May 15, 2015

Response to referee comments on "Uncertainties in isoprene photochemistry and emissions: implications for the oxidative capacity of past and present atmospheres and for trends in climate forcing agents".

We thank both reviewers for their valuable comments and suggestions. Their input has significantly improved the manuscript.

Referee's comments are *in italics*, our responses are in plain text, and changes to the manuscript are in blue. (Note: all page and line references are for the "acpd-15-2197-2015.pdf" manuscript version.)

REFEREE #1

General comments

It is evident throughout the text that the authors do not fully understand the IPCC concept of global radiative forcing.

The reviewer makes a good point that we did not clearly define the term 'radiative forcing' as used here. We address this issue in the revised text. Please see below under specific comments 2, 5-6.

Based on the comparisons in Section 3.2, readers would appreciate the addition of some clear and transparent statements in the Discussion Section on which model configuration is the most realistic, especially given the large number of sensitivity simulations.

We acknowledge that readers would appreciate pointers to the most realistic model, but we are reluctant to do so. As explained in the Discussion Section, our knowledge of both isoprene photochemistry and the CO_2-sensitivity of plant isoprene emissions is still evolving. The primary focus of our study is therefore to demonstrate the range of uncertainties in model estimates arising from such uncertainties. However, we now make clear that the C1 photochemical scheme is likely outdated (page 2224, line 16):

The primary goal of this model study is to explore the sensitivity of the oxidative capacity of present and past atmospheres to assumptions about isoprene emissions and the fate of its oxidation products. We are reluctant to offer "best guess" estimates in large part because the uncertainty in the CO_2-isoprene interaction is substantial and our knowledge of the photochemical cascade of isoprene oxidation is still evolving. Some studies have suggested that canopy-scale processes may complement or offset the leaf-scale response to atmospheric CO_2 levels (e.g., Sun et al., 2013). Also, it is likely that the application of the same CO_2-sensitivity parameterization to all PFTs leads to an overestimate of this effect. As discussed below, observations of the relevant chemical species that could constrain the oxidative capacity of past atmospheres are sparse. Laboratory and field measurements, however, strongly suggest that the C1 chemistry scheme is an inadequate representation of the isoprene photochemical cascade (Paulot et al., 2009a, b; Mao et al., 2013c). Therefore, model studies that depend on a simple, C1-like isoprene photo-oxidation scheme are likely outdated, particularly with respect to their ability to accurately simulate the tropospheric oxidative capacity. All of the models participating in the ACCMIP study in support of the IPCC AR5 used a C1-like isoprene photo-oxidation mechanism (Naik et al., 2013). Our results demonstrate that even under identical emission scenarios, the original and new isoprene photo-oxidation mechanisms yield different interpretations of various parameters such as changes in global mean OH and methane lifetime across the preindustrial-present day transition.

A further weakness of the study is that it stops at global burden changes and does not calculate radiative forcings, which may explain the authors' lack of understanding of the radiative forcing concept.

Radiative forcing calculations are beyond the scope of this work. The primary focus of our study is to explore the resulting uncertainties in tropospheric chemical composition. Therefore, our computational priorities are on chemical complexity. Because oxidants affect the abundance of climate forcing agents, we also discuss the implications of our findings for these species.

I recommend publication once the following major issues have been adequately addressed:

Major comments

1. A major concern is that ozone is treated as an oxidant and completely ignored as a climate forcing agent. The ozone results are some of the most interesting because the global burden is relatively insensitive to the isoprene emission CO_2-sensitivity and chemical mechanisms (as shown in Figure 2(b)). Yet the ozone burden increases dramatically by a factor of 2 across the cold to warm climate states. From my perspective, this result is critical. Ozone deserves a climate forcing section in the paper in its own right like methane and SOA.

The reviewer raises a good point and we have added a section on ozone (new Results section 3.5) as follows:

3.5 Implications for tropospheric ozone and radiative forcing

Isoprene and its oxidation products influence the formation and loss of tropospheric ozone (Beerling et al., 2007). As in Murray et al. (2014), we find decreasing tropospheric mean ozone burdens in each progressively colder scenario for each combination of isoprene photochemistry and emissions scenarios. The "best estimate" scenarios of Murray et al. (2014) – represented by our "C1-wo" simulations – suggest that relative to the preindustrial, the tropospheric mean ozone burden is 33% higher in the present, 27% lower at the warm LGM, and 19% lower at the cold LGM. These values do not vary more than 8% for the present day and 5% for the LGM when the isoprene photochemistry and/or emission schemes are varied.

Using the multi-model estimate of 0.042 W m^{-2} per DU change in the mean tropospheric column ozone across the preindustrial-present day transition (Stevenson et al., 2013), we estimate that across our sensitivity simulations, changes in the mean tropospheric column ozone relative to their respective preindustrial scenarios lead to forcing contributions of +0.3 W m^{-2} for the present day. If we extrapolate this relationship to the LGM-preindustrial transition, we estimate values of -0.3 W m^{-2} for the warm LGM and -0.2 W m^{-2} for the cold LGM. However, accurate quantification of the tropospheric ozone forcing at the LGM relative to the preindustrial would require the use of an online radiative transfer model that convolves changes in the ozone distribution with other radiatively active climate processes.

We have added a discussion of the implications of the above results in our Discussion section (page 2223, line 29):

Unlike SOA, we find that changes in tropospheric mean ozone burdens relative to the preindustrial are insensitive to the uncertainties in isoprene emissions and photochemistry tested in this study. Relative to the preindustrial, the absolute magnitude of the radiative forcing from the change in tropospheric ozone at the LGM may be comparable to that of the present day. However, most climate simulations of the LGM still use preindustrial ozone values as boundary conditions, including this study and the Paleoclimate Modelling Intercomparison Project 2 (PMIP2, Braconnot et al., 2012). Accurate quantification of the tropospheric ozone forcing at the LGM relative to the preindustrial requires the use of an online radiative transfer model that convolves changes in the ozone distribution with other radiatively active climate processes.

2a. The authors misunderstand the IPCC radiative forcing concept. Page 2224: "Our work demonstrates that besides changes in land use, changes in environmental factors controlling biogenic VOC emissions should also be included in calculations of the net radiative forcing. For example, Unger (2014) reported a decrease in biogenic VOC emissions of 37% due to expanding cropland, but did not include the effects of meteorological variables or CO_2-sensitivity on such emissions. In our study, biogenic VOC emissions decrease by just 8% in the present day relative to the preindustrial due to changing meteorology and land use change, and by 25% when the CO_2-sensitivity of isoprene emissions is also considered."

The experimental design in Unger (2014) was chosen to correspond exactly to that adopted in the IPCC Fifth Assessment Report (AR5) Chapter 8: Anthropogenic and Natural Radiative Forcing (Myhre et al., 2013). Importantly, the IPCC definition of global radiative forcing refers to a single perturbation in the climate system. Unger (2014) targets the historical cropland expansion as the single perturbation. The major advantage of adopting the IPCC experimental design is that the global radiative forcing values provided in Unger (2014) are fully consistent with the IPCC AR5 value for the surface albedo change due to land use (Myhre et al., 2013). A departure from the IPCC definition is required to account for the effects of multiple human perturbations on the BVOC global radiative forcing (for instance, when incorporating the effects of anthropogenic CO_2 and physical climate change on the plant emissions, and simultaneous changes to anthropogenic pollution emissions). This alternative approach has already been published in a recent related study (Unger, On the role of plant volatiles in anthropogenic global climate change, GRL, 2014b).

The authors should be aware that several research groups (in addition to Unger, 2014a,b) have been thinking and writing about the complex issues around how to tackle the human-induced radiative impacts of BVOC emissions and photochemistry changes. For instance, see also Heald et al., Contrasting the direct radiative effect *and direct radiative forcing of aerosols, ACP, 2014; and Heald and Spracklen, Land use change impacts on air quality and climate, in press, 2015.*

The reviewer raises an important point. To avoid confusion, we have clarified all text on radiative forcing and our discussion on page 2224, and we have added the two new references suggested by the reviewer. Please see the revised text in blue on page 5.

2b. What is more relevant and needed here in this work in the Discussion Section is a comparison of your results to those of the previous 3 IPCC-class vegetation-climate models for the preindustrial to present day change in isoprene that isolate the roles of individual global change drivers. You have included 2 of these already on Page 2207: "Previous studies, which employ different global biogenic VOC emission models and land cover products to the ones used in this study, find that biogenic VOC emissions were 20–26% higher in the preindustrial relative to the present day (Pacifico et al., 2012; Unger, 2013). In this study, we estimate this value to be 8% when the CO_2*-sensitivity of plant isoprene emissions is not considered, and 25% when the* CO_2*-sensitivity is considered." Another important result to include is Lathiere et al., Sensitivity of isoprene emissions from the terrestrial biosphere to 20th century changes in atmospheric* CO_2 *concentration, climate, and land use GBC, 2010. This study uses MEGAN isoprene emission algorithms embedded in ORCHIDEE.*

We now refer to Lathiere et al. (2010) in our study.

Your result is consistent with these 3 IPCC-class models for the net change in isoprene emissions (~25% decrease between preindustrial and present day) but the ICECAP model framework obtains the result for a different reason. In the 3 IPCC-class models, the historical human land cover change is the dominant driver of the reduction, whereas in your model framework the CO_2*-sensitivity effect is the dominant driver of the reduction. Can you explain this difference? (See Point (3) below about over-estimate of* CO_2*-sensitivity in global models). I recommend to check the basal isoprene emission factors in your model and the vegetation cover change fractions between the PI and PD. How does LAI change in your model in the different climate states? Are you over-estimating LAI changes?*

The reviewer raises good questions. In fact, Lathiere et al. (2010) found that the CO_2-sensitivity effect dominates the change in isoprene emissions between 1901-2002, with the impact of land use change about half that of the CO_2-sensitivity: rising atmospheric CO_2 levels reduce isoprene emissions over this time period by 21% and cropland expansion by 10%; climate change offsets these reductions by increasing isoprene emissions by 7% (Lathiere et al., 2010).

We now clarify that the basal isoprene emission factors per plant functional type used in our model do not change between any of the climate scenarios (Murray et al., 2014, Table 5). Isoprene emissions here respond to shifts in: (1) LAI and the distribution of PFTs as output by the BIOME4-TG equilibrium vegetation model in response to climate; (2) prescribed cropland extent; (3) temperature, PAR, etc., as it affects the MEGAN BVOC emission parameterization; and (4) atmospheric CO_2 levels (only for the "with" CO_2-sensitivity simulations). Differences in the dominant factor driving the modeled decrease in global isoprene emissions among the four studies are most likely due to differences in the time periods of the simulations, land use trends applied, changes in LAI and the distribution of PFTs, and the CO_2-sensitivity algorithm considered in each study. These differences are summarized in the table below.

	Time periodof simulation	**PI-to-PD change in crop cover (%)**	**PI-to-PD change in CO_2 (%)**	**Reference for CO_2-sensitivity algorithm**
This study	1770s-1990s	+10	+32	Possell & Hewitt, 2011
Lathiere et al. (2010)	1901-2002	?	+27	Possell et al., 2005
Pacifico et al. (2012)	1860-2000	+7	+29	Arneth et al., 2007
Unger (2013)	1880-2000	+22	+27	Wilkinson et al., 2009; Heald et al., 2009

The Possell and Hewitt (2011) scheme for CO_2-sensitivity of isoprene emissions likely represents an upper limit of this effect.

We have added a more detailed comparison based on the reviewer's recommendation. In response to all of the issues raised in the reviewer's comments 2a and 2b, the discussion section on Page 2224, line 1, now reads:

Besides SOA, changes in biogenic VOC emissions also affect the atmospheric concentrations of other climate forcing agents. Recent studies have demonstrated the importance of considering the net effect of human-induced changes in biogenic VOC emissions on global climate forcing over the industrial period (e.g., Unger, 2014a, b; Heald et al., 2014; Heald and Spracklen, 2015). Unger (2014a) quantified the global radiative impact of changes to the atmospheric concentrations of ozone, methane, and SOA due to a reduction in the emission of biogenic VOCs resulting from global cropland expansion between the 1850s and 2000s. She estimated a net cooling of -0.11 ± 0.17 W m^{-2}, which is comparable in magnitude but opposite in sign to the net forcing from the changes in surface albedo and land carbon release associated with cropland expansion. When other known anthropogenic influences on biogenic VOC emissions are also considered, the net global climate forcing is estimated to be -0.17 W m^{-2} (Unger 2014b). Our work demonstrates that reducing the uncertainties on such an estimate will require improvements in our knowledge of isoprene photochemistry and CO_2-sensitivity, as well as reconciling model estimates of land cover change over the industrial period.

We find that biogenic VOC emissions decrease by 8% in the present day relative to the preindustrial due to changing meteorology, redistribution of natural vegetation, and cropland expansion, and by 25% when the CO_2-sensitivity of isoprene emissions is also considered. The larger reduction is comparable to results from previous studies that have estimated a 20-26% reduction in biogenic VOC emissions from the late 19th century to the present day (Lathiere et al., 2010; Pacifico et al., 2012; Unger, 2013). Consistent with our study, Lathiere et al. (2010) determined that the CO_2-sensitivity effect dominates the change in isoprene emissions between 1901-2002, with the impact of land use change about half that of CO_2-sensitivity. In contrast, Pacifico et al. (2012) and Unger (2013) found cropland expansion to be the dominant driver of the reduction. This discrepancy likely arises for two reasons. First, our study applied an increase of approximately 10% in global cropland expansion (Guenther et al., 2012), which is smaller than the 22% change estimated by Unger (2013). Second, we apply a CO_2-sensitivity algorithm that most likely provides an upper limit of this effect for past climates (Possell and Hewitt, 2011).

Addition to section 2.2 (page 2205, line 10):

...into GEOS-Chem. The basal biogenic emission factors per plant functional types used in the BIOME4-TG model, which do not change between the climate scenarios, can be found in Murray et al. (2014), Table 5.

3. One of the main strengths of the study, and most interesting aspects, is testing the impacts of the isoprene CO_2-sensitivity parameterization by doing simulations with and without this effect. The CO_2-sensitivity parameterization is likely drastically too strong in current global models (including the one used in this study) in part because it has been applied uniformly to all PFTs. The "null" response is not typically reported in the plant physiology literature. Furthermore, some studies report increases in isoprene emission at high CO_2 (e.g. Sun et al., 2013).

We acknowledge in section 2.2 that the CO_2-sensitivity parameterization employed in our study most likely provides an upper limit of this effect for past climates, and in the Discussion section that our knowledge on this issue is still very much evolving. As stated in the original text, we chose the Possell and Hewitt (2011) parameterization because it is based on the widest range of plant taxa (page 2206, lines 20-24). As suggested by the reviewer, we now also discuss how uniform application of the CO_2-sensitivity to all PFTs will likely contribute to the overestimate (page 2224, line 22):

Also, it is likely that the application of the same CO_2-sensitivity parameterization to all PFTs leads to an overestimate of this effect.

We thank the reviewer for pointing out the Sun et al. (2013) study. They found increased isoprene emissions at high CO_2, which suggest that canopy-scale dynamics may offset leaf-scale processes, but did not perform any experiments at CO_2 levels relevant for our study (i.e., below 380 ppm). We have included this reference in our Discussion (page 2224, line 22):

Some studies have also suggested that canopy-scale processes may complement or offset the leaf-scale response to atmospheric CO_2 levels (e.g., Sun et al., 2013).

4. How are other plant terpenoid emissions treated in this study? Monoterpenes? Is CO_2-sensitivity applied to their emissions?

The CO_2-sensitivity has only been applied to plant isoprene emissions because its effect on other plant VOC emissions is less conclusive, with most studies observing no significant effect on monoterpene and sesquiterpene emitting species [Penuelas and Staudt, 2010]. Moreover, isoprene emissions constitute over 60% of total plant VOC emissions in all four climate scenarios (Murray et al., 2014, Figure 5). We have added a comment about this issue in Section 2.2 (page 2206, line 24).

We have not considered the effect of CO_2-sensitivity on other plant VOC emissions, such as monoterpenes and sesquiterpenes, due to lack of conclusive evidence of this effect (Penuelas and Staudt, 2010). In all four climate scenarios, isoprene constitutes more than 60% of total biogenic VOC emissions.

5. Misunderstanding radiative forcing again. Page 2202: "Uncertainties in the preindustrial-to-present day changes in biogenic SOA burdens lead to large uncertainties in the anthropogenic direct and indirect radiative forcing estimates (e.g., Scott et al., 2014; Unger, 2014)."

Authors need to be careful here. Scott et al. computes the present-day radiative effect of biogenic SOA (with and without SOA in the present-day atmosphere). Their result does not assess any human impacts on the biogenic SOA global radiative effect. In contrast, Unger computes the effects of the anthropogenic historical cropland expansion on biogenic SOA (i.e. an anthropogenic radiative forcing mechanism). Another more recent paper computes the effects of all anthropogenic influences on BVOC emissions and photochemistry between 1850s and 2000s and provides a biogenic SOA radiative forcing estimate (Unger, On the role of plant volatiles in anthropogenic global climate change, GRL, 2014b).

