone is the primary source of the OH radical, which in turn oxidises CO. Similar biases in CO were observed in the ACCMIP models; at 500 hPa, the

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multi-model mean is biased high compared with satellite observations over South America, Africa and Indonesia, and thought to be linked to biomass burning emissions (Naik et al., 2013). Furthermore, as seen in SOCOL, the multi-model mean is in good agreement with observations in the Southern Hemisphere. 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).

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SOCOL reproduces the elevated tropospheric NO_2 columns observed by OMI over North America, Europe and Asia, but overestimates their magnitude (Figs. 2g-i); this is linked in part to HNO_3 washout from the troposphere (as described above), and also leads to the general high ozone bias in SOCOL throughout the Northern Hemisphere, which is likely related to emissions. We note that potential discrepancies in emissions are a major source of uncertainty in our analyses. Indeed, Parrish et al. (2014) identify emissions as an issue in need of attention, given that CCMs consistently overestimate tropospheric ozone mixing ratios, and underestimate the magnitude of tropospheric ozone changes over the past 50-60 years.

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.

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Although SOCOL is subject to several biases in terms of absolute species concentrations, it captures the latitudinal and longitudinal distributions of ozone, CO and NO_2 convincingly. Furthermore, given that the changes in ozone, NO_x, NMVOCs and CO over the period 2010-

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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. We now proceed to discuss the distribution of ozone in the 1960s, and the model-simulated changes until 2100.

3.2 Tropospheric ozone chemistry

Although tropospheric ozone chemistry is comprehensive and complex, we outline below some fundamental reaction cycles, as they are useful in discussing SOCOL's spatial ozone distribution later in this section. In the troposphere, ozone is produced via reaction cycles that begin with oxidation of a NMVOC or CO, as shown below:

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$HO_2 + NO \rightarrow NO_2 + OH$ (R1)

$NO_2 + h\nu \rightarrow NO + O$

$\underline{O + O_2 + M \rightarrow O_3 + M}$

$CO + 2O_2 \rightarrow CO_2 + O_3$

The reaction HO_2 + NO is the rate-limiting step in ozone production and determines that the net effect of this cycle is ozone production with a gross production rate R1. Other ozone producing cycles follow the oxidation of VOCs, such as methane, formaldehyde, or isoprene and its degradation products, leading to:

$RO_2 + NO \rightarrow NO_2 + RO$ (R2)

where R represents the organic chain of the molecules RO_2 and RO.

In contrast, when air is NO_x-poor, rather than reacting with NO, as in the ozone production cycle R1 above, the generated peroxy radicals HO_2 (and generally RO_2), will instead react with ozone, as in the cycles below, which are catalytic in HO_x, with ozone net loss rates R3 and R4:

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$\underline{HO_2 + O_3 \rightarrow OH + 2O_2}$ (R3)

$CO + O_3 \rightarrow CO_2 + O_2$

$OH + O_3 \rightarrow HO_2 + O_2$ (R4)

$\underline{HO_2 + O_3 \rightarrow OH + 2O_2}$

$2O_3 \rightarrow 3O_2$

In the tropics, where humidity and solar actinic fluxes are high, the following reaction mechanism R5 can become the leading ozone loss reaction, even though it is not catalytic:

$O_3 + h\nu \rightarrow O(^1D) + O_2$ ($\lambda < 320$ nm)

$\underline{O(^1D) + H_2O \rightarrow 2OH}$ (R5)

$O_3 + H_2O + h\nu \rightarrow O_2 + 2OH$

In extremely NO_x-poor environments, ozone loss by R5 can occur to such a large extent that minima in tropospheric ozone ensue, as in over the Amazon Basin and tropical Pacific Ocean in Fig. 3a. Minima in tropical Western Pacific ozone have been observed in a number of measurement campaigns (Kley et al., 1996; Singh et al., 1996; Tsutsumi et al., 2003; Rex et al., 2014). Furthermore, Rex et al. (2014) showed, using ozone and OH measurements in combination with the GEOS-Chem CTM, that very low tropospheric ozone and OH abundances exist in the tropical Western Pacific. Rex et al. (2014) explained that low OH abundances are concomitant with low ozone abundances in the tropical Western Pacific because ozone is the principal source of OH, and ozone loss via R5 is so pronounced in this region. They also noted that low NO_x abundances further reduce OH because production of OH via $HO_2 + NO \rightarrow OH + NO_2$ becomes very slow (Gao et al., 2014). 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)). We suggest, therefore, that relatively high abundances of CO and VOCs from biomass burning are important for OH depletion, in combination with low NO_x abundances. 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. 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).

Figures 3c~~-~~ and d show the ratios of ozone production:loss, defined here as (R1 + R2)/(R3 + R4 + R5) and NO_x:NMVOCs+CO, respectively. We consider CO and NMVOCs together as they both undergo oxidation to initiate ozone production and destruction cycles. Here, NMVOCs are C2-C5 species that are related to isoprene, belonging to the reduced mechanism (MIM-1) outlined by Poeschl et al. (2000). One limitation of SOCOL is that the set of NMVOCs included is very small, namely formaldehyde, isoprene and the 15 other isoprene degradation products included in the MIM-1 isoprene oxidation mechanism. However, this subset of NMVOCs makes the mechanism detailed enough to accurately reproduce the diurnal cycle of important intermediate species like carbonyls, hydroperoxides and alkyl and peroxyl acyl nitrates, thus enabling the most relevant chemical processes for the tropospheric ozone budget to be represented (Poeschl et al., 2000). As shown in Figs. 3c-d, regions with high NO_x and low NMVOC+CO concentrations generally have high ozone production rates relative to ozone loss.

3.3 Projections for the 21st century

Given the projected changes in ozone precursor emissions, greenhouse gases and stratospheric ozone in the REF-C2 and fEmis simulations, how is tropospheric ozone projected to evolve through the 21st century? Further, are the projected changes dominated by changes in precursor emissions or by changes in climate? We focus our tropospheric analysis in the mid-troposphere, at 500 hPa. At this pressure the regional to hemispheric background ozone concentration is established, and the signal is ~~representative for~~broadly consistent with the surface, as seen when comparing Fig. 3a (ozone at 500 hPa) with Fig. 4 (surface ozone). Furthermore, most of the tropospheric ozone transport between low, middle and high latitudes happens in the mid-troposphere, as shown later in Fig. 7. 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).

Figure 5 shows the model-simulated free tropospheric concentrations of NO_x and NMVOCs+CO, as well as tropospheric and stratospheric ozone for the tropics and northern and southern midlatitudes. For the stratosphere, Fig. 5d shows that extratropical stratospheric column ozone is projected to increase through the 21st century in both the REF-C2 and fEmis simulations, owing to the phase-out of halocarbon gases under the Montreal Protocol on~~for~~ Substances that Deplete the Ozone Layer. Because of CO_2-induced cooling of the stratosphere (Bekki et al., 2011) and the increased rate of tropical upwelling (Avallone and Prather, 1996), the Northern and Southern Hemisphere stratospheric ozone columns increase to values slightly higher than those in 1980 by the end of the 21st century. Projected accelerated tropical upwelling is also expected to lead to slight decreases in tropical stratospheric ozone through the 21st century, as seen here.

In the troposphere, the REF-C2 simulation shows that concentrations of NO_x, NMVOCs and CO increase dramatically through the late 20th century (Figs. 5a-b), but eventually start to decrease towards the end of the 21st century. Although anthropogenic NMVOC and CO emissions are fixed at 1960 levels in the fEmis simulation, an increase of CO still occurs as it is an oxidation product of CH_4, and CH_4 itself is not fixed at 1960 levels, but rather follows RCP 6.0 (Masui et al., 2011).

Global-mean tropospheric ozone increases substantially through the 20th century in the REF-C2 simulation, by 23% until the 2020s, stays at these high values for about 40 years, and then decreases in the late 21st century (leading to an overall global-mean increase of 8% between 1960 and 2100). The global-mean tropospheric ozone burden decreases by 1% between 2000-2030, and 10% between 2000-2100. These decreases are similar to the ensemble mean of the ACCMIP models which performed the RCP 6.0 simulation, of 1% and 9% between 2000-2030 and 2000-2100, respectively (Young et al., 2013).

One seemingly inconsistent feature of Fig. 5 is that at northern midlatitudes, NO_x and NMVOC+CO concentrations decrease in the early 21st century, yet ozone concentrations in the REF-C2 simulation remain constant. To explain this feature, one must examine the spatial changes in ozone and its precursor emissions. Figures 6a-b show that NO_x and NMVOC+CO both decrease in the Northern Hemisphere over Europe (and North America, in the case of NO_x). Therefore, ozone decreases by up to 4% between the 2000s and 2020s over Europe (Fig. 6c). However, the decrease in NO_x of approximately 20% over Europe and North America is compensated for by up to a 40% increase in NO_x over Asia. In turn, this incurs an increase in ozone of up to 6% in the same region, and, because of ozone's long lifetime in the troposphere, the increase extends as far as the west coast of North America. The decreases in ozone and its precursor emissions over Europe and North America and the increases over Asia are statistically significant at the 95% level of confidence.

As shown in Fig. 6, changing regional emission patterns explain the substantial effect on northern midlatitude tropospheric ozone (Fig. 5c): by 1990, tropospheric ozone is 31% higher than in 1960, and such high abundances are sustained until 2060. Attempts by Europe and North America to reduce emissions are ~~partially~~ offset by increases from Asia. It is well known that ozone formed from precursor emissions in Asia can be transported across the Pacific Ocean to the US, and this has previously been shown by, amongst others, Auvray et al. (2007), Derwent et al. (2008) and Zhang et al. (2010). Europe may also expect to be affected by increased emissions from other Northern Hemisphere sources in the early to mid-21st century; Auvray and Bey (2005) showed that Asian and North American sources of ozone contribute 8% and 11% of the European annual ozone budget, respectively.

We further show decadal-mean ozone fluxes around the lower stratosphere and troposphere in Fig. 7. 15 of the 21 tracer regions are shown, with the remaining six regions located in the upper stratosphere above 30 hPa. Figure 7a quantifies ozone fluxes (Tg yr^{-1}) around the boundary layer (850-1000 hPa) and free troposphere (100-850 hPa between 30°N-30°S and 200-850 hPa elsewhere), ascent of air from the tropics into the stratosphere, and downwelling from the stratosphere at extratropical latitudes, for the 1960s. Figure 7b shows the same plot for the 2050s, with increases of more than 20% since the 1960s marked in red; this serves to highlight the increased export of ozone from tropical and northern midlatitude regions in the troposphere and boundary layer to surrounding regions (such as northern high latitudes), due to increased ozone production from precursor emissions in these regions between 1960-2050.

Decadal variability will also influence long-range transport of ozone within the troposphere through the 21st century. Under RCP 6.0, there is an increased tendency towards more El Niño conditions (consistent with the findings of e.g. Cai et al. (2014), although they examined RCP 8.5), which is linked with a strengthening of the flow of ozone-rich air from Europe and Asia across the Pacific Ocean towards Hawaii in Northern Hemisphere autumn (Lin et al., 2014). As El Niño conditions become increasingly prevalent, more eastward transport of ozone across the Pacific Ocean may be expected to occur.

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3.4 Ozone change with fixed precursor emissions

As shown in Figure 5b, holding CO and NMVOC emissions constant at 1960 levels does not equate to constant concentrations of those species in the troposphere through the 21st century, because methane is an important source of CO and an ozone precursor in its own right (e.g., Seinfeld and Pandis, 2006), and methane is not held constant in the fEmis simulation. Figure 5c shows that in the absence of NO_x, the tropospheric ozone concentration maximises in the 2080s in the fEmis simulation, which is approximately when methane concentrations maximise following RCP 6.0 (Fig. 1a).

To understand the effect on tropospheric ozone abundances if all ozone precursors, including methane, were held constant at 1960 levels, we ran an fEmis simulation with fixed methane (referred to as the fCH_4 simulation) for ~~2080~~1960-2100. 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.

Figure 5b shows that compared with 1960~~ of the fEmis and REF-C2 simulations~~, NMVOC+CO concentrations in the fCH$_4$ simulation are 5-10 ppb lower ~~in the 2080s~~by the end of the 21st century at northern midlatitudes and in the tropics, and decrease slightly at southern midlatitudes. In the 2080s, when methane concentrations maximise following RCP 6.0, ~~Compared with 2080 of the fEmis and REF-C2 simulations,~~ NMVOC+CO concentrations in the fCH4 simulation are significantly lower than in the fEmis and REF-C2 simulations: in the global average, NMVOC+CO concentrations are 4% lower in the fEmis simulation compared with the REF-C2, and 22% lower in the fCH$_4$ simulation compared with the REF-C2. This corroborates the finding of Wang and Prinn (1999), that controlling methane emissions is more effective in controlling NMVOC+CO concentrations in the troposphere, than controlling NMVOC+CO emissions themselves.