We acknowledge that we should have been more careful with our wording as well as our choice of references here. We have clarified all text on radiative forcing and climate impacts. We reference Carslaw et al. (2013) based on their statement that "Our results show that 45 per cent of the variance of aerosol forcing since about 1750 arises from uncertainties in natural emissions of volcanic sulphur dioxide, marine dimethylsulphide, biogenic volatile organic carbon, biomass burning and sea spray". We reference Scott et al. (2014) based on their statement that "the anthropogenic indirect radiative forcing between 1750 and the present day is sensitive to assumptions about the amount and role of biogenic SOA." This section now reads (page 2201, line 26):

The oxidation products of isoprene also substantially contribute to secondary organic aerosol (SOA) formation (Henze and Seinfeld, 2006). Biogenic SOA, like other aerosols, affects climate by scattering and absorbing solar radiation and by altering the properties and lifetimes of clouds, but the net climate effect is poorly characterized (Scott et al., 2014). Therefore, uncertainties in the preindustrial-to-present day changes in biogenic VOC emissions, and subsequently in SOA burdens, lead to large uncertainties in the anthropogenic indirect radiative forcing estimates over the industrial period (e.g., Carslaw et al., 2013; Scott et al., 2014).

We now reference Unger (2014a, b) in our Discussion section. Please see our response to comment #2 above.

6. Misunderstanding radiative forcing again. Page 2223: "The climate effects of biogenic SOA are not well characterized, but are thought to provide regional cooling (Scott et al., 2014)."

I could not find any scientific evidence being presented in Scott et al. (2014) that biogenic SOA plays a role in regional cooling. The Scott et al. (2014) paper *investigates the global direct and indirect radiative effects of biogenic SOA in the present day (with and without SOA) with a particular emphasis on the possible contributions from new particle formation.*

We thank the reviewer for pointing this out and have inserted new references here. This section now reads (page 2223 line 22):

The climate effects of biogenic SOA are not well characterized, but previous studies have estimated the regional direct radiative effect from biogenic SOA to be cooling (e.g., Lihavainen et al., 2009; Rap et al., 2013). Our work thus suggests that SOA reductions may have amplified regional warming in the present but minimized regional cooling at the LGM, relative to the preindustrial. Results from our sensitivity studies, however, underscore the large uncertainties in current model estimates of the anthropogenic indirect radiative forcing over the industrial period (e.g., Carslaw et al., 2013; Scott et al., 2014).

7. Why was the soil moisture dependence not included for isoprene emissions? Please explain.

Investigating the soil moisture dependence, although important, is beyond the scope of our present study, as the effect is still highly uncertain for biogenic isoprene emissions (Huang et al., 2015). This method also allows us to be as consistent as possible with Murray et al. (2014) in terms of model setup besides the parameters being investigated, as our primary goal is to isolate the sensitivity of model estimates to the CO_2-sensitivity algorithm. In MEGAN, environmental factors such as atmospheric CO_2 concentration and soil moisture are treated as scaling factors of the base emission rates (Section 2.2). Therefore, the relative differences with and without consideration of the CO_2-sensitivity are unlikely to change whether or not soil moisture dependence is considered.

8. Does this model account for changes in stratospheric ozone due to the different greenhouse gas concentrations? It is well established that stratospheric ozone increases with higher greenhouse gas levels due to the colder stratosphere that reduces the rates of the chemical destruction reactions (e.g. Waugh et al., 2009 and many others), which will have large implications for the stratosphere-troposphere exchange calculations as well as the tropospheric photolysis rate calculations.

Yes, the model accounts for chemical as well as dynamic changes in stratospheric ozone. As explained in the original manuscript (page 2203, line 22 and page 2221, line 17), "The ICECAP project is the first 3-D model framework to consider the full suite of key factors controlling the oxidative capacity of the troposphere at and since the LGM, including the effect of changes in the stratospheric column ozone on tropospheric photolysis rates." Murray et al. (2014) found that "reductions in greenhouse gases… decelerate the stratospheric residual circulation, … [leading to] an increase in tropical stratospheric ozone columns.") The GEOS-Chem model also includes online linearized stratospheric chemistry (McLinden et al., 2000). We have added this comment in section 2.1 (page 2204, line 17):

GEOS-Chem is a global 3-D chemical transport model (CTM) with a long history in simulating present-day tropospheric ozone-NO_x-CO-VOC-BrO_x-aerosol chemistry (http://www.goes-chem.org; Bey et al., 2001; Park et al., 2004; Parrella et al., 2012). The version used here includes online linearized stratospheric chemistry (McLinden et al., 2000), which allows for calculation of photolysis rates more consistent with changing climate and chemical conditions.

9a. Technical issues. The simulations are performed using only one year of archived meteorology for each time slice. Therefore, no assessment can be provided of uncertainty due to internal climate variability with this model framework.

As in Murray et al. (2014), we use four subsequent years of archived meteorology for each time slice. We have clarified this in the method section as follows (page 2209, line 5):

For each scenario, we use four subsequent years of archived meteorology from the GISS climate model. Each GEOS-Chem simulation is initialized with a 10-year spin-up, repeatedly using the first year of archived meteorology, to reach equilibrium with respect to stratosphere-troposphere exchange. We then perform three more years of simulations for analysis, using the three subsequent years of archived meteorology. All of the quantities considered here are global means or averages over large spatial regions. We find that the inter-annual variability of such quantities is small compared to the differences between the scenarios, and that three years is sufficient for our analysis.

9b. The AR4 GISS ModelE version is about 10 years old and at coarse spatial resolution (4°×5°; 23 vertical layers). Has the stratospheric-tropospheric exchange been captured properly in the framework, also given that only one year of meteorology is applied to calculate it?

We analyze three years of GEOS-Chem output. Please see our response to Comment 9a. Evaluation of the simulated stratosphere-troposphere exchange in ICECAP is discussed in Murray et al. (2014), section 2.5 and supplement. We have added a brief discussion to page 2205, line 14:

The ICECAP model overestimates transport from the stratosphere due to an overly vigorous Brewer-Dobson circulation (Murray et al., 2014). Rather than fixing the transport fluxes to better match present-day values, we accept this bias in order to allow the stratospheric columns of ozone to adjust freely to different climate scenarios. For example, Murray et al. (2014) found that reductions in greenhouse gases weakens the stratospheric residual circulation and leads to an increase in tropical stratospheric ozone columns.

10. Page 2208: "in which HO_2 uptake yields H_2O via coupling of Cu(I) /Cu(II) and Fe(II) / Fe(III) ions". How do we know about metal ions in the LGM and PI? Are they related to the dust distribution?

The reviewer raises a good point. Cu and Fe are ubiquitous components of crustal and combustion aerosols (Mao et al., 2013a) and are related to the dust distribution and volcanic activity. We have added the following information to the Introduction (page 2203, line 11):

Cu and Fe are ubiquitous components of crustal and combustion aerosols (Mao et al., 2013a). Observations and model studies suggest that during the LGM and preindustrial, natural dust distributions were higher than that in the present day (Mahowald et al., 2006). In particular, during the LGM, Fe(II) and Fe(III) ion concentrations in dust increased by at least two times relative to interglacial levels (Spolaor et al., 2013). Likewise, positive Cu anomalies during the last glacial period have been measured in ice cores (Oyarzun et al., 2005).

11. Table 1. That the global isoprene source from terrestrial ecosystems could be 50% higher in the LGM (when the temperate zone was covered in ice) compared to present day conflicts with common sense about the global Earth system plant productivity and behavior. Can you offer an explanation and justification?

Yes, this result is surprising. We have added an explanation to the Discussion section (page 2222, line 11). Note that we compare the LGM value with the preindustrial (rather than the present day) to match our practice for the rest of the paper, but the same reasoning applies.

This implementation increases global isoprene emissions in the warm LGM scenario by 15% relative to the preindustrial. At the LGM, lower sea levels expose extensive land area in equatorial Asia and Australia, which leads, in turn, to large regional increases in plant isoprene emissions (Murray et al., 2014, Figure 7). When we account for the potential increase in biogenic isoprene emissions at low CO_2 concentrations, this implementation swamps the effect of cooler temperatures in the warm LGM scenario.

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REFEREE #2

General Comments

The modeling work and subsequent analysis appears to have been a lot of work. However, it is not clear to me that this work has advanced scientific knowledge. The experimental setup includes new parameterizations for isoprene emissions, photochemistry, and CO_2 sensitivity, but then the results are not able to distinguish whether any of these are improvements over existing models (In the discussion the authors say "All of our sensitivity experiments are broadly consistent with ice-core records of D17O of sulfate and nitrate at the LGM and of CO in the preindustrial. For the present-day, the C1 chemistry scheme shows the best agreement with observation-based estimates of methane and methyl chloroform lifetimes, whereas C3 shows the best agreement with observation-based estimates of the inter-hemispheric (N = S) ratio of tropospheric mean OH. Thus, it is challenging to identify the most likely chemistry and isoprene emission scenarios.") Also, on page 2224 the entire paragraph starting with "The primary goal. . ." similarly describes how our current understanding of modern oxidative capacity of the atmosphere is limited by uncertain knowledge of the basic chemistry and mechanisms, so what can be learned from applying this uncertain knowledge to past environments?

The reviewer asks a fair question. We have significantly revised the text on page 2224 (line 16 onwards) to emphasize the scientific value of our analysis. We also make clear the C1 photochemical scheme is likely outdated. The revised text is as follows:

The primary goal of this model study is to explore the sensitivity of the oxidative capacity of present and past atmospheres to assumptions about isoprene emissions and the fate of its oxidation products. We are reluctant to offer "best guess" estimates in large part because the uncertainty in the CO_2-isoprene interaction is substantial and our knowledge of the photochemical cascade of isoprene oxidation is still evolving. Some studies have suggested that canopy-scale processes may complement or offset the leaf-scale response to atmospheric CO_2 levels (e.g., Sun et al., 2013). Also, it is likely that the application of the same CO_2-sensitivity parameterization to all PFTs leads to an overestimate of this effect. As discussed below, observations of the relevant chemical species that could constrain the oxidative capacity of past atmospheres are sparse. Laboratory and field measurements, however, strongly suggest that the C1 chemistry scheme is an inadequate representation of the isoprene photochemical cascade (Paulot et al., 2009a, b; Mao et al., 2013c). Therefore, model studies that depend on a simple, C1-like isoprene photo-oxidation scheme are likely outdated, particularly with respect to their ability to accurately simulate the tropospheric oxidative capacity. All of the models participating in the ACCMIP study in support of the IPCC AR5 used a C1-like isoprene photo-oxidation mechanism (Naik et al., 2013). Our results demonstrate that even under identical emission scenarios, the original and new isoprene photo-oxidation mechanisms yield different interpretations of various parameters such as changes in global mean OH and methane lifetime across the preindustrial-present day transition.

Quantifying the oxidative capacity of past atmospheres remains an ongoing challenge because the oxidants are not directly preserved in the ice-core record, and paleo-proxies that can provide a simple and robust constraint have not been readily identified (Levine et al., 2011; Alexander and Mickley, 2015). Our results call for greater attention and research efforts in the following measurements to help constrain model estimates of the oxidative capacity of past atmospheres:

1. Ice-core CO. Quantifying the amount of CO produced in situ from organic substrates trapped within the ice would facilitate the use of ice-core CO measurements as constraints for model results.
2. Ice-core $\Delta^{17}O(NO_3^-)$. Because of its greater sensitivity to oxidant abundances, ice-core measurements of $\Delta^{17}O(NO_3^-)$ may in fact provide a more robust proxy than $\Delta^{17}O(SO_4^{2-})$ for reconstructing the oxidation capacity of past atmospheres. For example, cloud amount and pH do not influence the isotopic composition of nitrate as they do for sulfate (Levine et al., 2011). In particular, measurements of $\Delta^{17}O(NO_3^-)$ in tropical ice cores, which are so far sparse, may be highly valuable given that the dominant natural sources of NO_x and production of OH are most prevalent in the tropics (Buffen et al., 2014).
3. Field campaigns focused on measurements of oxidant cycling in high-isoprene, low-NO_x environments. Such a suite of observations will help constrain the modeled sensitivity of tropospheric oxidants to past climate changes.

The main scientific value of our study lies in its demonstration of the importance of biogenic VOC emissions and the fate of their oxidation products in influencing chemistry-climate interactions across the last glacial-interglacial time interval and the industrial era. Because of existing uncertainties in isoprene emissions and photochemistry, there are larger uncertainties in model estimates of the oxidative capacity of past atmospheres than previously acknowledged. These uncertainties, in turn, limit our confidence in estimating radiative forcing due to changes in short-lived species such as SOA over time, as well as our ability to identify the factors controlling global mean OH levels between the LGM and the present day.

Constraining the anthropogenic radiative forcing over the industrial period inherently depends on our ability to quantify the chemical composition of the preindustrial atmosphere. In particular, assessing the radiative forcing from changes involving biogenic processes is an ongoing challenge in the modeling community, but has importance in the coming decades as policymakers face decisions that depend critically on accurate knowledge of the atmospheric oxidative capacity. For example, recent studies have demonstrated the importance of considering the net effect of human-induced changes in biogenic VOC emissions on global climate forcing over the industrial period (e.g., Unger, 2014a, b; Heald et al., 2014; Heald and Spracklen, 2015). Tackling the long-standing issue of the dynamics of future global methane sources and sinks is also crucial for the next generation of climate projections (Quiquet et al., 2015; Kirschke et al., 2013). However, including detailed photochemical mechanisms in chemistry-climate models is computationally expensive. In the ACCMIP models involved in the IPCC assessments of the preindustrial and present day, the tropospheric chemical mechanisms of non-methane hydrocarbons were represented in varying degrees of complexity (Lamarque et al., 2013), and the isoprene photo-oxidation mechanisms did not consider HO_x-recycling under low-NO_x conditions (Naik et al., 2013). Chemistry-climate models attempting to explain methane trends since the Last Glacial Maximum have also historically depended on relatively simple schemes for isoprene photo-oxidation (e.g., Valdes et al., 2005; Kaplan et al., 2006). Our work points to the value of incorporating into such models both current knowledge and the associated uncertainties regarding biogenic isoprene emissions and photochemistry.

Based on this, what additional constraints does this model inter-comparison study provide? They may have explored the model space of these new mechanisms, but is this a useful endeavor if we don't really expect the mechanisms to be right in the first place (i.e. "knowledge of the photochemical cascade of isoprene oxidation is still evolving" on pg 2224, ln 26)? Perhaps this is a useful endeavor, but if so the authors should make a forceful argument for it and explicitly state what new insights are learned by doing this work. Another question is why try to examine the LGM and preindustrial conditions if we know that the model doesn't work for modern conditions ("All of our present- day sensitivity experiments underestimate methane and methyl chloroform lifetimes inferred from observations. Our findings corroborate those of the recent Atmospheric Chemistry and Climate Model Intercomparison Project that uncertainties in our understanding of the long-term trends in OH and methane lifetime will persist unless natural precursor emissions and chemical mechanisms are well constrained" on pg 2225, line 21)?

The current manuscript appears to be a minor update in a model that is not validated against observations. If a clear and compelling argument was included in the manuscript that described how this work advanced our scientific understanding of the oxidative capacity of the atmosphere, provided insight into what types of observations are necessary to constrain models better (e.g. Levine et al (2011) – "In search of an *ice core signal to differentiate between source-driven and sink-driven changes in atmospheric methane", DOI: 10.1029/2010jd014878), or something of that nature it could be a valuable contribution. Without a substantial revision like this, I would not recommend it for publication.*

The reviewer makes several useful suggestions. In response to the previous comment, we have amended the text in our Discussion section to emphasize the insights gained by our study (please see above). We have also added a discussion of what observations may be useful for constraining the oxidative capacity of past atmospheres (please see above, 2nd paragraph of revised text).

Regarding model evaluation, the ICECAP model was evaluated against observations in Murray et al. (2014). We now include this information on page 2205, line 13:

A detailed description of the ICECAP model framework and its evaluation against observations can be found in Murray et al. (2014). The present-day simulation has been evaluated against a suite of sonde, aircraft, satellite, and surface measurements of trace gases, aerosols, and radionuclides. The simulated LGM climate scenarios have also been evaluated against pollen-based climate reconstruction from Bartlein et al. (2011).

Specific Comments

1. The title of the paper (and in multiple instances in the paper) is slightly misleading since the authors do no actually look at any "trends" in this manuscript, they look at three time slices and compare them. They could fix this by saying, for example "Uncertainties in isoprene photochemistry and emissions: implications for the oxidative capacity of past and present atmospheres as well as climate forcing agents" or something like that. I will highlight a few locations where they have misused the word "trend" in the manuscript, but there are likely more that I missed.

We have revised other instances in the text in which the word "trend" is used (please see the relevant comments below). The title now reads:

"Uncertainties in isoprene photochemistry and emissions: Implications for the oxidative capacity of past and present atmospheres and for climate forcing agents"

2. Pg 2199 line 6-8: The word "trend" implies a time series and this study uses time slices. I would remove the word "trend", for example "Our work focuses on changes in conditions between the LGM, preindustrial, and present day" or something like that.

This sentence now reads:

Our work focuses on two climate transitions: from the Last Glacial Maximum (LGM, 21 000 years BP) to the preindustrial (1770s); and from the preindustrial to the present day (1990s).

3. Pg 2200 ln 27: Sentence structure issue. Suggest rewording to: "Direct measurement of their past abundances is nearly impossible." And also, the authors could change 'nearly' to 'not currently'.

This sentence now reads:

However, due to the high reactivity of most atmospheric oxidants, direct measurement of their past abundances is not currently possible for most species.

As before, we then go on to discuss the uncertainties in the direct measurements of past abundances of ozone and H_2O_2.