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Figure 5c shows that tropospheric ozone concentrations in the 2080s of the fCH$_4$ simulation are approximately the same as in the 1960s. In the global mean, ozone in the fCH$_4$ simulation is 16% lower than in the REF-C2 simulation and 10% lower than in the fEmis simulation. Methane has been shown to be an important ozone precursor historically, with both Shindell et al. (2009) and Lang et al. (2012) finding it to be responsible for most of the tropospheric ozone increase from pre-industrial to present times. Studies that have modelled projected tropospheric ozone under the different RCPs find methane to be the largest factor defining differences between the projections, because the RCPs assume huge reductions in NO$_x$ and NMVOCs, but project growth in methane, especially in RCP 8.5 (Wild et al., 2012; Eyring et al. 2013b; Young et al., 2013).

3.5 Impacts of climate change and stratospheric ozone recovery

Although the fEmis simulation was designed to assess the impacts of climate change on the atmosphere (Eyring et al., 2013a), there is a discrepancy with respect to methane's dual roles as a greenhouse gas and ozone precursor when it comes to analyzing tropospheric ozone, as discussed in the preceding section. However, given that ozone in the fCH$_4$ simulation is the same in the 1960s and 2090s (Fig. 5c), this implies that the effects of climate change and stratospheric ozone recovery on ozone in the mid-troposphere are either negligible, or offset one another.

Climate change is thought to lead to tropospheric ozone decreases, due to increasing temperature and humidity, which accelerates the ozone destruction reactions (e.g. Toumi et al., 1996; Grewe et al., 2001; Doherty et al. 2013; Morgenstern et al., 2013). Figure 8a shows the ozone change at 500 hPa in the fEmis simulation between the 1960s and 2090s. The change is statistically significant at the 95% confidence level almost everywhere. Here, with NO_x, NMVOCs and CO fixed in the fEmis simulation, ozone increases up to 6 ppb ~~almost everywhere~~ (a global-mean increase of 6%). The only exceptions are south of 50°S, where it remains unchanged and over the equatorial Pacific, where decreases of up to 2 ppb are seen. As discussed in Section 3.2, the $H_2O + O(^1D)$ reaction (R5) is very important for ozone loss over the remote tropical Pacific Ocean, and this reaction becomes faster over the period 1960-2100 as the troposphere becomes increasingly warm and humid (e.g. Zeng et al., 2010; Stevenson et al., 2013). Figure 8b shows the change in the ozone production:loss ratio (R1+R2)/(R3+R4+R5) between the 1960s and 2090s. This ratio decreases everywhere due to the increased rate of ozone loss reactions, particularly at northern midlatitudes. Clearly temperature and humidity play an important role for ozone in the tropical Pacific (leading to less ozone), however ozone production resulting from the increase in methane is more important elsewhere, despite the increased rate of the ozone destruction reactions.

Alongside methane, two further factors contribute to the ozone increase in the fEmis simulation, although their influence is small: NO_x emissions from lightning, and STE. STE is projected to increase through the 21st century, because (a) as lower stratospheric ozone abundances increase, there is more ozone in the stratosphere available to be transported to the troposphere, and (b) the overall meridional circulation, the Brewer-Dobson circulation, is projected to strengthen (thus transporting more ozone from the stratosphere to the troposphere) (Hegglin and Shepherd, 2009; Zeng et al., 2010). Figure 8c shows the contribution of stratospheric ozone to the ozone budget at 500 hPa in the 1960s, calculated using the lower-stratospheric ozone tracers. The tracers define the lower stratosphere as the region between 30-200 hPa for 30-90°N and 30-90°S, and between 30-100 hPa for 30°N-30°S (Fig. 7), given that the tropopause sits at a lower pressure level in the tropics. In the 1960s, STE contributes between 0.1 – 5% of ozone present at 500 hPa. We calculate a total flux from the lower stratosphere to the troposphere of 462 Tg yr^{-1} in the 1960s. This is lower than the mean value from the model studies reviewed by Wild (2007) of 636 Tg yr^{-1}, but still within one standard deviation from their mean. Figure 8d shows the change in the contribution of stratospheric ozone to ozone at 500 hPa between the 1960s and 2090s in the fEmis simulation. STE contributes up to one additional ppb at southern midlatitudes, and this is statistically significant at the 95% confidence level.

As discussed in Section 3.2, methane leads to ozone production in the presence of NO_x. Along with humidity and STE, lightning NO_x emissions may increase in a warmer climate, either due to increased frequency of thunderclouds (and therefore lightning), or more intense thunderstorms (Schumann and Huntrieser 2007; Price 2013). Figure 9a shows lightning NO_x emissions from SOCOL averaged over the 1960s, and shows that most lightning is produced over Africa and South America. Lightning NO_x emissions increase over the continents by 61% between 1960-2100 (Fig. 9b), and by 48% between 2000-2100. Smyshlyaev et al. (2010) found that ozone increased between 10-20% when lightning NO_x emissions increased by 2 Tg(N) year^{-1} (depending on latitude and season), and up to 90% with a 20 Tg(N) year^{-1} increase in lightning NO_x. Banerjee et al. (2014) calculated increases in lightning NO_x emissions of 33% (2 Tg(N) year^{-1}) and 78% (4.7 Tg(N) year^{-1}) between 2000-2100 in simulations using RCP 4.5 and RCP 8.5, respectively. 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. Banerjee et al. (2014)~~.~~ also showed that under RCP 8.5, the increase in lightning NO_x emissions of 78% caused ozone increases of up to 30% in the troposphere (maximizing between the equator and 30 °S). Although we cannot quantify ozone increases induced by lightning NO_x emissions in our simulations, the studies referred to here indicate the likely magnitude of increase (20-30%). Together with STE, ozone increases induced by lightning NO_x emissions are largely offset by the temperature-induced increased rates of ozone destruction in the troposphere. ~~However,~~ Finally, we note that the results also depend on the chosen lightning parameterization, which is coupled to the cloud top heights;~~.~~ Grewe (2009) showed that lightning NO_x emissions might also slightly decrease, when stronger but fewer convective events occur in a future climate. ~~Although we cannot quantify any ozone increases induced by lightning NO_x emissions, they are likely to be small, and,~~

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~~together with STE, offset by the temperature-induced increased rates of ozone destruction reactions in the troposphere, similar to the findings of Morgenstern et al. (2013).~~

4 Conclusions

We have presented three~~wo~~ CCM simulations covering the period 1960-2100, where the only factors differing in the model setup were the ozone precursor emissions (NO_x, NMVOCs, ~~and~~ CO and CH_4). The tropospheric extension to the SOCOL CCM is still new and with 17 NMVOCs only moderately sophisticated relative to some of the better-established tropospheric chemistry models, however the results presented here compare favorably with previous work.