4. Pg 2201 ln 3: the word 'but' seems out of place. Was this supposed to be 'and'?

We have amended the text:

Atmospheric oxidants, except for H_2O_2, are not directly preserved in the ice-core record. Even for H_2O_2, however, post-depositional processes impede quantitative interpretation of this record (Hutterli et al., 2002).

5. Pg 2203 ln 9: missing a space between H_2O and uptake.

Fixed.

6. Pg 2204 ln 9: Trends again.

This sentence now reads:

We also discuss the implications for changes in short-lived climate forcers and for interpreting the ice-core methane record.

7. Pg 2204 ln 10-13: This sentence claiming novelty may be true, but it seems out of place for a modeling study that is only a small expansion of a previous model. There is nothing particularly novel about this work – it is using a previously published model to look at something that is being extensively studied at time periods that are common to look at. I would suggest replacing "To our knowledge, this is the first model study to consider in a systematic manner. . ." with "Here we examine . . .".

This sentence now reads:

We examine, in a systematic manner, the effects of all of the above developments on the chemical composition of the troposphere over the last glacial-interglacial time interval and the industrial era.

8. Pg 2205 ln 16: They list ca 1990s as their "present day" and then refer to "present day" throughout the paper. I, however found "present day" to be confusing because they were comparing their model to data and models from a range of recent time periods in multiple places in the paper. It would be helpful for the reader if they could refer to the 1990s more frequently, especially when they are discussing multiple time periods. For example pg 2212, line 7 – indicate what year the CH_4 value is from. Pg 2213, lines 1-5 the authors are comparing model/data output from different time periods to their "present day" which confused me because I had forgotten what time *period that was, and I was unclear which time interval was the best to compare against their model.*

We have now clarified all instances of the use of "present day" in Section 3.2, Comparison with observations. Throughout the rest of the paper, present day refers to the 1990s as defined in our Abstract and Introduction.

(Page 2212, line 5 – Page 2213, line 11):

For methane, the global burden is calculated from the mean surface concentration using a conversion factor of 2.75 Tg CH_4 ppbv^{-1} from Prather et al. (2012). In our present-day simulations (ca. 1990s), we prescribe the mean surface concentration as 1743 ppbv. The combination of new isoprene and original HO_2 uptake chemistry (C2) has the largest simulated tropospheric mean OH burden (Fig. 2) and so yields the shortest methyl chloroform and methane lifetimes: 4.1 years and 8.9 years, respectively. Prinn et al. (2005) inferred an average methyl chloroform lifetime of $6.0^{+0.5}_{-0.4}$ years for the years 1978-2004 based on observations of methyl chloroform and knowledge of its emissions. Our model results are all lower than this range, but comparable to recent multi-model estimates of 5.7 ± 0.9 years for 2000 (Naik et al., 2013). Based on observations and emission estimates, the mean methane lifetime against loss from tropospheric OH is estimated to be $10.2^{+0.9}_{-0.7}$ years between 1978-2004 by Prinn et al. (2005), and 11.2 ± 1.3 years for 2010 by Prather et al. (2012). The values given by the C1 and C3 chemistry schemes fall within these ranges. The lowest value given by C2 does not fall within the ranges derived from observations, but is still within the range of estimates reported by recent multi-model studies for 2000-2001: 10.2 ± 1.7 years (Fiore et al., 2009), 9.8 ± 1.6 years (Voulgarakis et al., 2013) and 9.7 ± 1.5 years (Naik et al., 2013). Reconciling the magnitude of the inferred OH burden with modeled results remains an ongoing challenge (Holmes et al., 2013).

We also assess our model results for present-day OH by evaluating the simulated inter-hemispheric ratios (N/S) of tropospheric mean OH. Estimates of this ratio based on methyl chloroform measurements from 1980-2000 range between 0.85-0.98, whereas the recent ACCMIP multi-model study finds a mean ratio of 1.28 ± 0.10 for 2000 (Naik et al., 2013; and references therein). In our present-day sensitivity experiments, we calculate ratios of 1.20 for C1, 1.11 for C2, and 1.07 for C3. The C1 value falls within the ACCMIP range, but the C3 value best matches the ratio inferred from observations. Models participating in the ACCMIP study did not consider HO_x-recycling pathways through reactions of peroxy and HO_2 radicals (Naik et al., 2013). As previously described, HO_x-recycling in the absence of NO_x can occur in our new isoprene photochemistry scheme (C2), which leads to a lower present-day N/S ratio of tropospheric mean OH. The ratio decreases further and becomes more comparable with the observations when the upper limit of efficacy of HO_2 uptake by aerosols is considered (C3). This result is due to the large anthropogenic aerosol loadings in the Northern Hemisphere.

9. Pg 2205 ln 16: What is the temperature difference between preindustrial & present in their model? They say that the preindustrial is colder than the present on pg 2217, ln 21 and the temperature difference should be explicitly stated here.

Page 2205, line 15 now reads:

As in Murray et al. (2014), we perform simulations for four different climate scenarios: present day (ca. 1990s); preindustrial (ca. 1770s); and two different representations of the LGM (~19-23 kyr) to span the range of likely conditions. The simulated average global surface air temperatures are 14.9 °C for the present day, 14.3 °C for the preindustrial, 10.7 °C for the warm LGM, and 6.1 °C for the cold LGM (Murray et al., 2014, Table 4).

10. Pg 2205 ln 23-25: Earlier in this paragraph they state that they choose two different representations of the LGM that span the range of "likely conditions". I'm not aware of anyone who still thinks tropical SSTs at the LGM were -6.1 °C colder than preindustrial conditions. This would imply extremely cold temperatures elsewhere around the world that is not supported by any recent literature that I'm aware of (see IPCC AR5, chapter 5, table 5.2 for a comprehensive list). Since this is one of their 4 model conditions, I would like to see a much more robust argument for why they think this could be in the range of "likely conditions" at the LGM. This is an important issue with the experimental design of this work because later in the manuscript they calculate regression lines through all of these climatic conditions, but if this climatic condition is not realistic then it probably should not be included in those regression lines.

The Webb et al. (1997) reconstruction yields a change of global surface air temperature of -8.2 °C in our model relative to the preindustrial, at the high end of the range of temperature changes reported by Holden et al. (2010), and slightly greater than that of Gilder et al. (2014). We have amended the text as follows:

The "warm LGM" uses the SST reconstructions from the Climate: Long range Investigation, Mapping, and Prediction project (CLIMAP, 1976), with an average change in SST within 15° of the equator relative to the preindustrial ($\Delta\mathrm{SST}_{15°\mathrm{S}\text{-}°\mathrm{N}}$) of -1.2°C. The "cold LGM" uses SSTs from Webb et al. (1997) who found $\Delta\mathrm{SST}_{15°\mathrm{S}\text{-}°\mathrm{N}}$ of -6.1°C. By imposing an ocean heat transport flux in an earlier version of the GISS model, Webb et al. (1997) achieved a better match with certain paleo-proxies of temperature such as corals (Guilderson et al., 1994; Stute et al., 1995). The warm LGM SSTs yields a change of mean global surface air temperature of -3.6 °C relative to the preindustrial, while the cold LGM SSTs yields a change of -8.2 °C. These values lie within the range of temperature changes reported by Holden et al. (2010), and they span the approximately -7 °C change inferred from Gildor et al. (2014) for the LGM relative to the present day. A more recent estimate from the MARGO project found $\Delta\mathrm{SST}_{15°\mathrm{S}\text{-}°\mathrm{N}}$ of -1.7 ± 1.0 °C (Waelbroeck et al., 2009), which is more similar to the warm LGM than the cold LGM scenario used in this study.

11. Pg 2206 ln 25-pg 2207 ln 8: These two paragraphs are a little confusing & I had to read them many times to understand them, and I'm still not sure that I fully get it. The authors switch between values they find in their models to values from other studies to values they are using in their models. I think the manuscript would benefit from them providing a little more explanation in these two paragraphs, or rearranging the text in some way to increase clarity.

We thank the reviewer for pointing this out. We have revised the second paragraph and moved it to the Discussion section following Reviewer 1's comment #2. The first paragraph discusses values used in our model study, and now reads as follows (page 2206, line 25):

In this study, we follow the Tai et al. (2013) implementation, which uses the empirical relationship from Possell and Hewitt (2011). Table 1 summarizes the prescribed CO_2 mixing ratios, and the estimated total annual isoprene burdens with and without consideration of the CO_2-sensitivity of plant isoprene emissions, for each climate scenario. When the CO_2-sensitivity is considered, we find relative increases in the total biogenic isoprene source of 4% for the present day, 28% for the preindustrial, 78% for the warm LGM, and 77% for the cold LGM scenarios.

12. Pg 2207 ln 23: "Our work tests the sensitivity of the model results to these updates in the isoprene photo-oxidation mechanism." Ok, so how will the authors determine in the update provides any improvement in our understanding or a better explanation of the natural world? What data will they compare against? This should be listed here.

Model evaluation of the new isoprene photochemical mechanism can be found in Mao et al., 2013c. We have amended the text as follows (page 2207, line 12):

Here we apply recent updates to the mechanism by Mao et al. (2013c) and Paulot et al. (2009a, b), which Mao et al. (2013c) evaluated in GEOS-Chem through comparison with present-day observations of ozone, isoprene, and oxidation products.

13. Pg 2209 ln 3: Is 10 years long enough for all of their model parameters to come into equilibrium? If methane has an atmospheric lifetime of ~10 years, are sources and sinks in equilibrium at the end of 10 years? Does CH_4 change with time in the model? Regardless, the authors should have a statement addressing equilibrium conditions in the model here.

Methane does not change with time in the model. As stated on page 2215, line 22, "In GEOS-Chem, atmospheric methane concentrations are prescribed from observations – the tropospheric mean concentrations are 1743 ppbv for the present day, 732 ppbv for the preindustrial, and 377 ppbv for the LGM scenarios (Murray et al., 2014, Table 3)." The troposphere equilibrates in 1-2 years when methane is not interactive, and it is standard practice to spin up for at least one year in the GEOS-Chem CTM. One metric that we use to check for tropospheric equilibrium is convergence of the annual mean concentration of CO in the 10-year spin-up.

We now describe the model spin-up in Section 2.4 (page 2205, line 3):

For each climate scenario, we use four subsequent years of archived meteorology from the GISS climate model. Each GEOS-Chem simulation is initialized with a 10-year spinup, repeatedly using the first year of archived meteorology, to reach equilibrium with respect to stratosphere-troposphere exchange. We then perform three more years of simulations for analysis, using the three subsequent years of archived meteorology. All of the quantities considered here are global means or averages over large spatial regions. We find that the inter-annual variability of such quantities is small compared to the differences between the climate scenarios, and that three years is sufficient for our analysis.

In GEOS-Chem, atmospheric methane concentrations are prescribed with imposed meridional gradients derived from observations, except for the tropical LGM in which model results are used (Murray et al., 2014, Table 3). The tropospheric mean values are 1743 ppbv for the present day, 732 ppbv for the preindustrial, and 377 ppbv for the LGM scenarios.

14. Pg 2210 ln 1-3: This is the difference in Fig 2 between C1 and C2 curves, correct (you might mention this explicitly to help guide the reader)? I see a large difference in NO3 in the present, but there is not much difference in the past. (This is discussed in detail later, but this sentence is incorrect)

The reviewer raises a good point. The sentence now reads:

Implementation of the new isoprene oxidation mechanism leads to large changes in tropospheric oxidant burdens of OH and O_3, but not H_2O_2 and NO_3, for the past atmospheres.

15. Pg 2210 ln 3-4: Do the authors mean the uncertainty in the mechanism itself, or the differences between including the mechanism and not including it? I think they mean the latter, but wrote the former.

Fixed. The sentence now reads:

For a given climate scenario, the largest source of uncertainties in global mean OH arises from differences between the original and new isoprene photo-oxidation mechanisms.

16. Pg 2212 ln 7: What year does the CH_4 value come from? Is it from the middle of the 1990s (present day)? How is it derived? Is it an average of all of the flask measurement sites, or is it a modeled value? If it's an average of flask measurement sites, is it weighted to account for unequally spaced stations?

We now refer the reader to this information in Murray et al. (2014), Table 3. Please see comment #13.

As reported in Murray et al. (2014), our present-day methane values are from flask observations of the NOAA Global Monitoring Division database from the years 1992-1995 (http://www.esrl.noaa. gov/gmd/) (Dlugokencky et al., 2008). We use a subset of the data from stations expected to be representative of background air, and assign them into latitude bins of 30-90 °S, 0-30 °S, 0-30 °N, and 30-90 °N. Within each latitude bin, the data are averaged. The spatial variability in atmospheric methane concentrations is relatively small and unimportant when comparing globally averaged values.

17. *Pg 2212 ln 11-12: Didn't Montzka et al 2011 (DOI: 10.1126/science.1197640) show that Prinn et al 2005 had shortcomings in their assumptions about methyl chloroform emissions which led to a smaller inter-annual variability in OH? Is there*

an updated lifetime & lifetime uncertainty estimate that would provide a better comparison?

The Montzka et al. (2011) study derived a mean inter-annual variability (IAV) in OH of 2.3 ± 1.5% for the period 1998–2007. This value is much smaller than the pre-1995 mean IAV of 7-9% derived by Prinn et al. (2005) and Krol et al. (2008). Montzka et al. (2005) suggest that this difference arises because of the reduced uncertainties in the analysis of MCF data during 1998-2007 rather than a substantial reduction in the IAV of atmospheric oxidative capacity after 1997. However, the ability to capture inter-annual variability (IAV) is different from the ability to capture the mean lifetime, which is not what Montzka et al. (2011) were looking at but is what Prinn et al. (2005) were explicitly calculating.

The only updated methyl chloroform lifetime estimate we were able to find is from the supplement of Prather et al. (2012). However, we choose to use the Prinn et al. (2005) value for the following reasons. First, the Prinn et al. (2005) value is calculated for the time period 1978-2004 which is more relevant to our 1990s present-day simulation than the year 2010 from Prather et al. (2012). Second, the Prinn et al. (2005) value was estimated from a full inverse method analysis, whereas the method used by Prather et al. (2012) required assumptions to be made about the other minor loss rates of MCF. Finally, we note that the Prinn et al. (2005) value is not statistically different from the Prather et al. (2012) value: $6.0^{+0.5}_{-0.4}$ and 6.3 ± 0.4 years, respectively.

18. Pg 2212 ln 14-16: The lifetimes listed are from tropospheric OH loss, not total loss. This is stated at the beginning of the section, but I think it would be worth emphasizing again. I checked Prather et al 2012 & they list a lifetime of 9.1 +/- 0.9 years in their abstract without referring to total or OH loss. I had to dig into their supplemental information to find the correct figure that is listed here. I think it is worth helping the reader out as much as possible because this is a subtle difference.

We thank the reviewer for pointing this out. Page 2212, line 14 now reads:

Based on observations and emission estimates, the mean methane lifetime against loss from tropospheric OH is estimated to be $10.2^{+0.9}_{-0.7}$ years between 1978-2004 by Prinn et al. (2005), and 11.2 ± 1.3 years for 2010 by Prather et al. (2012).

19. Pg 2213 ln 4-5: Does their choice of the 1990s as their present day bias their result? Would it be different if they chose the 2000s? 1980s? Similarly, they report a range of observed ratios – which one is the most appropriate to compare against their model (the observations are from different time periods)? Which one of their models provides the best match with observations? The title of this section is "3.2 Comparison with observations" but they do not provide any comparisons here, they just list the observations and then list their model results hoping that the reader makes the comparisons themselves.

The focus of our work is to compare the pre- and post-Industrial decades. As seen in the ACCMIP models, there are differences between the 1980s and 2000s. We chose the 1990s as our "present day" and have consistently used input model parameters that are representative of this time period, such as the appropriate anthropogenic emission inventories.

In section 3.2, we use available and appropriate values for the inter-hemispheric OH ratio from the literature to compare to our present-day model results. We have revised this paragraph to make a more direct comparison (page 2212, line 21):

We also assess our model results for present-day OH by evaluating the simulated inter-hemispheric ratios (N/S) of tropospheric mean OH. Estimates of this ratio based on methyl chloroform measurements from 1980-2000 range between 0.85-0.98, whereas the recent ACCMIP multi-model study finds a mean ratio of 1.28 ± 0.10 for 2000 (Naik et al., 2013; and references therein). In our present-day sensitivity experiments, we calculate ratios of 1.20 for C1, 1.11 for C2, and 1.07 for C3. The C1 value falls within the ACCMIP range, but the C3 value best matches the ratio inferred from observations. Models participating in the ACCMIP study did not consider HO_x-recycling pathways through reactions of peroxy and HO_2 radicals (Naik et al., 2013). As previously described, HO_x-recycling in the absence of NO_x can occur in our new isoprene photochemistry scheme (C2), which leads to a lower present-day N/S ratio of tropospheric mean OH. The ratio decreases further and becomes more comparable with the observations when the upper limit of efficacy of HO_2 uptake by aerosols is considered (C3). This result is due to the large anthropogenic aerosol loadings in the Northern Hemisphere.

20. Pg 2213 ln 12-pg 2214 ln 2: This paragraph puzzles me. They write that ". . .CO can thus be a useful tool for evaluating the ability of chemistry transport models to simulate the tropospheric oxidative capacity. . ." but then at the end of the paragraph they write that ". . .However, in situ production of CO from organic substrates trapped within the ice may complicate the comparison between ice-core CO and model results." So, which is it? Fig 4 assumes that this comparison is robust, but then they undercut their argument. This gives me the impression that there is not robust observations that can be used to validate the model that then gives me the impression that the model is not validated.

The present-day ICECAP model was evaluated against observations in Murray et al. (2014), and we now include this information on page 2205, line 13 (please see our response under the general comments).

Regarding the CO ice-core measurements, our view is that it is wise to include caveats, when appropriate, for observations used in model evaluation. We now include the word "preindustrial" for clarification on page 2213, line 28:

However, in situ production of CO from organic substrates trapped within the ice may complicate the comparison between ice-core CO and preindustrial model results (Fain et al., 2014; Guzman et al., 2007; Haan and Raynaud, 1998).

21. Pg 2214 ln 19-24: Please add these values to Table 4 so that the reader can more easily compare observations to the model result.

We have revised Table 4 accordingly (see next page):

Table 4. Modeled percent changes in the surface $[O_3]/[OH]$ and $[O_3]/[RO_2]$ ratios for the present day relative to the preindustrial, and in the surface [OH] concentration for the warm and cold LGM relative to the preindustrial, for different model sensitivity experiments. Surface $[O_3]/[OH]$ and [OH] values are averaged over the 46-66°S latitude band to compare with values inferred from ice-core measurements of $\Delta^{17}O(SO_4^{2-})$ by Sofen *et al.* (2014) and Alexander *et al.* (2002). Surface $[O_3]/[RO_2]$ are averaged over the 34-54°S and 62.5-72.5°W (extratropical South America) to compare with values inferred from ice-core measurements of $\Delta^{17}O(NO_3^-)$ by Sofen *et al.* (2014). Observation-derived estimates are shown in the last row.

Chemistry Scheme[a]	CO_2-sensitivity of plant isoprene emissions	Present day - Preindustrial	Present day - Preindustrial	Warm LGM - Preindustrial	Cold LGM - Preindustrial
		Percent change in surface $[O_3]/[OH]$ over 46-66°S (%)	Percent change in surface $[O_3]/[RO_2]$ over S. America (%)	Percent change in surface [OH] over 46-66°S (%)	Percent change in surface [OH] over 46-66°S (%)
C1	without	35	2.3	68	87
	with	39	-0.3	105	106
C2	without	42	5.1	93	95
	with	42	2.8	105	101
C3	without	38	2.5	102	109
	with	40	-0.4	120	117
Observation-derived estimates		260	-60 to -90	40[b]	40[b]

[a] See Table 2 for a full description of the different chemistry schemes tested in this study.

[b] Percent increase in sulfate formed from gas-phase oxidation by OH

22. Pg 2214 ln 28: ". . .values ranging from 3 to 42%" this should be ". . .values ranging from 35 to 42%"

Fixed. The sentence (page 2214, line 26) now reads:

For $[O_3]/[OH]$, the signs of change are all consistent with the ice-core measurements, but our model greatly underestimates the values inferred from observations, with values ranging from 35% to 42%.

23. Pg 2214 ln 28-pg 2215 ln 2: Please also list the time intervals that the observations come from. After reading this many times I think the authors are comparing the model to the values listed at the beginning of the paragraph, but it is hard to follow. Maybe it would be clearer if the authors discussed OH observations and model and then discussed D17O(NO3) observations and models rather than mixing them together. Trying to piece this together, WAIS observations indicates that O3/OH changed by +260%, yet their modeled range is 35-42% implying a large model-data disagreement. Similarly, WAIS observations indicate the O3/RO2 changed by -60 to -90%, but their model range is -0.4 to 5.1 which is also a large model-data disagreement. Is this correct?

Yes, we indeed find large model-data disagreements for these comparisons with preindustrial observations. We have added the time intervals that the observations come from, simplified the discussion of the O_3/OH and O_3/RO_2 ratios, and revised the text according to the reviewer's suggestions:

Table 4 lists the simulated percent changes in surface $[O_3]/[OH]$ and $[O_3]/[RO_2]$ in the present day scenarios relative to their respective preindustrial scenarios. Measurements of $\Delta^{17}O(SO_4^{2-})$ from the WAIS Divide ice core imply that the $[O_3]/[OH]$ ratio in the Southern ocean MBL may have increased by 260% since the early 19th century. Our model results greatly underestimate the values inferred from observations, with values ranging from 35% to 42%. Measurements of $\Delta^{17}O(NO_3^-)$ suggest that the $[O_3]/[RO_2]$ ratio in the Southern Hemisphere extratropical troposphere may have decreased by 60-90% between the 1860s and 2000, assuming no change (≤ 5 %) in OH (Sofen et al., 2014). As with the $[O_3]/[OH]$ ratio, the model cannot capture the sensitivity of $[O_3]/[RO_2]$ to recent climate change, with changes in the ratio ranging from -0.4% to +5.1%, depending on the scenario. These mismatches may be due to deficiencies in our current understanding and model representation of remote marine boundary layer sulfate formation, as suggested by Sofen et al. (2014), and potential model underestimates of the sensitivity of oxidant abundances to climate change (Alexander and Mickley, 2015).

24. Pg 2215 ln 7-13: Confused again. The way I read this, the observations "contributed up to 40% more" and then the authors say "our simulated percent changes. . .are more comparable to the observations, with values ranging from 68-120% for the warm LGM and 87-117% for the cold LGM." The way read this, their model results do not overlap with the observations.

We have revised the text to emphasize the consistency of the model results for OH with values inferred from observations for the LGM scenarios (page 2215, line 7):

On glacial-interglacial timescales, measurements of $\Delta^{17}O(SO_4^{2-})$ from the Vostok ice core imply that gas-phase oxidation by OH contributed up to 40% more to sulfate production during the last glacial period relative to the interglacial periods before and after (Alexander et al., 2002). Our simulated percent changes in surface OH concentrations over the Southern Ocean between the LGM and preindustrial scenarios range from 68% to 120% for the warm LGM and 87% to 117% for the cold LGM scenarios (Table 4). Given the uncertainties in the model, these values are remarkably consistent with those inferred from the $\Delta^{17}O(SO_4^{2-})$ measurements, both in terms of sign and magnitude.

25. Pg 2215 ln 19: At the end of reading section "3.2 Comparison with observations" I'm wondering if any of their models provide good agreement with any observations, and also if these observations are even robust proxies to compare against in the first place.

Testing model results for the preindustrial and LGM against existing proxies is crucial, especially for quantities such as LGM OH, and we have added a summary paragraph at the end of this section:

In summary, we find that all three chemistry schemes yield present-day methyl chloroform lifetimes 24-35% shorter than that inferred from observations (Prather et al., 2012). For methane, the C1 and C3 lifetimes fall within the range inferred from observations (Prinn et al., 2005; Prather et al., 2012), while the C2 chemistry scheme yields a value 21% too short compared to the value from Prather et al. (2012). For the OH N/S ratio, the C3 chemistry falls closest to the observations (Montzka et al., 2000;

Prinn et al., 2001; Krol and Lelieveld, 2003; Bousquet et al., 2005). Compared to preindustrial ice-core measurements of CO, application of the C1 scheme with CO_2 sensitivity yields the best match, with the other scenarios underestimating CO by 16-33%. Slow, in situ production of CO in ice cores may, however, inflate the observed CO values. Isotopic signatures in sulfate and nitrate provide a means to test the preindustrial and LGM model estimates of the oxidation capacity. For example, for all scenarios, we find relatively good agreement of the modeled change in OH since the LGM compared to that derived from measured $\Delta^{17}O(SO_4^{2-})$.

We have also added a discussion of what observations may be useful for constraining the oxidative capacity of past atmospheres. Please see above under general comments.

26. Pg 2215 ln 26-27: Logical progression of the sentence. "Preindustrial to LGM" would imply a "decrease" in methane emissions, but "LGM to preindustrial" would imply an "increase" in emissions. If the logical progression is fixed, they don't need to have "at the LGM" at the end of the sentence.

Fixed. This sentence now reads:

The approximately doubled methane concentration across the LGM-to-preindustrial transition implies an increase in methane emissions or in its lifetime against oxidation, or some combination of both factors.

27. Pg 2216 discussion of CH_4 lifetimes: Something that I find to be curious about this discussion is that they are showing a fairly large range of CH_4 lifetimes across the models, but that doesn't translate to a large range in emissions. For example, take the range of lifetimes in the warm LGM of ~17 years to ~8 years (so, 8 years is ~50% of 17 years). At steady state & assuming a constant burden of CH_4 in the atmosphere, the lifetime of methane should be proportional to emissions (emissions = Burden/lifetime), ie there should be a 50% difference between the emissions in C1 with CO_2 sensitivity and C2 without CO_2 sensitivity in the central panel of Fig 5 right panels. To my eyes though, there is only a ~10% difference between them, although the scale is very coarse. There is a good chance that there is a nuance in understanding Fig 5 that I am not getting, but if that's the case I would encourage the authors to explain this a little more because it could be a common misunderstanding.

The reviewer is correct that changes in emissions should be proportional to changes in the total methane loss by OH, or inversely proportional to changes in the lifetime. However, the reviewer is misinterpreting our figures. The left panel shows the calculated methane lifetimes against oxidation by tropospheric OH. The right panels show the changes relative to each respective preindustrial scenario. Indeed, there is a ~50% difference in the implied emissions between the warm LGM C1-w and C2-wo. The values are 62 Tg CH_4 y^{-1} and 127 Tg CH_4 y^{-1}, respectively. For clarification, we now include the values associated with calculating the methane budget in a new table (Table 5, see next page).

Table 5. Global methane burden and lifetime against tropospheric oxidation by OH ($\tau_{CH_4,OH}$).

Climate	Chemistry	CO_2-sensitivity	CH_4 burden (Tg)[a]	Loss by OH in troposphere (Tg y^{-1})	$\tau_{CH_4,OH}$ (y)
Present day	C1	w	4780	465	10.3
	C2	w	4780	539	8.9
	C3	w	4780	497	9.6
Preindustrial	C1	wo	2000	184	10.9
		w	2000	165	12.1
	C2	wo	2000	238	8.4
		w	2000	230	8.7
	C3	wo	2000	223	9.0
		w	2000	214	9.4
warm LGM	C1	wo	1040	91	11.5
		w	1040	62	16.8
	C2	wo	1040	127	8.2
		w	1040	112	9.3
	C3	wo	1040	120	8.7
		w	1040	102	10.1
cold LGM	C1	wo	1040	66	15.8
		w	1040	48	21.7
	C2	wo	1040	87	11.9
		w	1040	79	13.1
	C3	wo	1040	81	12.9
		w	1040	72	14.5

[a] Global burden calculated from mean surface concentration using a conversion factor of 2.75 Tg CH4 ppbv^{-1} (Prather et al., 2012).

We have revised the text in this section to facilitate the interpretation of our results. We also made corrections to several typos for the values quoted in the text (page 2216, line 1 – page 2217, line 9):

Table 5 and the left panels of Fig. 5 show the global methane lifetimes against oxidation by tropospheric OH for each combination of climate, chemistry, and isoprene emission scenarios. In Fig. 5, the dotted orange line represents results using the “best estimate” lightning and fire emission scenarios of Murray et al. (2014). Consideration of the CO_2-sensitivity of plant isoprene emissions alone leads to large increases in the past global isoprene emissions, which in turn depress the tropospheric mean OH burden, thereby lengthening the methane lifetimes by 1.2 years for the preindustrial, 5.3 years for the warm LGM, and 5.9 years for the cold LGM. Conversely, implementation of the new isoprene photo-oxidation scheme leads to larger OH burdens, resulting in decreases in the methane lifetimes – by 1.4 years for the present day, 2.6 years for the preindustrial, 3.3 years for the warm LGM, and 3.9 years for the cold LGM. Implementation of the new HO_2 uptake scheme dampens the OH burden, which in turn slightly increases the methane lifetimes for each climate scenario.

We compare the sensitivity of changes relative to the preindustrial in the global methane lifetimes and in the implied emissions in the right panels of Fig. 5. The values shown are relative to their respective preindustrial scenarios (e.g., C1-w Present day relative to C1-w Preindustrial). Results from the "best estimate" scenarios of Murray et al. (2014) suggest that relative to the preindustrial, the global methane lifetime is reduced by 0.7 years in the present, and is increased by 0.5 years at the warm LGM. (As discussed in Sect. 2.1, comparison with paleo-observations suggests that their "low-fire, variable-lightning, warm LGM" scenario was the best representation of the LGM atmosphere.) This minimal increase in the lifetime at the LGM puts a higher burden on sources in explaining the glacial-interglacial variability of atmospheric methane concentration. Assuming no large changes occurred in the minor loss mechanisms, methane emissions scale with changes in its loss by OH in the troposphere (Table 5). As defined in section 3.2, the total loss rate of methane with respect to OH oxidation in the troposphere (Tg yr^{-1}) is calculated from the integral: $\int_{\mathrm{surface}}^{\mathrm{tropopause}} k_{\mathrm{CH_4+OH}}(T)[\mathrm{OH}][\mathrm{CH_4}]\,dx\,dy\,dz$. For their "best estimate" scenarios, Murray et al. (2014) reports that total methane emissions are 150% higher in the present relative to the preindustrial and are reduced by 50% at the warm LGM.

Consideration of the CO_2-sensitivity of plant isoprene emissions alone results in the global methane lifetime being reduced by 1.9 years in the present, and increased by 4.6 years in the warm LGM, relative to the respective preindustrial scenario. This result suggests that methane emissions are reduced by 62% at the warm LGM relative to the preindustrial, which places an even larger burden on sources than in Murray et al. (2014) in explaining the glacial-interglacial variability of atmospheric methane concentration. On the other hand, implementation of the new isoprene photo-oxidation scheme, either with or without consideration of the CO_2-sensitivity of plant isoprene emissions, results in relatively small changes in methane lifetimes across the glacial-interglacial or preindustrial-to-present day timescales. The resulting estimates of the reductions in methane emissions at the warm LGM relative to the preindustrial (between 46-62%) are consistent with the Murray et al. (2014) finding.

Also, we have added a clarifying note to the captions of Figures 3, 5-6:

"… changes in […] relative to their respective preindustrial scenarios (e.g., C1-w Present day relative to C1-w Preindustrial)."

28. The message that I took away initially after looking at Fig 5 is that regardless of which model characteristics you use, and even with a range of lifetimes, there is little variability in the magnitude of CH_4 emissions in the LGM. Is this the message that the authors wish to convey with this figure?

The main point we want to convey is that there is little variability – with respect to uncertainties in isoprene emissions and photochemistry – in the implied relative LGM-preindustrial difference in methane emissions. We have added a statement about this (page 2218, line 10):

In summary, we find little variability in the implied relative LGM-preindustrial difference in methane emissions with respect to the uncertainties in isoprene photochemistry and emissions tested in this study. However, the range of values derived from the loss of methane by OH across our sensitivity simulations exceeds the 29-42% decrease in wetland emissions simulated by the PMIP2 ensemble members (Weber et al., 2010), and the 16 and 23% decreases in natural methane emissions simulated by Kaplan et al. (2006) and Valdes (2005), respectively.

29. One suggestion is that it may make the figure easier to interpret if there were separate scales for pre-industrial, warm LGM, and cold LGM, although perhaps the authors prefer having one scale.

We thank the reviewer for the suggestion but would prefer to have one scale, so that comparisons between the four different climate scenarios can be readily made.

30. Pg 2217 ln 11: Doesn't the C1 with CO_2 sensitivity have a change of +9% relative to PI conditions (Fig 5, right panel, cold LGM)? Is this somehow excluded from the range of values presented here (-0.4 to +4.6 years), and if so why?

We had left out the word "warm" to describe LGM. This particular sentence has been removed. Please see the revised text under comment #28.

31. Pg 2217 ln 21: How much colder is the preindustrial compared to present day? This wasn't mentioned above and is important for this logical argument. Looking at Fig 6 left panels, it looks to me that the global SOA burden is actually higher in all of the models during the preindustrial compared to the present, which goes against the line of logic in this line of the manuscript.

We have now added the simulated temperature values for each climate scenario in the manuscript. (Please see comment #9.) The global SOA burden is slightly higher in the preindustrial than the present day because the total terrestrial plant VOC emissions is slightly higher in the preindustrial than the present day, even without consideration of the CO_2-sensitivity (Table 1 and Murray et al., 2014, Figure 5c).

32. Pg 2218 ln 3-6: I got really confused in this for example case, but eventually I think I figured it out. Initially I thought it referred to Fig 6B (right panels) since that figure is describing the relative change in SOA burden, which is also exactly the wording in this "for example" case. Instead I think the authors are comparing the relative change in the C1 lines in the Fig 6a between the "with" & "without" models. It would be helpful for the reader if there was a little more direction/explanation in this description. Something like this: "For example, under the C1 chemistry scheme, the relative increases in the SOA burden between the models with and without CO2 sensitivity are 24% for the preindustrial, 93% for the warm LGR, and 80% for the cold LGM scenarios as seen in the Fig 6 left panels."

We thank the reviewer for the suggestion. The revised text now reads:

For example, when the CO_2-sensitivity is considered under the C1 chemistry scheme (i.e. C1-w compared to C1-wo), the relative increases in the simulated SOA burden are 24% for the preindustrial, 93% for the warm LGM, and 80% for the cold LGM scenarios, as shown in the left panels of Fig. 6.

33. Pg 2219 ln 18: It would be useful if the authors reported the R^2 values for C2 and C3, even (especially) if they are not statistically significant.