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In the REF-C2 simulation, which used RCP 6.0 greenhouse gases and ozone precursors, the maximum impact of ozone precursors on tropospheric ozone occurs between 1990 and 2060, when global-mean ozone in the free troposphere increases by 23% from 1960 levels. Although decreasing emissions of ozone precursor gases over Europe and North America lead to local reductions in ozone in the early 21st century, large increases in precursor gas emissions from Asia, combined with ozone's ability to be transported on inter-continental scales within the troposphere, lead to a 70 year period between 1990-2060 in which ozone abundances at northern midlatitudes are constantly elevated. In the late 21st century, reductions in ozone precursor gases, especially NO_x, lead to decreases in tropospheric ozone globally. However, global-mean concentrations are still 8% higher in the 2090s compared with the 1960s.

In the fEmis (fixed ozone precursor emissions) simulation, global-mean ozone increases by 6% between 1960-2100, mostly because methane concentrations were not held constant. A ~~short~~ fCH_4 sensitivity simulation ~~for 2080-2100~~ with all ozone precursors (including methane) held constant shows that tropospheric ozone concentrations are the same in 2100 as in 1960. Increased flux of ozone from the stratosphere to the troposphere, and increased emissions of NO_x from lightning in a warmer climate contribute to increases in tropospheric ozone through the 21st century, although their effects are largely offset by temperature-induced increased rates of ozone destruction in the troposphere ~~effects are relatively small~~.

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Other climate-change related factors we have not examined include biogenic emissions, which are thought to increase with temperature, but are not considered in our simulations because SOCOL does not include an interactive scheme for biogenic emissions. Notably, we have considered only a single climate change scenario (RCP 6.0), and the impacts of climate change will differ under different climate scenarios. We furthermore reiterate that emissions of ozone precursor gases are also a significant source of uncertainty in our results.

Overall, and given the assumptions inherent in the climate and ozone precursor emissions scenarios we used, anthropogenic NO_x emissions have the largest influence on tropospheric ozone in our simulations. Methane has the second largest influence, which is approximately one-third that of anthropogenic NO_x emissions. We therefore conclude that emission policies globally have the largest role to play in determining tropospheric ozone evolution through the 21st century.

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Table 1. Summary of boundary conditions used for the SOCOL CCM simulations

	REF-C2 (1960-2100)	fEmis (1960-2100)	fCH$_4$ (1960~~2080~~-2100)
Greenhouse gases (CO$_2$, N$_2$O, CH$_4$)	Observations until 2005 then RCP 6.0 (Masui et al., 2011).	Same as REF-C2.	CO$_2$ and N$_2$O same as REF-C2; CH$_4$ fixed at 1960 levels.
Ozone ~~and aerosol~~ precursor emissions	~~Observations~~ Historical emissions until 2000 (Lamarque et al., 2010), then RCP 6.0.	Fixed at 1960 levels.	Fixed at 1960 levels.
SSTs	Observations until 2005 (Rayner et al., 2003), then RCP 6.0 (Meehl et al., 2013).	Same as REF-C2.	Same as REF-C2.
ODSs	~~Observations +~~ ~~the~~The A1 scenario from WMO (2011), which includes observations until 2009.	Same as REF-C2.	Same as REF-C2.

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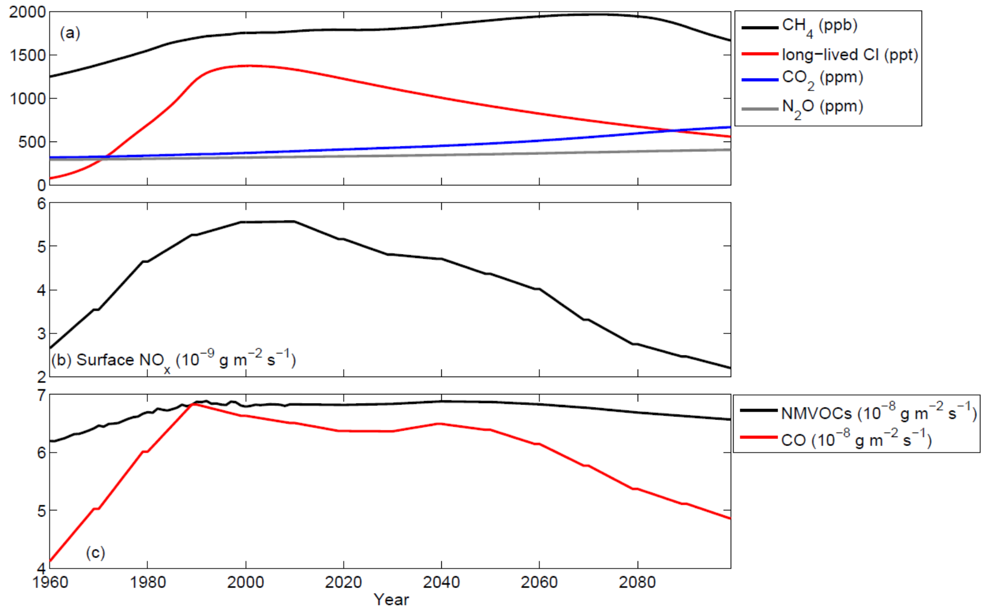
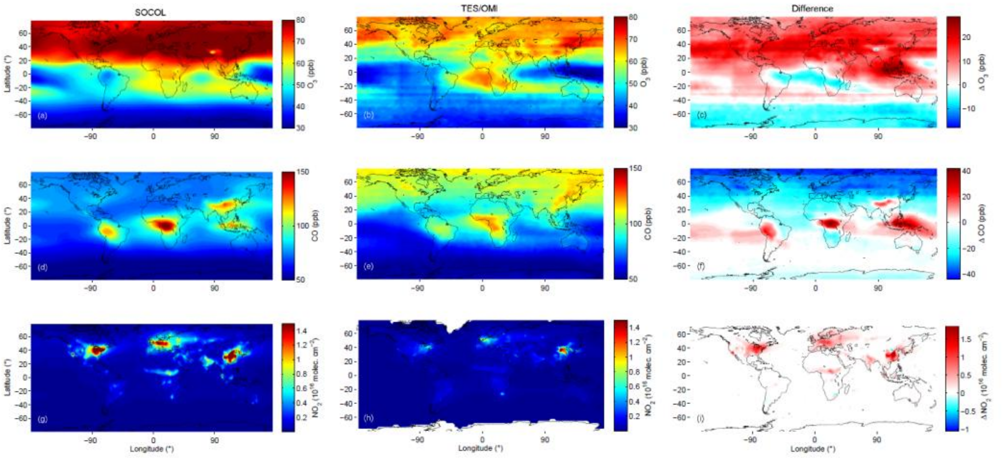