We now report the correlation coefficient, *r,* instead of R^2, for all of the chemistry schemes. The text on page 2219, line 18 now reads:

Only the C1 data subset shows a statistically significant correlation coefficient (r = 0.87, n = 7, p<0.01); a reduced major axis regression fit is shown by the orange line in Fig. 7. The breakdown in linearity for the C2 (r = 0.36) and C3 (r = 0.34) subsets can by explained by examining the classical tropospheric NO_x-HO_x-CO-ozone chemistry, upon which the linear relationship is derived.

We also report the r values for C2 and C3 in the caption of Figure 7:

We do not find a statistically significant correlation between OH and $J_{O_3} q\, S_N / (S_C{}^{3/2})$ for the C2 (r = 0.36) and C3 (r = 0.34) subsets.

34. Pg 2220 ln 4: Technically speaking, they show n=3 in Fig 7 since Present Day is run only WITH the CO_2 sensitivity. Granted it should be nearly the same, but I think they should explicitly say this.

We understand the reviewer's concern, but the regression analysis was performed with 4 data points, using the present-day C1-w value to be representative of the C1-wo value. We now remind the reader that we did not technically perform a separate C1-wo simulation for the present-day scenario:

In this study, the only subset of simulations exhibiting a statistically significant correlation between OH and J_{O_3} is C1-wo (r = 0.98, n = 4, p = 0.02). Note that we are assuming the present-day C1-w simulation to be representative of the C1-wo scenario.

35. On another note, it strikes me that n=4 is not a very statistically meaningful sample size. In addition, technically only one of their LGM scenarios represents reality, the other one is probably too cold. The question that I'm trying to get at is, is n of 3 or 4 a large enough sample size to find a meaningful statistically significant linear relationship? If the authors had done this modeling experiment for conditions at every 1000 years between present and the LGM, that would be a much higher n, and would have much more statistical power.

We acknowledge that n=3 (or 4) is a small sample size but the small p values indicate that the correlations are unlikely due to chance.

36. Pg 2220 ln 8-10: "In Fig. 7 it can be seen that the slopes of the relationship appear to change. . ." I can't see this in the figure, and don't see anywhere that the slopes are listed in the text.

The reviewer is correct that the slopes are not explicitly shown in Figure 7. We have corrected the text as follows:

As can be seen by inspection of Fig. 7, the relationship between OH and $J_{O_3} q\, S_N / (S_C{}^{3/2})$ differs between the LGM-to-preindustrial and preindustrial-to-present day transitions for all of the three data subsets. With the present-day values excluded, we test whether the slope and intercept values are significantly different between the chemistry schemes by fitting a multiple regression model with $J_{O_3} q\, S_N / (S_C{}^{3/2})$ as a continuous explanatory variable and chemistry scheme as a categorical explanatory variable.

37. Pg 2220 ln 16-17: Isn't this already shown in Fig 2A? Or can the authors mention Fig 2A here to show that this is consistent with the results shown in Fig 2A?

Yes, the reviewer is correct that the results are consistent. We have revised the text as follows (page 2220, line 15):

The value of the intercept is largest for the C2 ensemble, followed by C3, and then C1. This sequence follows from our finding in Fig. 2, described in Section 3.1, that the new isoprene photo-oxidation mechanism leads to larger tropospheric mean OH burdens for each climate scenario compared to those simulated by the original mechanism. Implementation of the new HO_2 uptake scheme dampens this increase, but values remain above those from the C1 ensemble.

38. Pg 2221 ln 21: Did the authors leave out a word at the end of this sentence? ". . .a new photo-oxidation PATHWAY"?

Fixed. The sentence now reads:

…, and considers the effects of a new isoprene photo-oxidation mechanism (Paulot et al., 2009a, b) and a potentially larger role for heterogeneous HO_2 uptake (Mao et al., 2013a).

39. Pg 2221 ln 23-25: Again this claim of novelty seems out of place. See earlier comment.

This sentence now reads:

We perform a systematic evaluation of the sensitivity of the chemical composition of past atmospheres to these developments.

40. Pg 2223 ln 9-10: Isn't the point of this type of modeling study to identify the most likely chemistry and isoprene emission scenarios?

No, that is not the main purpose of this study because as we discuss earlier and in our paper, knowledge of the CO_2-sensitivity of isoprene emissions and the fate of its oxidation products is still evolving. Our primary goal is demonstrate how existing uncertainties in isoprene emissions and photochemistry lead to larger uncertainties in model estimates of the oxidative capacity of past atmospheres than previously acknowledged.

41. Pg 2223 ln 12: Same question as on Pg 2217 ln 11, see above.

We had left out the word "warm" to describe LGM. This particular sentence has been removed.

42. Pg 2225 ln 17-21: I don't think that the range of uncertainties in their results demonstrates the inadequacy of the current understanding of isoprene emissions and photochemistry. It seems to me that the current inadequacy in our understanding of isoprene emissions and photochemistry make it challenging (or impossible?) to constrain the oxidative capacity of the past and present atmospheres, its controlling factors, and the radiative forcing of trends in short-lived species such as SOA over time.

The reviewer raises a good point. We have substantially revised the text in this last paragraph following the reviewer's comments. Please see above under general comments.

This particular sentence now appears at the end of the abstract as follows:

This study demonstrates how inadequacies in our current understanding of isoprene emissions and photochemistry impede our ability to constrain the oxidative capacities of the present and past atmospheres, its controlling factors, and the radiative forcing of short-lived species such as SOA over time.

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Uncertainties in isoprene photochemistry and emissions: ~~implications~~ Implications for the oxidative capacity of past and present atmospheres and for ~~trends in~~ climate forcing agents

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Abstract

Isoprene and its oxidation products are major players in the oxidative chemistry of the troposphere. Current understanding of the factors controlling biogenic isoprene emissions and of the fate of isoprene oxidation products in the atmosphere has been evolving rapidly. We use a climate-biosphere-chemistry modeling framework to evaluate the sensitivity of estimates of the tropospheric oxidative capacity to uncertainties in isoprene emissions and photochemistry. Our work focuses on ~~trends across two time horizons~~two climate transitions: from the Last Glacial Maximum (LGM, 21 000 years BP) to the preindustrial (1770s); and from the preindustrial to the present day (1990s). We find that different oxidants have different sensitivities to the uncertainties tested in this study, with OH being the most sensitive: changes in the global mean OH levels for the LGM-to-preindustrial transition range between −29 % and +7 %, and those for the preindustrial-to-present day transition range between −8 % and +17 %, across our simulations. ~~Our results suggest that the observed glacial-interglacial variability in atmospheric methane concentrations is predominantly driven by changes in methane sources as opposed to changes in OH, the primary methane sink. However, the magnitudes of change are subject to uncertainties in the past isoprene global burdens, as are~~ We find little variability in the implied relative LGM-preindustrial difference in methane emissions with respect to the uncertainties tested in this study. Conversely, estimates of the ~~change~~ preindustrial-to-present day and LGM-to-preindustrial changes in the global burden of secondary organic aerosol (SOA) ~~relative to the preindustrial~~are highly sensitive. We show that the linear relationship between tropospheric mean OH and tropospheric mean ozone photolysis rates, water vapor, and total emissions of NO_x and reactive carbon – first reported in Murray et al. (2014) – does not hold across all periods with the new isoprene photochemistry mechanism. ~~Our results demonstrate that~~ This study demonstrates how inadequacies in our ~~understanding of present-day OH and its controlling factors must be addressed in order to improve model estimates of the oxidative capacity of past and present atmospheres.~~ current understanding of isoprene emissions and photochemistry impede our ability to constrain the oxidative

capacities of the present and past atmospheres, its controlling factors, and the radiative forcing of some short-lived species such as SOA over time.

1 Introduction

A key player in the coupling between climate change and atmospheric chemical composition is the oxidative capacity of the troposphere, primarily characterized by the burden of the four most abundant and reactive oxidants: OH, ozone, H_2O_2, and NO_3. Estimates of the oxidative capacity of past atmospheres remain uncertain due to the limited number of historical and paleo-observations, which hinders our ability to understand the chemical, climatic, and ecological consequences of past changes in the oxidative capacity. Multiple factors govern the abundance of tropospheric oxidants, including emissions of reactive volatile organic compounds (VOCs). Isoprene (2-methyl-1,3-butadiene, C_5H_8), primarily emitted by plants, is the most abundant VOC in the present-day atmosphere after methane (Pike and Young, 2009). Recent studies have suggested the need to revise our understanding of the environmental factors controlling biogenic isoprene emissions and of its atmospheric photo-oxidation mechanism (e.g., Paulot et al., 2009a, b; Possell and Hewitt, 2011). These advances call into question the validity of existing model estimates of the oxidative capacity of past atmospheres. In this study, we use a climate-biosphere-chemistry modeling framework (Murray et al., 2014) to explore the sensitivity of the simulated oxidative capacity to uncertainties in isoprene emissions and photochemistry, and the implications for radiative forcing on preindustrial-present and on glacial-interglacial timescales. To our knowledge, this study is the first systematic evaluation of the effects of these recent developments on model estimates of the chemical composition of past atmospheres.

The atmospheric oxidative capacity determines the lifetime of many trace gases important to climate, chemistry, and human health (e.g., Isaksen and Dalsøren, 2011; Fiore et al., 2012). It may also induce oxidative stress or alter the deposition of oxidized nutrients to terrestrial and marine ecosystem (Sitch et al., 2007; Paulot et al., 2013). Furthermore, oxidants modify the radiative effects of aerosols by influencing their evolution, lifetime, and physical properties (Sofen et al., 2011). However, due to the high reactivity of most atmospheric oxidants, direct measurement of their ~~abundance is nearly impossible for the past~~past abundances is not currently possible for most species. Late 19th-century surface ozone measurements exist but their accuracy has been debated (Pavelin et al., 1999). Atmospheric oxidants, except for H_2O_2, are not directly preserved in the ice-core record~~, but~~. Even for H_2O_2, however, post-depositional processes impede quantitative interpretation of ~~the H_2O_2~~ this record (Hutterli et al., 2002). As summarized in Murray et al. (2014), Table 1, prior modeling studies that investigated past changes in the abundance of tropospheric oxidants disagree on the magnitude and even the sign of change. Such discrepancies call into question our ability to quantify the relative roles of sources and sinks in driving past variations in atmospheric methane concentration. Previous studies attributed these variations to changes in wetland emissions, the dominant natural source of methane to the atmosphere (e.g., Khalil and Rasmussen, 1987; Brook et al., 2000). However, more recent modeling studies suggested that potential variations in OH – the primary sink for methane – may be larger than previously thought, driven by changes in biogenic VOC emissions (e.g., Kaplan, 2002; Valdes, 2005; Harder et al., 2007).

Tropospheric oxidants are strongly coupled through atmospheric photochemical reactions, and their ~~abundance responds~~ abundances respond to meteorological conditions, changes in surface and stratospheric boundary conditions, and changes in emissions of key chemical species such as reactive nitrogen oxides ($\mathrm{NO_x} = \mathrm{NO} + \mathrm{NO_2}$) and VOCs. Present-day natural emissions of VOCs, which far exceed those from anthropogenic sources on a global scale, are dominated by plant isoprene emissions, which have an estimated global source ranging from approximately 500 to 750 Tg yr^{-1} (Lathière et al., 2005; Guenther et al., 2006). This large emission burden is accompanied by high reactivity; isoprene has an atmospheric chemical lifetime on the order of minutes to hours (Pike and Young, 2009). Isoprene and its oxidation products react with OH, ozone, and the nitrate radical, and are thus major players in the oxidative chemistry of the troposphere (Beerling et al., 2007). The oxidation products of isoprene also substantially contribute to secondary organic aerosol (SOA) formation (Henze and Seinfeld, 2006). Biogenic SOA, like other aerosols, affects climate by scattering and absorbing solar radiation ~~,~~ and by altering the properties and lifetimes of clouds, but the net climate effect is poorly characterized (Scott et al., 2014). ~~Uncertainties~~ Therefore, uncertainties in the preindustrial-to-present day changes in biogenic ~~SOA burdens~~ VOC emissions, and subsequently in SOA burdens, lead to large uncertainties in the anthropogenic ~~direct and~~ indirect radiative forcing estimates over the industrial period (e.g., ~~Scott~~ Carslaw et al., ~~2014; Unger~~2013; Scott et al., 2014).

Results from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) demonstrate that uncertainties remain in our understanding of the long-term trends in OH and methane lifetime, and that these uncertainties primarily stem from a lack of adequate constraints on natural precursor emissions and on the chemical mechanisms in the current generation of chemistry-climate models (Naik et al., 2013). Recent field and laboratory findings have called into question prior estimates of global burdens of isoprene for the past and future atmospheres, and have revealed new details of the isoprene photo-oxidation mechanism. First, isoprene emission from plants is well known to be strongly dependent on plant species and, for a given species, on environmental factors including temperature, light availability, and leaf age (Guenther et al., 2012). However, recent empirical studies have shown that isoprene emission by several plant taxa is also inversely correlated with atmospheric CO_2 levels, but this relationship is not yet well-constrained (e.g., Wilkinson et al., 2009; Possell and Hewitt, 2011). The biochemical mechanism for this effect remains unresolved, but evidence suggests that CO_2 concentration plays a role in partitioning carbon-substrate availability between the chloroplast and cytosol of a plant cell, and in mobilizing stored carbon sources (Trowbridge et al., 2012). Such bio-mechanisms involving a CO_2-dependence of isoprene emissions may have evolved in plants long ago.

Second, recent field studies in major isoprene-emitting regions, such as the Amazon forest (Lelieveld et al., 2008), South East Asia (Hewitt et al., 2010), and China (Hofzumahaus et al., 2009), reported large discrepancies between measured and modeled HO_x ($OH + HO_2$) concentrations, suggesting that VOC oxidation under low-NO_x conditions may recycle OH more efficiently than previously understood. These findings motivated numerous theoretical and experimental studies, which in turn led to extensive updates in the gas-phase isoprene photo-oxidation mechanism, in which there is greater regeneration and recycling of HO_x and NO_x under high-NO_x conditions, and of HO_x under low-NO_x conditions (e.g., Paulot et al., 2009a, b). In general, greater OH-recycling enhances the efficiency of atmospheric oxidation, while greater NO_x-recycling enhances the efficiency of ozone production. However, the improved mechanism is still unable to fully reconcile measured and modeled OH concentrations (Mao et al., 2012). Moreover, global and regional modeling studies indicate that the heterogeneous HO_2 uptake by aerosols presents a potentially important HO_x sink. There remains, however, considerable uncertainty in the magnitude of this sink and its impact on tropospheric chemistry (Thornton et al., 2008). Mao et al. (2013a) proposed a new scheme in which HO_2 uptake by aerosols leads to H_2O rather than H_2O_2 formation, via coupling of Cu(I) / Cu(II) and Fe(II) / Fe(III) ions. Since H_2O_2 can be readily photolyzed to regenerate OH, this new mechanism provides a more efficient HO_x removal pathway. Cu and Fe are ubiquitous components of crustal and combustion aerosols (Mao et al., 2013a). Observations and model studies suggest that during the LGM and preindustrial, natural dust distributions were higher than that in the present day (Mahowald et al., 2006). In particular, during the LGM, Fe(II) and Fe(III) ion concentrations in dust increased by at least two times relative to interglacial levels (Spolaor et al., 2013). Likewise, positive Cu anomalies during the last glacial period have been measured in ice cores (Oyarzun et al., 2005).

In support of the ICE age Chemistry And Proxies (ICECAP) project, Murray et al. (2014) developed a new climate-biosphere-chemistry modeling framework for simulating the chemical composition of the present and past tropospheres, focusing on preindustrial-to-present and glacial-interglacial transitions. The Last Glacial Maximum (LGM, ∼ 19–23 kyr) spans the coldest interval of the last glacial period (∼ 11.5–110 kyr) and is relatively well recorded in ice-core and sediment records, making the LGM-to-preindustrial transition a convenient glacial-interglacial analogue. Disparities in existing model studies of past tropospheric oxidant levels are partly due to differences in the model components of the Earth system allowed to vary with climate, and the differing degrees of complexity in the representation of those components (Murray et al., 2014). The ICECAP project is the first 3-D model framework to consider the full suite of key factors controlling the oxidative capacity of the troposphere at and since the LGM, including the effect of changes in the stratospheric column ozone on tropospheric photolysis rates. Murray et al. (2014) found that: (1) the oxidative capacities of the preindustrial and LGM atmospheres were both lower than that of the present day; (2) tropospheric mean OH levels appear to be well buffered in the LGM-to-preindustrial transition – a result at odds with most prior studies; (3) past changes in atmospheric methane concentrations were predominantly source-driven; and (4) the key parameters controlling the oxidative capacity over LGM-present day timescales are tropospheric mean ozone photolysis rates, water vapor abundance, and total emissions of NO_x and reactive carbon.

In light of recent developments in our understanding of the isoprene photo-oxidation mechanism and of the sensitivity of plant isoprene emissions to atmospheric CO_2 levels, we build on the model study by Murray et al. (2014) to explore the sensitivity of the simulated tropospheric oxidative capacity at and since the LGM, and the ramifications for our understanding of the factors controlling the oxidative capacity. We also discuss the implications for ~~trends~~ changes in short-lived climate forcers and for interpreting the ice-core methane record. ~~To our knowledge, this is the first model study to consider,~~ We examine, in a systematic manner, the ~~effect~~ effects of all of the above developments on the chemical composition of the troposphere over the last glacial-interglacial time interval and the industrial era.