Figure 1. Boundary conditions used in the REF-C2 simulation (global-mean concentrations/emission fluxes). (a) CO_2, CH_4, N_2O mixing ratios following RCP 6.0, and long-lived chlorine mixing ratios following the WMO A1 scenario for ODSs. (b) Surface NO_x emission fluxes, following RCP 6.0. (c) Surface CO and NMVOC emission fluxes, following RCP 6.0.



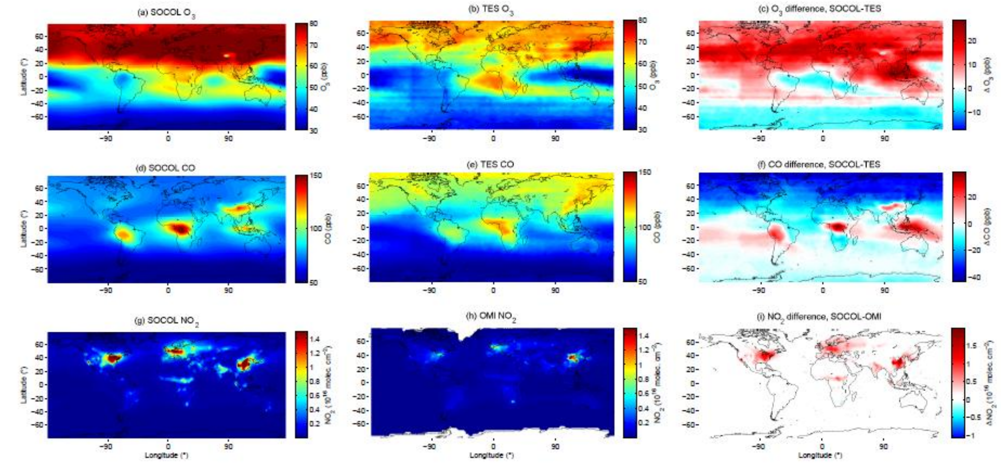
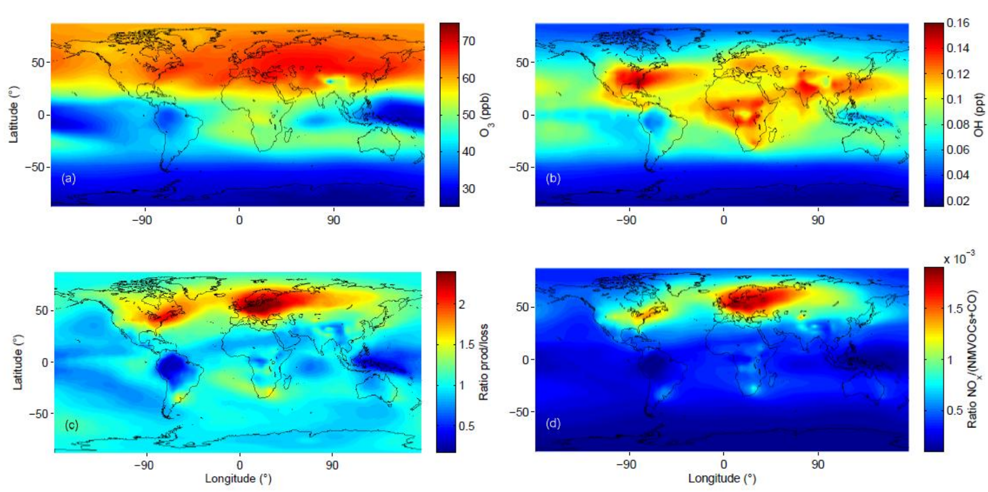


Figure 2. Comparisons of SOCOL model results (from the REF-C2 simulation) with observations, averaged over 2005-2009, for: (a) SOCOL ozone, 500 hPa; (b) TES ozone, 464 hPa; (c) ozone difference (panel (a) minus (b)); (d) SOCOL CO, 500 hPa; (e) TES CO, 464 hPa; (f) CO difference (panel (d) minus (e)); (g) SOCOL tropospheric column NO_2; (h) OMI tropospheric column NO_2; (i) NO_2 difference (panel (g) minus (h)).



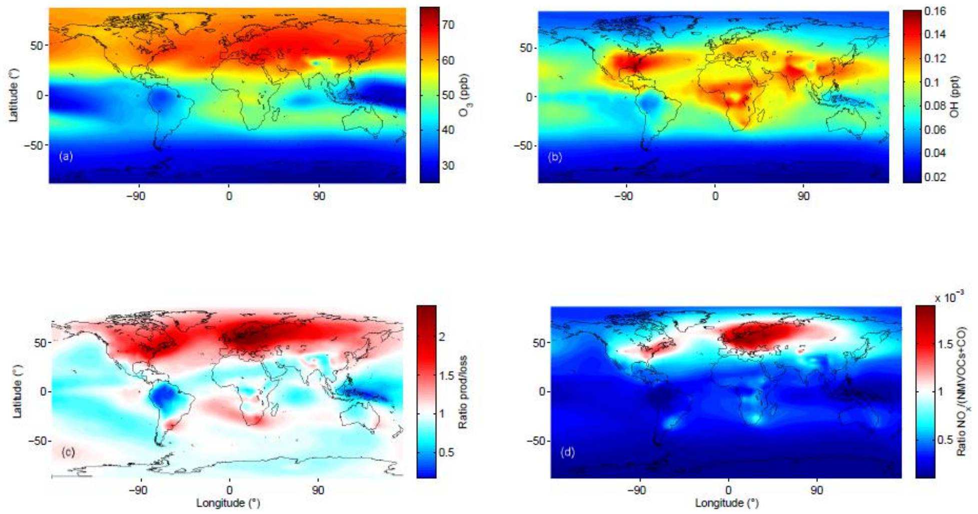


Figure 3. Results from the REF-C2 simulation, 1960-1969 average, 500 hPa. (a) Ozone; (b) OH; (c) Ratio of ozone production over loss; (d) Ratio of NO_x: NMVOCs+CO.