2 Method: model framework, model developments, and project description

2.1 The ICECAP model framework

Figure 1 illustrates the stepwise, offline-coupled climate-biosphere-chemistry model framework of the ICECAP project. This setup relies on four global models. GEOS-Chem is a global 3-D chemical transport model (CTM) with a long history in simulating present-day tropospheric ozone-NO_x-CO-VOC-BrO_x-aerosol chemistry (http://www.geos-chem.org; Bey et al., 2001; Park et al., 2004; Parrella et al., 2012)~~, and~~. The version used here includes online linearized stratospheric chemistry (McLinden et al., 2000), which allows for calculation of photolysis rates more consistent with changing climate and chemical conditions. We use version 9-01-03 with modifications as described in Murray et al. (2014) and below. ICECAP is driven by meteorological fields from ModelE, a climate model developed at the

NASA Goddard Institute of Space Studies (GISS). ModelE and related models at GISS have been used extensively in paleo-climate studies (e.g., LeGrande et al., 2006; Rind et al., 2001, 2009). Here we use the ModelE version with a horizontal resolution of 4° latitude by 5° longitude, and 23 vertical layers extending from the surface to 0.002 hPa in the atmosphere. Climate in ModelE is forced by prescribed greenhouse gas levels, orbital parameters, topography, and sea ice and sea surface temperatures (SSTs) relevant to each time slice of interest. The final components are the BIOME4-trace gas (BIOME4-TG) equilibrium terrestrial biosphere model (Kaplan et al., 2006) and the Lund-Potsdam-Jena Lausanne-Mainz fire (LPJ-LMfire) dynamic global vegetation model (Pfeiffer et al., 2013). BIOME4-TG is used to determine static vegetation distributions, while LPJ-LMfire simulates biomass burning regimes. Meteorology from ModelE drives both these models, and the resulting land-cover characteristics and dry matter burned are implemented into GEOS-Chem. The ~~offline-coupling approach of ICECAP allows sensitivity experiments to be performed relatively quickly. Also, by performing simulations in a stepwise manner,~~ basal biogenic emission factors per plant functional types used in the ~~chain of cause and effect can be readily diagnosed.~~BIOME4-TG model, which do not change between the climate scenarios, can be found in Murray et al. (2014), Table 5.

A detailed description of the ICECAP model framework and its evaluation against observations can be found in Murray et al. (2014). The present-day simulation has been evaluated against a suite of sonde, aircraft, satellite, and surface measurements of trace gases, aerosols, and radionuclides. The simulated LGM climate scenarios have also been evaluated against pollen-based climate reconstruction from Bartlein et al. (2011). The ICECAP model overestimates transport from the stratosphere due to an overly vigorous Brewer-Dobson circulation (Murray et al., 2014). Rather than fixing the transport fluxes to better match present-day values, we accept this bias in order to allow the stratospheric columns of ozone to adjust freely to different climate scenarios. For example, Murray et al. (2014) found that reductions in greenhouse gases weakens the stratospheric residual circulation and leads to an increase in tropical stratospheric ozone columns.

As in Murray et al. (2014), we perform simulations for four different climate scenarios: present day (ca. 1990s); preindustrial (ca. 1770s); and two different representations of the LGM (∼19–23 kyr) to span the range of likely conditions. The simulated average global surface air temperatures are 14.9 °C for the present day, 14.3 °C for the preindustrial, 10.7 °C for the warm LGM, and 6.1 °C for the cold LGM (Murray et al., 2014, Table 4). The two LGM scenarios differ in the degree of cooling of tropical SSTs. Such differences have implications for LGM dynamics because of the influence of tropical SSTs on meridional temperature gradients and low-latitude circulation (Rind et al., 2009). The "warm LGM" uses ~~the~~ SST reconstructions from the Climate: ~~long~~ Long range Investigation, Mapping, and Prediction project (CLIMAP, 1976), with an average change in SST within 15° of the equator relative to the preindustrial ($\Delta SST_{15^\circ S-^\circ N}$) of −1.2 °C. The "cold LGM" uses SSTs from Webb et al. (1997) who found $\Delta SST_{15^\circ S-^\circ N}$ of −6.1 °C~~by~~. By imposing an ocean heat transport flux in an earlier version of the GISS ~~climate model.~~ model, Webb et al. (1997) achieved a better match with certain paleo-proxies of temperature such as corals (Guilderson et al., 1994; Stute et al., 1995). The warm LGM SSTs yields a change of mean global surface air temperature of −3.6 °C relative to the preindustrial, while the cold LGM SSTs yields a change of −8.2 °C. These values lie within the range of temperature changes reported by Holden et al. (2010), and they span the approximately −7 °C change inferred from Gildor et al. (2014) for the LGM relative to the present day. A more recent estimate ~~based on SST reconstructions~~ from the MARGO project found $\Delta SST_{15^\circ S-^\circ N}$ of -1.7 ± 1.0 °C (Waelbroeck et al., 2009), which is more ~~comparable~~ similar to the warm LGM than the cold LGM scenario used in this study.

Murray et al. (2014) also tested the sensitivity of their model results to uncertainties in lightning and fire emissions. Comparison with paleo-observations suggests that their "low-fire, variable-lightning, warm LGM" scenario was the best representation of the LGM atmosphere, in which lightning NO_x emissions are parameterized to reflect changes in convective cloud top heights, and the LPJ-LMfire fire emissions are scaled to match observational records inferred from the Global Charcoal Database (Power et al., 2007, 2010). The model simulations in this study are performed using the Murray et al. (2014) "best estimate" fire and lightning emission scenarios relevant for each climate.

2.2 Uncertainties in biogenic isoprene emissions

Biogenic VOC emissions in GEOS-Chem are calculated interactively by the Model of Emissions of Gases and Aerosols from Nature (MEGAN v2.1) (Guenther et al., 2012). The canopy-level flux of isoprene is computed as a function of plant function type (PFT)-specific basal emission rate, scaled by activity factors (γ_i) to account for environmental controlling factors including temperature, light availability, leaf age, and leaf area index (LAI). Tai et al. (2013) recently implemented an additional activity factor, γ_C, to account for the effect of atmospheric CO_2 concentrations. They used the empirical relationship from Possell and Hewitt (2011): $\gamma_\mathrm{C} = a/(1+abC)$, where the fitting parameters a and b have values of 8.9406 and 0.0024 ppm^{-1}, respectively, and C represents the atmospheric CO_2 concentration ($\gamma_\mathrm{C} = 1$ at $C = 370$ ppm). To date, Possell and Hewitt (2011) studied the widest range of plant taxa and atmospheric CO_2 concentrations. Their CO_2-isoprene emission response curve shows a higher sensitivity at ~~sub-ambient~~ CO_2 concentrations below present-day levels than others from similar studies (e.g., Wilkinson et al., 2009), likely providing an upper limit of this effect for past climates. We have not considered the effect of CO_2-sensitivity on other plant VOC emissions, such as monoterpenes and sesquiterpenes, due to lack of conclusive evidence of this effect (Penuelas and Staudt, 2010). In all four climate scenarios, isoprene constitutes more than 60 % of total biogenic VOC emissions.

In this study, we follow the Tai et al. (2013) implementation, which uses the empirical relationship from Possell and Hewitt (2011). Table 1 summarizes the prescribed CO_2 mixing ratios, and the estimated total annual isoprene burdens with and without consideration of the CO_2-sensitivity of plant isoprene emissions, for each climate scenario. ~~Using the Possell and Hewitt (2011) relationship~~When the CO_2-sensitivity is considered, we find relative increases in the total biogenic isoprene source of 4 % for the present day, 28 % for the preindustrial, 78 % for the warm LGM, and 77 % for the cold LGM scenarios~~, relative to estimates that do not take into account the CO_2-sensitivity~~.

~~Previous studies, which employ different global biogenic VOC emission models and land cover products to the ones used in this study, find that biogenic VOC emissions were 20–26higher in the preindustrial relative to the present day (Pacifico et al., 2012; Unger, 2013). In this study, we estimate this value to be 8when the CO_2-sensitivity of plant isoprene emissions is not considered, and 25when the CO_2-sensitivity is considered.~~

2.3 Uncertainties in the fate of the oxidation products of isoprene

2.3.1 Isoprene photo-oxidation mechanism

Murray et al. (2014) used the original GEOS-Chem isoprene photo-oxidation mechanism which is largely based on Horowitz et al. (1998). Here we apply recent updates to the mechanism by Mao et al. (2013c) and Paulot et al. (2009a, b)~~.~~, which Mao et al. (2013c) evaluated in GEOS-Chem through comparison with present-day observations of ozone, isoprene, and oxidation products. Daytime oxidation of isoprene by OH leads to the formation of hydroxyl-peroxy radicals ($ISOPO_2$). The new scheme includes a more explicit treatment of the production and subsequent reactions of organic nitrates, acids, and epoxides from reactions of the $ISOPO_2$ radicals. Such reactions lead to greater HO_x- and NO_x-regeneration and recycling than in the original mechanism, especially under low-NO_x conditions, which is of particular relevance for past atmospheres (Mao et al., 2013c). The new scheme also includes an update for the aerosol reactive uptake coefficient of NO_3 radicals, in which the value is increased from 10^{-4} to 0.1 (Mao et al., 2013c). Beyond Mao et al. (2013c), we also change the stoichiometry of the ($ISOPO_2 + HO_2$) reaction to that recommended by the laboratory study of Liu et al. (2013), which has smaller uncertainties and leads to relatively smaller yields (by ~50 %) of HO_x, methyl vinyl ketone (MVK), and methacrolein (MACR) from this pathway. Our work tests the sensitivity of model results to these updates in the isoprene photo-oxidation mechanism.

2.3.2 Heterogeneous HO_2 uptake by aerosols

As parameterized in the standard GEOS-Chem model, gaseous HO_2 uptake by aqueous aerosols leads to H_2O_2 formation and has a $\gamma(HO_2)$ value typically less than 0.1, where $\gamma(HO_2)$ is a measure of the efficacy of uptake, defined as the fraction of HO_2 collisions with aerosol surfaces resulting in reaction. (Note that γ traditionally refers to both the aerosol uptake efficiency and biogenic emissions flux activity factor.) Atmospheric observations, however, suggest that HO_2 uptake by aerosols may in fact not produce H_2O_2 (de Reus et al., 2005; Mao et al., 2010). In light of these findings, Mao et al. (2013a) implemented a new uptake scheme in GEOS-Chem, in which HO_2 uptake yields H_2O via coupling of Cu(I) / Cu(II) and Fe(II) / Fe(III) ions, and we follow that approach here. As in Mao et al. (2013a), we use the upper limit of $\gamma(HO_2) = 1.0$ for all aerosol types to evaluate the implications of this uptake for the HO_x budgets and for the fate of the oxidation products of isoprene.

2.4 Outline of model sensitivity experiments

Table 2 summarizes the different climate, chemistry and plant isoprene emission scenarios tested in this model study. For each climate scenario, we apply to GEOS-Chem the archived meteorology and land cover products from the "best estimate" fire and lightning emission scenarios from Murray et al. (2014). We test three different chemistry schemes in GEOS-Chem: C1 uses the original isoprene chemistry and original HO_2 uptake; C2 uses the new isoprene chemistry and original HO_2 uptake; and C3 uses the new isoprene chemistry and new HO_2 uptake mechanisms. Each chemistry scheme is tested either with (w) or without (wo) inclusion of the CO_2-sensitivity of biogenic isoprene emissions, except for the present day. As Table 1 shows, consideration of the CO_2-sensitivity for the present day results in only a 4 % change in the global isoprene burden ($\gamma_C = 1$ at $C = 370$ ppm), and so we assume that the present-day model simulations with consideration of the CO_2-sensitivity of biogenic isoprene emissions are representative of their respective "without" scenarios. Our "C1-wo" model simulations match the isoprene emissions and photochemistry schemes used by Murray et al. (2014)~~in their “best estimate” scenarios~~. We perform 21 simulations in total.

For each climate scenario, we use four subsequent years of archived meteorology from the GISS climate model. Each GEOS-Chem simulation is initialized ~~over 10 years~~with a 10-year spin-up, repeatedly using the first year of archived meteorology, to reach equilibrium with respect to stratosphere-troposphere exchange. We then perform ~~3~~ three more years of simulations for analysis~~.~~, using the three subsequent years of archived meteorology. All of the quantities considered here are global means or averages over large spatial regions. We find that the inter-annual variability of such quantities is small compared to the differences between the climate scenarios, and that three years is sufficient for our analysis.

In GEOS-Chem, atmospheric methane concentrations are prescribed with imposed meridional gradients derived from observations, except for the tropical LGM in which model results are used (Murray et al., 2014, Table 3). The tropospheric mean values are 1743 ppbv for the present day, 732 ppbv for the preindustrial, and 377 ppbv for the LGM scenarios.

3 Results

3.1 Tropospheric mean oxidant burdens

Figure 2 shows the simulated tropospheric mean mass-weighted burdens of OH, ozone, H_2O_2, and NO_3 for each combination of climate, chemistry and plant isoprene emission scenarios. The dotted orange line represents results using the “best estimate” lightning and fire emission scenarios of Murray et al. (2014). The plots show the varying sensitivity of oxidant levels to assumptions about the tropospheric chemical mechanism and the global isoprene burden.

Consideration of the CO_2-sensitivity of plant isoprene emissions yields larger isoprene emissions for the preindustrial and LGM scenarios (Table 1). For a given chemistry scheme and climate scenario, this leads to a decrease in the tropospheric mean OH burden, an increase in H_2O_2, and small changes in ozone and NO_3. This result can be understood by considering the classical tropospheric ozone-HO_x-NO_x-CO catalytic cycle (e.g., Rohrer et al., 2014, Fig. 1). In general, daytime oxidation of VOC by reaction with OH leads to formation of oxidized organic products and HO_2. Efficient HO_x-cycling depends on the presence of NO_x. Since low-NO_x conditions prevail in past atmospheres, an increased isoprene burden represents a net OH sink but an HO_2 source. The self-reaction of HO_2 leads to H_2O_2 formation. Under low-NO_x conditions, tropospheric ozone production is relatively insensitive to changes in the reactive carbon burden. The tropospheric NO_3 burden also shows little change since the abundances of its precursors ($NO_2 + O_3$) hardly vary with the global isoprene burden.

Implementation of the new isoprene oxidation mechanism leads to large changes in tropospheric oxidant burdens of OH, O_3, ~~and NO_3,~~ but not H_2O_2 and NO_3, for the ~~present and~~ past atmospheres. ~~Uncertainties in the isoprene mechanism are the~~ For a given climate scenario, the largest source of uncertainties in global mean OH arises from differences between the original and new isoprene photo-oxidation mechanisms. Increases in the tropospheric mean OH burdens result from greater HO_x-regeneration in the new isoprene photo-oxidation cascade (Mao et al., 2013c). The ozone production efficiency – the number of ozone molecules produced per molecule of NO_x consumed (Liu et al., 1987) – is greater in the new isoprene mechanism, leading to increases in the tropospheric ozone burdens. This is because the newly added reactions of recycling of isoprene nitrates, formed in the ($ISOPO_2$+NO) reaction pathway, can lead to NO_x-regeneration, thereby representing a less permanent NO_x sink than nitric acid (Paulot et al., 2012). The present-day burden of NO_3 shows a large decrease in response to the new isoprene oxidation scheme, while those of the past atmospheres show little change. The muted NO_3 response for the past atmospheres is due to two competing effects in the new scheme: (1) an increased aerosol reactive uptake coefficient of NO_3 radicals (from 10^{-4} to 0.1) leading to greater NO_3 depletion (Mao et al., 2013c); and (2) increased abundances in both NO_3 precursors ($NO_2 + O_3$) enhancing its formation. The latter effect is due to greater NO_x-recycling and regeneration in the new scheme through isoprene nitrate recycling, and hence greater ozone production efficiency and increased lifetime of NO_x reservoir species. For the present-day, the increased abundances of NO_3 precursors are smaller than those of the past atmospheres. Finally, implementation of the new scheme of HO_2 uptake by aerosols leads to significant decreases in the tropospheric mean OH and H_2O_2 burdens in all simulations. This is due to both the higher efficacy of uptake than previously assumed and the formation of H_2O, instead of H_2O_2, as a by-product of the uptake, yielding a more efficient HO_x removal pathway.

Despite uncertainties in the isoprene emissions and photochemistry, we find reduced levels of ozone, H_2O_2, and NO_3 in each combination of chemistry and isoprene emission scenarios for the past atmospheres relative to the present-day, a result consistent with Murray et al. (2014). However, their conclusion that OH is relatively well buffered on glacial-interglacial timescales relative to other tropospheric oxidants does not hold for some of the uncertainties explored in this study. Figure 3 shows the simulated percent changes in the tropospheric mean OH burden for the present-day, warm LGM, and cold LGM scenarios, relative to their respective preindustrial scenarios ~~.~~ (e.g., C1-w Present day relative to C1-w Preindustrial). Consideration of the CO_2-sensitivity of plant isoprene emissions alone (C1-w) leads to 23 and 29 % reductions in the tropospheric mean OH burden in the warm and cold LGM scenarios, relative to that of the preindustrial, while the present-day burden is 17 % greater than that of the preindustrial. When the new chemistry schemes are applied without consideration of the CO_2-sensitivity, the modeled changes in OH relative to the preindustrial are less dramatic but have opposite signs to those calculated under the C1-w scenarios for the present day and warm LGM. When all effects are considered (C2-w and C3-w), changes in the tropospheric mean OH burden across the warm LGM-to-preindustrial and preindustrial-to-present day transitions do not exceed 5 %, a result consistent with Murray et al. (2014). The varying sensitivity of the tropospheric mean OH burden to assumptions about the isoprene photochemistry and emissions has implications for our understanding of past methane and SOA burdens and radiative forcing calculations, as discussed in Sects. 3.3–3.4.