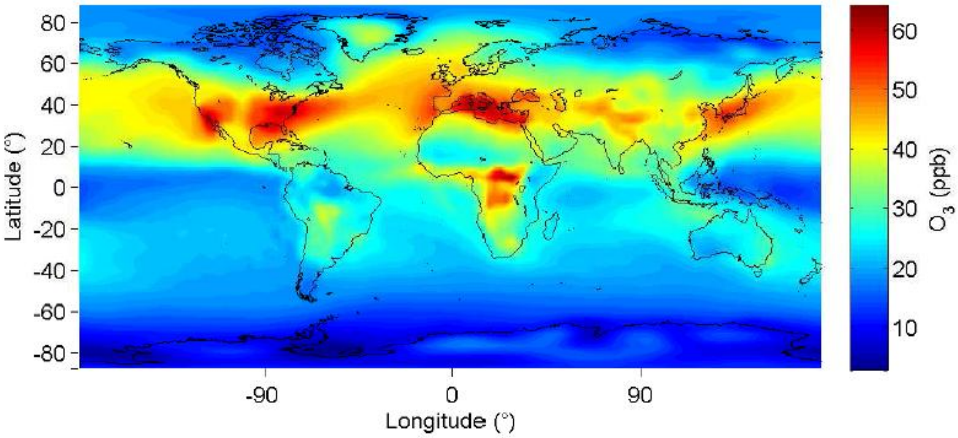
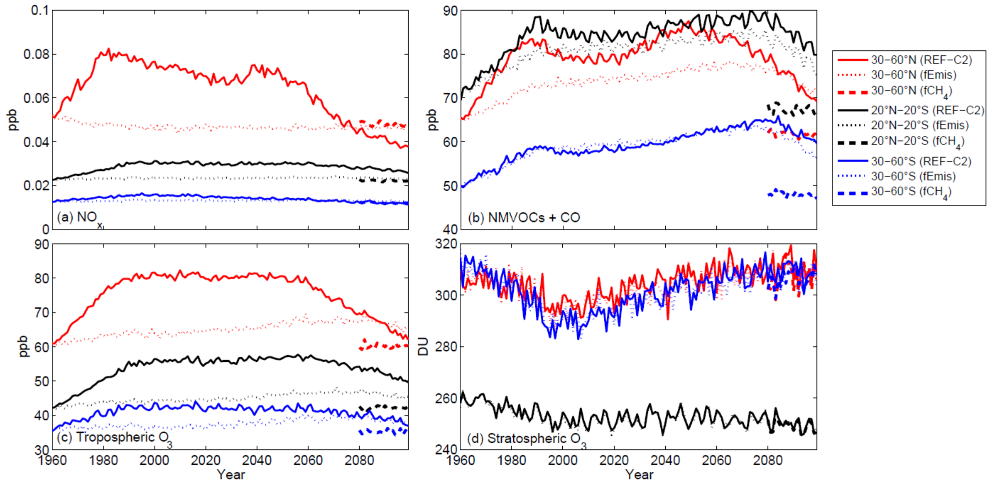


Figure 4. As for Figure 3a, but for the surface instead of 500 hPa.



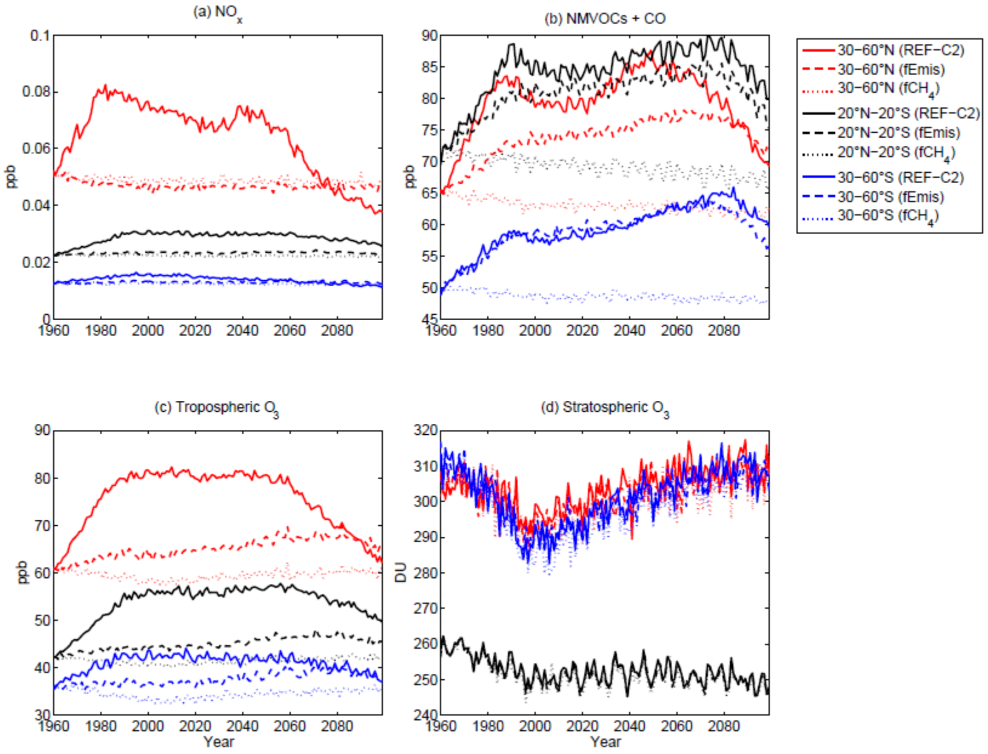


Figure 5. Timeseries of northern midlatitude (30-60°N, red lines), tropical (20°-20°S, black lines) and southern midlatitude (30-60°S, blue lines): (a) NO$_x$ (500 hPa); (b) NMVOCs + CO (500 hPa); (c) tropospheric ozone (500 hPa); (d) stratospheric column ozone. Solid lines: for

the REF-C2 simulation. Dashed~~Dotted~~ lines: fEmis simulation. ~~Thick dashed lines (2080-2100)~~Dotted lines: fCH_4 simulation.

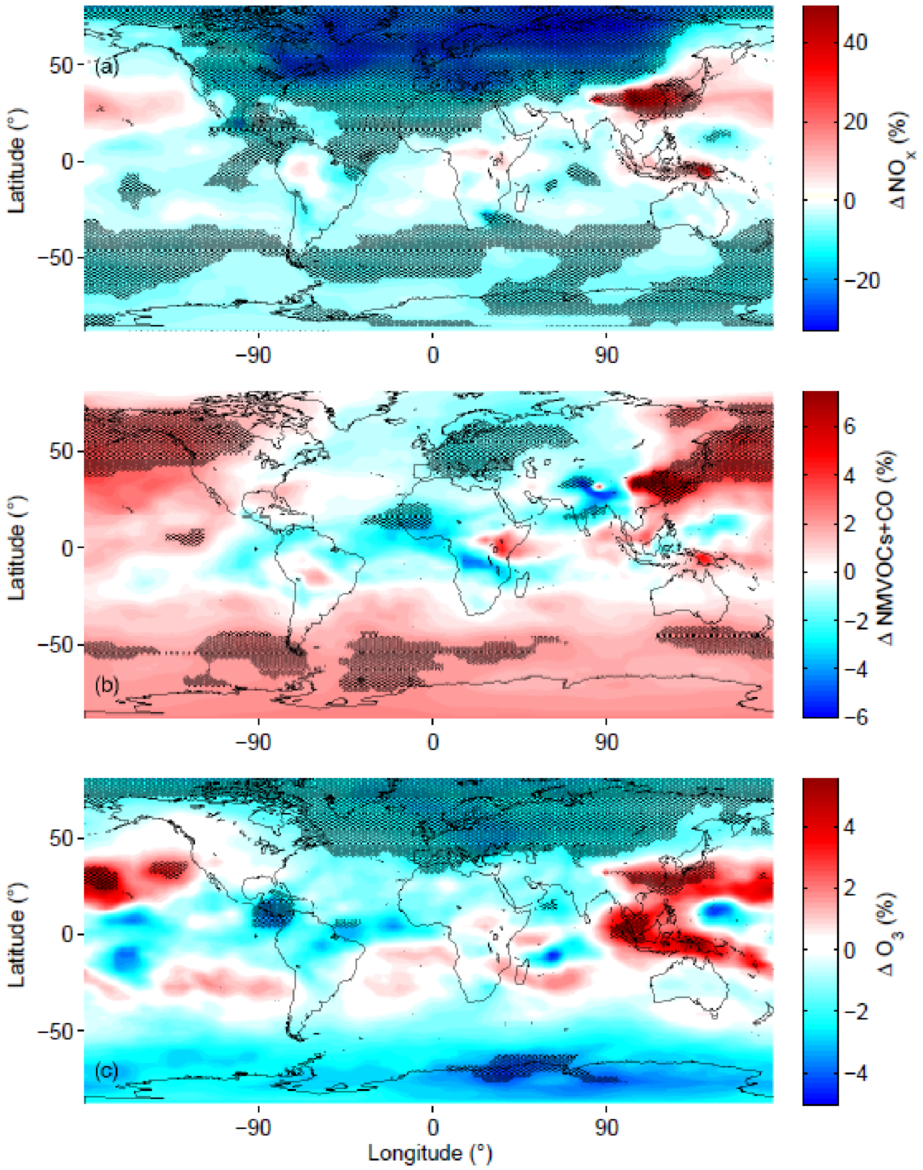


Figure 6. Changes between the 2000s and 2020s decades (2020s minus 2000s) in the REF-C2 simulation at 500 hPa for: (a) NO_x; (b) NMVOCs+CO; (c) ozone. Shading indicates that the difference is statistically significant at the 95% level of confidence.