3.2 Comparison with observations

We evaluate the results of the model sensitivity experiments against four different categories of observations. First, Table 3 compares the simulated methyl chloroform (CH_3CCl_3) and methane lifetimes against loss from tropospheric OH under different chemistry schemes with observations for the present day. The global lifetimes of methyl chloroform and of methane against oxidation by tropospheric OH ~~is~~ are calculated as the global burden divided by the total loss rate summed over all grid boxes in the troposphere:

$$\tau_{X,\mathrm{OH}} = \frac{\int_{\mathrm{surface}}^{\mathrm{TOA}} [X]\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z}{\int_{\mathrm{surface}}^{\mathrm{tropopause}} k_{\mathrm{X+OH}}(T)[\mathrm{OH}]\,[X]\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z}, \tag{1}$$

where X represents either methyl chloroform or methane, and $k_{X+\mathrm{OH}}(T)$ is the temperature-dependent rate constant of the reaction. We assume that the mixing ratio of methyl chloroform is uniform throughout the troposphere and is 92 % lower than the total atmospheric concentration (Bey et al., 2001; Prather et al., 2012). For methane, the global burden is calculated from the mean surface concentration ~~– prescribed as 1743ppbv for the present day –~~ using a conversion factor of 2.75 Tg CH_4 ppbv^{-1} from Prather et al. (2012). In our present-day simulations (ca. 1990s), we prescribe the mean surface concentration as 1743 ppbv.

The combination of new isoprene and original HO_2 uptake chemistry (C2) has the largest simulated tropospheric mean OH burden (Fig. 2) and so yields the shortest methyl chloroform and methane lifetimes: 4.1 and 8.9 years, respectively. Prinn et al. (2005) inferred ~~a~~ an average methyl chloroform lifetime of $6.0^{+0.5}_{-0.4}$ years ~~from~~ for the years 1978–2004 based on observations of methyl chloroform and knowledge of its emissions. Our ~~model results~~ present-day model results range between 4.1–4.8 years, which are all lower than ~~this range~~ the range derived from observations, but comparable to recent multi-model estimates of 5.7 ± 0.9 years for 2000 (Naik et al., 2013). Based on observations and emission estimates, ~~Prinn et al. (2005) derived a~~ the mean methane lifetime ~~of~~ against loss from tropospheric OH is estimated to be $10.2^{+0.9}_{-0.7}$ years between 1978–2004 ~~, and Prather~~ by Prinn et al. (~~2012)derived a methane lifetime of~~ 2005), and 11.2 ± 1.3 years for ~~2010. Although only the C1 value falls within this range, the slightly lower~~ 2010 by Prather et al. (2012). The values given by the ~~C2~~ C1 (10.3 years) and C3 ~~chemistry schemes are~~ (9.6 years) chemistry schemes fall within these ranges. The lowest value given by C2 (8.9 years) does not fall within the ranges derived from observations, but is still within the range of estimates reported by recent multi-model studies: 10.2 ± 1.7 years (Fiore et al., 2009), 9.8 ± 1.6 years (Voulgarakis et al., 2013) and 9.7 ± 1.5 years (Naik et al., 2013). Reconciling the magnitude of the inferred OH burden with modeled results remains an ongoing challenge (Holmes et al., 2013).

~~We~~ Second, we also assess our model results for present-day OH by evaluating the simulated inter-hemispheric ratios (N / S) of tropospheric mean OH. Estimates of this ratio based on methyl chloroform measurements from 1980–2000 range between 0.85–0.98 ~~,~~ (Montzka et al., 2000; Prinn et al., 2001; Krol and Lelieveld, 2003; Bousquet et al., 2005), whereas the recent ACCMIP multi-model study finds a mean ratio of 1.28 ± 0.10 for 2000 (Naik et al., 2013~~; and references therein). For the years 2004–2011, Patra et al. (2014) finds an estimate of 0.97±0.12 by optimizing model results to fit methyl chloroform measurements.~~). In our present-day sensitivity experiments, we ~~find a ratio~~ calculate ratios of 1.20 for C1, 1.11 for C2, and 1.07 for C3. The ~~models~~ C1 value falls within the ACCMIP range, but the C3 value best matches the ratio inferred from observations. Models participating in the ACCMIP study did not consider HO_x-recycling pathways through reactions of peroxy and HO_2 radicals (Naik et al., 2013). As previously described, HO_x-recycling in the absence of NO_x can occur in our new isoprene photochemistry scheme (C2), which leads to a lower present-day N / S ratio of tropospheric mean OH. The ~~decrease in this ratio is amplified~~ ratio decreases further and becomes more comparable with the observations when the upper limit of efficacy of HO_2 uptake by aerosols is considered (C3)~~, because of~~. This result is due to the large anthropogenic aerosol loadings in the Northern Hemisphere.

~~Figure 4 shows a comparison of CO surface concentrations over Antarctica between observations and our model results~~ Third, we we compare modeled CO for the preindustrial and present-day simulations ~~.~~ against observed CO surface concentrations over Antarctica (Fig. 4). CO influences the oxidative capacity of the troposphere through reaction with its primary sink, OH, which can subsequently affect the ozone budget (Fiore et al., 2012). In this context, CO can thus be a useful tool for evaluating the ability of chemistry transport models to simulate the tropospheric oxidative capacity (Haan and Raynaud, 1998). CO has a tropospheric lifetime of ∼2 months (Novelli et al., 1998), and CO surface concentrations over Antarctica are thus influenced by oxidation processes throughout much of the Southern Hemisphere (Haan and Raynaud, 1998; van der Werf et al., 2013) . The NOAA Global Monitoring Division measured a mean CO surface concentration of 49 ± 2 ppbv for the 1990s, which is matched by all of our present-day simulations tested with different chemistry schemes. Wang et al. (2010) recently provided a 650-year Antarctic ice-core record of concentration and isotopic ratios of atmospheric CO. They measured CO surface concentrations at the South Pole of 48 ± 4 ppbv for the year 1777 (±110 years). Only one (C1-w) out of the six preindustrial simulations tested with different chemistry and isoprene emission schemes falls within the range of the observed value. However, in situ production of CO from organic substrates trapped within the ice may complicate the comparison between ice-core CO and preindustrial model results (Faïn et al., 2014; Guzmán et al., 2007; Haan and Raynaud, 1998).

Finally, we compare our preindustrial and LGM model results to isotopic signatures in the ice-core record. Oxidants transfer unique isotopic signatures to the oxidation products, and we can take advantage of these signatures in our model evaluation if they are preserved in the ice-core record. The $\Delta^{17}O$ ($= \delta^{17}O - 0.52 \times \delta^{18}O$) of sulfate, known as $\Delta^{17}O(SO_4^{2-})$, and of nitrate, $\Delta^{17}O(NO_3^-)$, measure the departure from mass-dependent fractionation in its oxygen isotopes and reflect the relative importance of different oxidants in their atmospheric production pathways (Savarino et al., 2000). Sulfate formation primarily involves ozone, H_2O_2, and OH, while the main oxidants relevant to nitrate formation are ozone, RO_2 ($R = H$ atom or organic group), OH, and BrO (Sofen et al., 2014). Such oxygen triple-isotope measurements have been used to infer the atmospheric formation pathways of sulfate and nitrate in the present from atmospheric sulfate and nitrate (e.g. Lee et al., 2001; Michalski, 2003), and in the past from ice-core sulfate and nitrate (e.g., Alexander et al., 2002, 2004). The dominant source region for Antarctic sulfate is the Southern Ocean marine boundary layer (MBL) (Sofen et al., 2011), while that for Antarctic nitrate is extra-tropical South America (Lee et al., 2014). We thus qualitatively compare our model results for these respective regions with Antarctic ice-core measurements of $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$.

Table 4 lists the simulated percent changes in surface $[O_3]/[OH]$ and $[O_3]/[RO_2]$ in the present day scenarios relative to their respective preindustrial scenarios. Measurements of $\Delta^{17}O(SO_4^{2-})$ from the WAIS Divide ice core imply that the $[O_3]/[OH]$ ratio in the Southern ocean MBL may have increased by 260 % since the early 19th century~~, while measurements~~. Our model results greatly underestimate the values inferred from observations, with values ranging from 35 % to 42 %. Measurements of $\Delta^{17}O(NO_3^-)$ suggest that the $[O_3]$~~/~~/$[RO_2]$ ratio in the Southern Hemisphere extratropical troposphere may have decreased by ~~60–90~~60-90 % between the 1860s and 2000, assuming no change ($\leq$ 5 %) in OH (Sofen et al., 2014). ~~Table 4 lists the simulated percent changes in surface~~ As with the $[O_3]/[OH]$ ~~and~~ ratio, the model cannot capture the sensitivity of $[O_3]$~~/RO_2 in the present day scenarios relative to their respective preindustrial scenarios. For O_3 /, the signs of changeare all consistent with the ice-core measurements, but our model greatly underestimates the values inferred from observations, with values ranging from 3 to 42. Our model also underestimates the changes in O_3/~~ $[RO_2]$ ~~compared to observations. Our modeled increase (5–10~~to recent climate change, with changes in the ratio ranging from -0.4 % ~~) in OH abundance in the extra-tropical South American boundary layer in the present day would further lower $\Delta^{17}O(NO_3^-)$, which is qualitatively consistent with the observations. However, accounting for both modeled decreases in O_3/and OHstill underestimates the observed decrease in $\Delta^{17}O(NO_3^-)$ by 75–85~~to $+5.1$ %~~.~~, depending on the scenario. These mismatches may be due to deficiencies in our current understanding and model representation of remote marine boundary layer sulfate formation~~and of nitrate~~

~~formation~~, as suggested by Sofen et al. (2014)~~.~~, and potential model underestimates of the sensitivity of oxidant abundances to climate change (Alexander and Mickley, 2015).

On glacial-interglacial timescales, measurements of ~~Δ^{17}~~Δ^{17}O(SO_4^{2-}) from the Vostok ice core imply that gas-phase oxidation by OH contributed up to 40 % more to sulfate production during the last glacial period relative to the interglacial periods before and after (Alexander et al., 2002). ~~Here our~~ Our simulated percent changes in surface OH concentrations over the Southern Ocean between the LGM and preindustrial scenarios ~~are more comparable to the observations, with values ranging~~ range from 68 % to 120 % for the warm LGM and 87 % to 117 % for the cold LGM scenarios (Table 4). ~~Ongoing measurements of the Δ^{17}O in ice-core sulfate and nitrate over the last glacial-interglacial cycle will allow for further modelevaluation. Measurements of Δ^{17}O(NO_3^-) may in fact be a more robust proxy than those of~~ Given the uncertainties in the model, these values are remarkably consistent with those inferred from the Δ^{17}O(SO_4^{2-}) ~~for reconstructing the oxidation capacity of past atmospheres because of its greater sensitivity to oxidant abundances. For example, cloud amount and pH do not influence the isotopic composition of nitrate as they do for sulfate (Levine~~ measurements, both in terms of sign and magnitude.

In summary, we find that all three chemistry schemes yield present-day methyl chloroform lifetimes 24–35 % shorter than that inferred from observations (Prather et al., 2012). For methane, the C1 and C3 lifetimes fall within the range inferred from observations (Prinn et al., ~~2011)~~2005; Prather et al., 2012), while the C2 chemistry scheme yields a value 21 % too short compared to the value from Prather et al. (2012). For the OH N / S ratio, the C3 chemistry falls closest to the observations (Montzka et al., 2000; Prinn et al., 2001; Krol and Lelieveld, 2003; Bousquet et al., 2005). Compared to preindustrial ice-core measurements of CO, application of the C1 scheme with CO_2 sensitivity yields the best match, with the other scenarios underestimating CO by 16-33 %. Slow, in situ production of CO in ice cores may, however, inflate the observed CO values. Isotopic signatures in sulfate and nitrate provide a means to test the preindustrial and LGM model estimates of the oxidation capacity. For example, for all scenarios, we find relatively good agreement of the modeled change in OH since the LGM compared to that derived from measured Δ^{17}O(SO_4^{2-}).

3.3 Implications for the methane budget

The global methane lifetime against oxidation by tropospheric OH, $\tau_{\mathrm{CH_4,OH}}$, is calculated as defined by Eq. (1). In GEOS-Chem, atmospheric methane concentrations are prescribed from observations – the tropospheric mean concentrations are 1743 ppbv for the present day, ~~731~~732 ppbv for the preindustrial, and 377 ppbv for the LGM scenarios (Murray et al., 2014, Table 3). The approximately doubled methane concentration across the LGM-to-preindustrial transition implies ~~a decrease~~ an increase in methane emissions or in its lifetime against oxidation, or some combination of both factors~~, at the LGM~~.

~~The~~ Table 5 and the left panels of Fig. 5 show the global methane lifetimes against oxidation by tropospheric OH for each combination of climate, chemistry, and isoprene emission scenarios. ~~The~~ In Fig. 5, the dotted orange line represents results using the "best estimate" lightning and fire emission scenarios of Murray et al. (2014). Consideration of the CO_2-sensitivity of plant isoprene emissions alone leads to large increases in the past global isoprene emissions, which in turn depress the tropospheric mean OH burden, thereby lengthening the methane lifetimes by 1.2 years for the preindustrial, ~~5.4~~5.3 years for the warm LGM, and ~~5.8~~5.9 years for the cold LGM. Conversely, implementation of the new isoprene photo-oxidation scheme leads to larger OH burdens, resulting in decreases in the methane lifetimes – by 1.4 years for the present day, 2.6 years for the preindustrial, ~~3.2~~3.3 years for the warm LGM, and ~~4.0~~3.9 years for the cold LGM. Implementation of the new HO_2 uptake scheme dampens the OH burden, which in turn slightly increases the methane lifetimes for each climate scenario.

We compare the sensitivity of ~~the changes~~ changes relative to the preindustrial in the global methane lifetimes and in the implied emissions ~~relative to the preindustrial~~ in the right panels of Fig. 5. The values shown are relative to their respective preindustrial scenarios (e.g., C1-w Present day relative to C1-w Preindustrial). Results from the "best estimate" scenarios of Murray et al. (2014) suggest that relative to the preindustrial, the global methane lifetime is reduced by 0.7 years in the present, and is increased by ~~0.4~~0.5 years at the ~~LGM.~~ warm LGM. (As discussed in Sect. 2.1, comparison with paleo-observations suggests that their “low-fire, variable-lightning, warm LGM” scenario was the best representation of the LGM atmosphere.) This minimal increase in the lifetime at the LGM puts a higher burden on sources in explaining the glacial-interglacial variability of atmospheric methane concentration. Assuming no large changes occurred in the minor loss mechanisms, methane emissions scale with changes in its loss by OH in the troposphere (Table 5). As defined in Sect. 3.2, the total loss rate of methane with respect to OH oxidation in the troposphere ($\mathrm{Tg\,yr^{-1}}$) is calculated from the integral: $\int_{\text{surface}}^{\text{tropopause}} k_{\mathrm{CH_4+OH}}(T)[\mathrm{OH}]\,[\mathrm{CH_4}]\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$. For their “best estimate” scenarios, Murray et al. (2014) reports that total methane emissions are 150 % higher in the present relative to the preindustrial and are reduced by 50 % at the ~~LGM. In our study, consideration~~ warm LGM.

Consideration of the CO_2-sensitivity of plant isoprene emissions alone ~~shortens the methane lifetime~~ results in the global methane lifetime being reduced by 1.9 years in the present~~relative to the preindustrial, and lengthens it~~, and increased by 4.6 years ~~at the LGM~~in the warm LGM, relative to the respective preindustrial scenario. This result suggests that methane emissions are reduced by ~~63~~62 % at the warm LGM relative to the preindustrial, which places an even larger burden on sources than in Murray et al. (2014) in explaining the glacial-interglacial variability of atmospheric methane concentration. On the other hand, implementation of the new isoprene photo-oxidation scheme, either with or without consideration of the CO_2-sensitivity of plant isoprene emissions, results in relatively small changes in methane lifetimes across the glacial-interglacial or preindustrial-to-present day timescales. The resulting estimates of the reductions in methane emissions at the warm LGM relative to the preindustrial (between ~~46–52~~46–62 %) are consistent with the Murray et al. (2014) ~~finding~~“best estimate” of 50 %.

In summary, ~~the calculated change in global methane lifetime at the LGM relative to the preindustrial ranges between −0.4 to +4.6 years across our ensemble of sensitivity simulations. This range implies a reduction~~ we find little variability in the implied relative LGM-preindustrial difference in methane emissions ~~greater than or comparable to the estimated value of 50by Murray et al. (2014) in their “best estimate” scenario. Our estimates~~

~~are also greater than the~~ with respect to the uncertainties in isoprene photochemistry and emissions tested in this study. However, the range of values derived from the loss of methane by OH across our sensitivity simulations exceeds the 29–42 % decrease in wetland emissions simulated by the PMIP2 ensemble members (Weber et al., 2010), and the 16 and 23 % decreases in natural methane emissions simulated by Kaplan et al. (2006) and Valdes (2005), respectively.