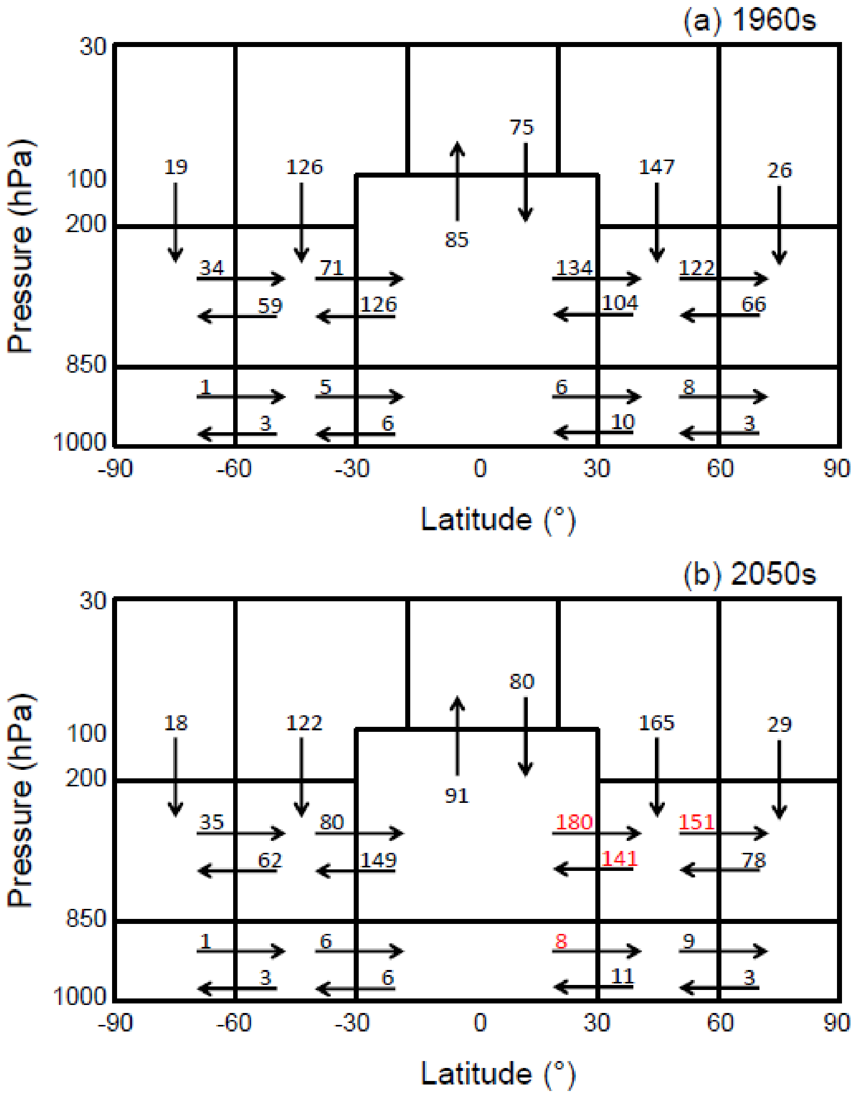


Figure 7. Decadal-mean ozone fluxes (Tg year^{-1}) between defined tracer regions for (a) the 1960s and (b) the 2050s in the REF-C2 simulation. Red text in panel (b) indicates an increase of more than 20% from the same quantity in (a).

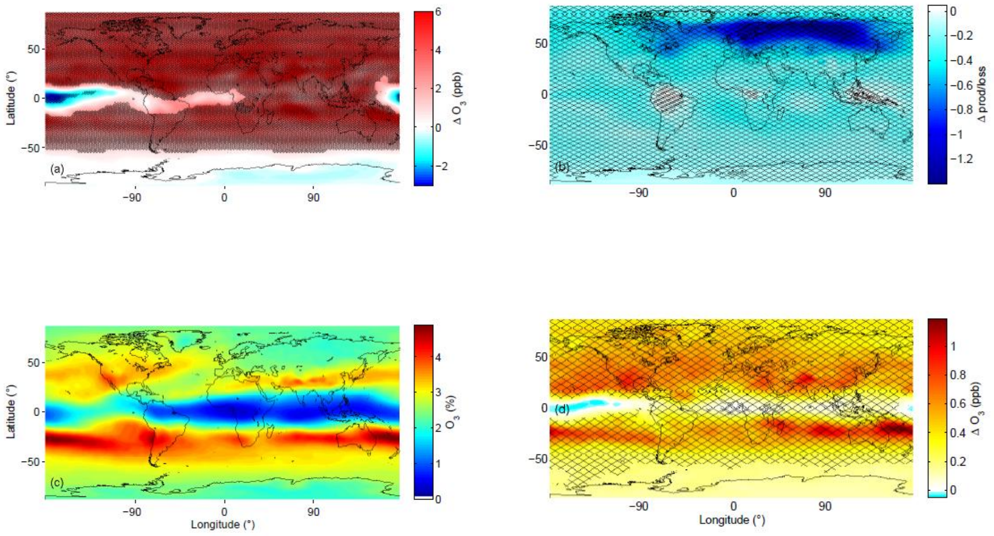


Figure 8. (a) Change in ozone at 500 hPa in the fEmis simulation, 2090s minus 1960s; (b) Change in the ratio of ozone production over loss in the fEmis simulation, 2090s minus 1960s; (c) Percentage of ozone at 500 hPa which was produced in the lower stratosphere in the fEmis simulation, 1960s decade; (d) Absolute change in the amount of ozone at 500 hPa which was produced in the lower stratosphere in the fEmis simulation, 2090s minus 1960s. Shading indicates that the difference is statistically significant at the 95% level of confidence.

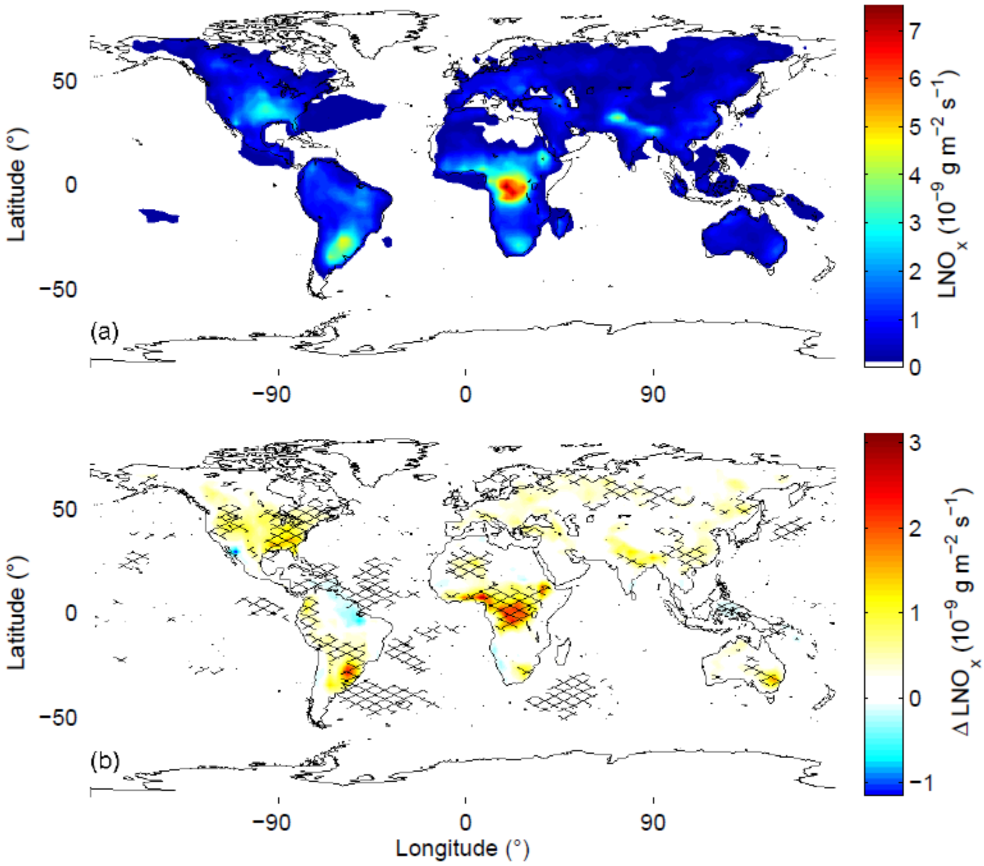


Figure 9. (a) Lightning NO_x emissions in the fEmis simulation, averaged over the 1960s; (b) Change in lightning NO_x emissions in the fEmis simulation, 2090s minus 1960s. Shading indicates that the difference is statistically significant at the 95% level of confidence.