3.4 Implications for SOA burdens and radiative forcing

Isoprene oxidation products substantially contribute to SOA formation (Henze and Seinfeld, 2006), and so our results have implications for ~~trends in SOA burden and radiative forcing~~past changes in SOA burdens. Increasingly cooler global temperatures relative to the present day in the preindustrial, warm LGM, and cold LGM scenarios are expected to decrease biogenic isoprene emissions. However, such reductions are dampened or offset when the sensitivity to atmospheric CO_2 is also considered, since biogenic isoprene emissions are enhanced at CO_2 concentrations below present-day levels. The left panel of Fig. 6 shows the global SOA burdens for each combination of climate, chemistry, and isoprene emission scenarios. The dotted orange line represents results using the "best estimate" lightning and fire emission scenarios of Murray et al. (2014). Consideration of the CO_2-sensitivity of plant isoprene emissions alone leads to large increases in the past global isoprene burdens, which subsequently increases SOA at the preindustrial and LGM. For example, when the CO_2-sensitivity is considered under the C1 chemistry scheme (i.e. C1-w compared to C1-wo), the relative increases in the simulated SOA burden are 24 % for the preindustrial, 93 % for the warm LGM, and 80 % for the cold LGM ~~scenario when the CO_2-sensitivity of plant isoprene emissions is considered compared to the cases when it is not.~~scenarios , as shown in the left panels of Fig. 6. Conversely, for a given isoprene emission scenario, changes to the isoprene photo-oxidation and HO_2 uptake schemes lead to much smaller changes in the SOA burdens in each climate scenario.

The right panel of Fig. 6 shows the percent changes in tropospheric mean SOA burdens relative to their respective preindustrial scenarios ~~.~~ (e.g., C1-w Present day relative to C1-w

Preindustrial). The "best estimate" scenarios of Murray et al. (2014) – represented by our "C1-wo" simulations – suggest that relative to the preindustrial, the total SOA burden is 5 % lower in the present, 42 % lower at the warm LGM, and 50 % lower at the cold LGM. These values, while relatively robust to variations in the isoprene photo-oxidation and HO_2 uptake schemes, are sensitive to estimates of the global isoprene burdens for the past atmospheres; consideration of the CO_2-sensitivity of plant isoprene emissions enhances the present-to-preindustrial difference but reduces the LGM-to-preindustrial differences in the global SOA burden. For example, under the C1 chemistry scheme, consideration of the CO_2-sensitivity of plant isoprene emissions leads to decreases of 23 % in the total SOA burden in the present, but only of 10 and 28 % in the warm and cold LGM scenarios, relative to the preindustrial.

3.5 Implications for tropospheric ozone and radiative forcing

Isoprene and its oxidation products influence the formation and loss of tropospheric ozone (Beerling et al., 2007). As in Murray et al. (2014), we find decreasing tropospheric mean ozone burdens in each progressively colder scenario for each combination of isoprene photochemistry and emissions scenarios. The "best estimate" scenarios of Murray et al. (2014) – represented by our "C1-wo" simulations – suggest that relative to the preindustrial, the tropospheric mean ozone burden is 33 % higher in the present, 27 % lower at the warm LGM, and 19 % lower at the cold LGM. These values do not vary more than 8 % for the present day and 5 % for the LGM when the isoprene photochemistry and/or emission schemes are varied.

We can estimate what these changes imply in terms of radiative forcing from tropospheric ozone using the relationship of 0.042 $W\,m^{-2}$ per DU change in the mean tropospheric column ozone (Stevenson et al., 2013). Averaging across our sensitivity simulations, changes in the mean tropospheric column ozone relative to their respective preindustrial scenarios lead to forcing contributions of $+0.3\,W\,m^{-2}$ for the present day, $-0.3\,W\,m^{-2}$ for the warm LGM, and $-0.2\,W\,m^{-2}$ for the cold LGM, relative to the preindustrial.

Using the multi-model estimate of 0.042 W m^{-2} per DU change in the mean tropospheric column ozone across the preindustrial-present day transition (Stevenson et al., 2013), we estimate that across our sensitivity simulations, changes in the mean tropospheric column ozone relative to their respective preindustrial scenarios lead to forcing contributions of $+0.3$ W m^{-2} for the present day. If we extrapolate this relationship to the LGM-preindustrial transition, we estimate values of -0.3 W m^{-2} for the warm LGM and -0.2 W m^{-2} for the cold LGM. However, accurate quantification of the tropospheric ozone forcing at the LGM relative to the preindustrial would require the use of an online radiative transfer model that convolves changes in the ozone distribution with other radiatively active climate processes.

3.6 Factors controlling variability in the tropospheric oxidative capacity

Murray et al. (2014) identified the key parameters that appear to control global mean OH levels on glacial-interglacial timescales. In this section, we explore the robustness of their result to the uncertainties in isoprene photochemistry and emissions tested in this study. Using the steady-state equations of the ozone-NO$_x$-HO$_x$-CO system, Wang and Jacob (1998) derived a linear relationship between the global mean OH burden and the ratio $S_\mathrm{N}/\left(S_\mathrm{C}^{3/2}\right)$, where S_N and S_C are the tropospheric sources of reactive nitrogen (Tmol N yr^{-1}) and of reactive carbon (Tmol C yr^{-1}), respectively. Murray et al. (2014) found that on glacial-interglacial timescales, the linear relationship can be maintained if two additional factors, which Wang and Jacob (1998) had assumed constant in their derivation, are also considered: (1) the mean tropospheric ozone photolysis frequency, $J_{\mathrm{O_3}}$ (s^{-1}) and (2) the tropospheric water vapor concentration, represented by the specific humidity, q (g H$_2$O kg air^{-1}). In other words,

$$[\mathrm{OH}] \propto J_{\mathrm{O_3}}\, q\, S_\mathrm{N}/\left(S_\mathrm{C}^{3/2}\right) \qquad (2)$$

Figure 7 shows a plot of the tropospheric mean OH burden for each simulation as a function of $J_{\mathrm{O_3}}\, q\, S_\mathrm{N}/\left(S_\mathrm{C}^{3/2}\right)$, divided into panels according to the chemistry scheme. As in Murray et al. (2014), S_C is calculated as the sum of emissions of CO and NMVOCs and an implied source of methane equal to its loss rate by OH. While Murray et al. (2014) assumed that each molecule of isoprene yields an average 2.5 carbons that go on to react in the gas phase, this assumption has been found to not be robust for different isoprene oxidation schemes, and so we assume that each isoprene molecule undergoes 100 % gas-phase oxidation for all of the three chemistry schemes tested in this study.

Only the C1 data subset shows a statistically significant correlation coefficient ($r = 0.87$, $n = 7$, $p < 0.01$); a reduced major axis regression fit is shown by the orange line ~~(~~in Fig. ~~7).~~ 7. The breakdown in linearity for the C2 ($r = 0.36$) and C3 ($r = 0.34$) subsets can by explained by examining the classical tropospheric NO_x-HO_x-CO-ozone chemistry, upon which the linear relationship is derived. In this classical chemistry system, HO_x-cycling is coupled to NO_x-cycling. However, the new isoprene photo-oxidation mechanism includes additional pathways for HO_x-regeneration and recycling in the absence of NO_x. The new mechanism thus permits HO_x-cycling to occur without subsequent production of ozone through NO_2 photolysis, thereby weakening the sensitivity of OH to each of the individual components of $J_{\mathrm{O_3}}\,q\,S_\mathrm{N}/\left(S_\mathrm{C}^{3/2}\right)$. For example, Murray et al. (2014) found that the global mean OH independently varied weakly but most strongly with the photolysis component ($J_{\mathrm{O_3}}$) in their simulations. In this study, the only subset of simulations exhibiting a statistically significant correlation between OH and $J_{\mathrm{O_3}}$ is C1-wo (~~$R^2 = 0.99$~~$r = 0.98$, $n = 4$~~).~~ , $p = 0.02$). Note that we are assuming the present-day C1-w simulation to be representative of the C1-wo scenario. This scheme employs the original isoprene and HO_2 uptake schemes without consideration of the CO_2-sensitivity of plant isoprene emissions – i.e., the same as that used by Murray et al. (2014).

~~In~~ As can be seen by inspection of Fig. 7, ~~it can be seen that the slopes of the relationship appear to change between~~ the relationship between OH and $J_{\mathrm{O_3}}\,q\,S_\mathrm{N}/\left(S_\mathrm{C}^{3/2}\right)$ differs between the LGM-to-preindustrial and preindustrial-to-present day transitions for all of the three data subsets. ~~We~~ With the present-day values excluded, we test whether the slope and intercept values are significantly different between the chemistry schemes by fitting a multiple regression model with $J_{\mathrm{O_3}} q S_{\mathrm{N}} / \left(S_{\mathrm{C}}^{3/2}\right)$ as a continuous explanatory variable and chemistry scheme as a categorical explanatory variable. We find that the three correlations have different values for the intercepts whereas the values for the slopes do not significantly differ (Fig. 7, dashed grey lines). The value of the intercept is largest for the C2 ensemble, followed by C3, and then C1~~, indicating that mean OH is sensitive to the chemistry scheme used~~. This sequence follows from our finding in Fig. 2, described in Section 3.1, that the new isoprene photo-oxidation mechanism leads to larger tropospheric mean OH burdens for each climate scenario compared to those simulated by the original mechanism. Implementation of the new $\mathrm{HO_2}$ uptake scheme dampens this increase, but values remain above those from the C1 ensemble~~(Sect. 3.1).~~. We postulate two main reasons why the slope of OH to $J_{\mathrm{O_3}} q S_{\mathrm{N}} / \left(S_{\mathrm{C}}^{3/2}\right)$ appears to be lower across the industrial era than across the glacial-interglacial period. First, it is likely that heterogeneous reactions that can also act as $\mathrm{HO_x}$ sinks but are not considered in the derivation of the linear relationship, such as $\mathrm{N_2O_5}$ hydrolysis and $\mathrm{HO_2}$ uptake by aerosols, become more important under present-day conditions. In the present day, tropospheric aerosol mass loading is 17–20 % higher than the preindustrial, and 36–52 % higher than the warm and cold LGM scenarios. Second, there is a dramatic shift in the altitudinal distribution of tropospheric $\mathrm{NO_x}$ emissions. The ratio of lightning to surface $\mathrm{NO_x}$ emissions is 0.16 for the present day, 0.50 for the preindustrial, 0.73 for the warm LGM, and 0.79 for the cold LGM. The much lower present-day ratio is primarily due to large anthropogenic surface $\mathrm{NO_x}$ emissions, especially in the Northern Hemisphere (Murray et al., 2014, Fig. 5). This could lead to relatively more efficient $\mathrm{NO_x}$ removal by wet and dry deposition, and by formation of organic nitrates, which would both reduce primary and secondary OH production. However, these hypotheses need to be examined in greater detail, and an evaluation of potential weaknesses of the linear relationship between OH and $J_{\mathrm{O_3}} q S_{\mathrm{N}} / \left(S_{\mathrm{C}}^{3/2}\right)$ that operate independently of the classic photo-oxidation mechanism is described by Murray et al. (2015).

4 Discussion and conclusions

Using a detailed climate-biosphere-chemistry framework, we evaluate the sensitivity of modeled tropospheric oxidant levels to recent advances in our understanding of biogenic isoprene emissions and of the fate of isoprene oxidation products in the atmosphere. We focus on this sensitivity for the present day (ca. 1990s), preindustrial (ca. 1770s), and the Last Glacial Maximum (LGM, ∼19–23 kyr). The 3-D global ICECAP model employed here considers the full suite of key factors controlling the oxidative capacity of the troposphere, including the effect of changes in the stratospheric column ozone on tropospheric photolysis rates (Murray et al., 2014). Our study, which revisits Murray et al. (2014), takes into account the sensitivity of plant isoprene emissions to atmospheric CO_2 levels, and considers the effects of a new isoprene photo-oxidation mechanism (Paulot et al., 2009a, b) and a potentially larger role for heterogeneous HO_2 uptake Mao et al., 2013a). ~~To our knowledge, this is the first model study to~~ We perform a systematic evaluation of the sensitivity of the chemical composition of past atmospheres to these developments.

We simulate two possible realizations of the LGM, one significantly colder than the other, to bound the range of uncertainty in the extent of tropical cooling at the LGM. For each climate scenario, we test three different chemistry schemes: C1, the original isoprene chemistry and original HO_2 uptake; C2, the new isoprene chemistry and original HO_2 uptake; and C3, the new isoprene chemistry and new HO_2 uptake mechanisms. Each chemistry scheme is tested with or without inclusion of the CO_2-sensitivity of biogenic isoprene emissions, except for the present day for which consideration of the CO_2-sensitivity results in only a 4 % change in the global isoprene burden. We find that consideration of the CO_2-sensitivity of biogenic emissions enhances plant isoprene emissions by 27 % in the preindustrial and by 77–78 % at the LGM, relative to respective estimates that do not take into account the CO_2-sensitivity. This implementation increases global isoprene emissions in the warm LGM scenario by 15 % relative to the preindustrial. At the LGM, lower sea levels expose extensive land area in equatorial Asia and Australia, which leads, in turn, to large regional increases in plant isoprene emissions (Murray et al., 2014, Figure 7). When we account for the potential increase in biogenic isoprene emissions at low CO_2 concentrations, this implementation swamps the effect of cooler temperatures in the warm LGM scenario.

We find that different oxidants have varying sensitivity to the assumptions tested in this study, with OH being the most sensitive. Although Murray et al. (2014) estimated that OH is relatively well buffered on glacial-interglacial timescales, we find that this result is not robust to all of the assumptions tested in this study, especially with respect to uncertainties in the isoprene photo-oxidation mechanism. Changes in the global mean OH levels for the LGM-to-preindustrial transition range between -29 and $+7\,\%$, and those for the preindustrial-to-present day transition range between -8 and $+17\,\%$, across our sensitivity simulations. However, consistent with Murray et al. (2014), we find reduced levels of ozone, H_2O_2, and NO_3 for the past atmospheres relative to the present-day in our ensemble of sensitivity simulations. That study also reported a linear relationship between OH and tropospheric mean ozone photolysis rates, water vapor, and total emissions of NO_x and reactive carbon ($J_{\mathrm{O_3}}\,q\,S_{\mathrm{N}}/\left(S_{\mathrm{C}}^{3/2}\right)$) on LGM-to-present day timescales. We find that the new isoprene photo-oxidation mechanism causes a breakdown in this linear relationship across the entire period, as the new mechanism permits HO_x-cycling to occur without subsequent production of ozone through NO_2 photolysis, thereby weakening the feedback on OH production per RO_2 consumed. We propose that the sensitivity of OH to changes in $J_{\mathrm{O_3}}\,q\,S_{\mathrm{N}}/\left(S_{\mathrm{C}}^{3/2}\right)$ may be lower for the preindustrial-to-present day than the LGM-to-preindustrial transition. This is most likely because NO_x and HO_x loss processes not considered in the classical NO_x-HO_x-CO-ozone system (from which the linear relationship is derived) become more important under present-day conditions. ~~All of our sensitivity experiments are broadly consistent with ice-core records of $\Delta^{17}O$ of sulfate and nitrate at the LGM and of CO in the preindustrial. For the present-day, the C1 chemistry scheme shows the best agreement with observation-based estimates of methane and methyl chloroform lifetimes, whereas C3 shows the best agreement with observation-based estimates of the inter-hemispheric (N/S) ratio of tropospheric mean OH. Thus, it is challenging to identify the most likely chemistry and isoprene emission scenarios.~~

~~We find that the calculated change in global methane lifetime at the~~ We find little variability in the implied relative LGM-preindustrial difference in methane emissions with respect to the uncertainties in isoprene photochemistry and emissions tested in this study. The resulting estimates of the reductions in methane emissions at the warm LGM relative to the preindustrial ~~ranges between −0.4 to +4.6 years across our ensemble of sensitivity simulations. This range implies a reduction in methane emissions greater than or~~ (between 46–62 %) are comparable to the ~~best estimate value of 50by~~ Murray et al. (2014) ~~, which corroborates their finding that the observed glacial-interglacial variability in atmospheric methane is predominantly driven by changes in its sources as opposed to its sink with OH.~~ "best estimate" of 50 %. However, the range of our implied values exceed those derived from prior model studies of wetland emission changes (Valdes et al., 2005; Kaplan et al., 2006; Weber et al. 2010). Our findings also have implications for radiative forcing estimates of SOA on preindustrial-present and glacial-interglacial timescales. For example, the "best estimate" scenarios of Murray et al. (2014) suggest that relative to the preindustrial, the total SOA burden is 5 % lower in the present and 42 % lower at the LGM. Here, we find decreases ranging between 2–23 % in the present and 10–44 % at the LGM relative to the preindustrial across our sensitivity experiments. The climate effects of biogenic SOA are not well characterized, but are thought to provide regional cooling (Scott et al., 2014). Our work thus suggests that SOA reductions may have amplified regional warming in the present but minimized regional cooling at the LGM, relative to the preindustrial. Results from ~~the~~ this sensitivity studies, however, underscore the large uncertainties in current model estimates of SOA radiative forcing across long time scales (e.g., Scott et al., 2014; Unger and Yue, 2014; Unger, ~~2014).~~

~~Unger (2014) recently quantified the~~ 2014a). Unlike SOA, we find that changes in tropospheric mean ozone burdens relative to the preindustrial are insensitive to the uncertainties in isoprene emissions and photochemistry tested in this study. Relative to the preindustrial, the absolute magnitude of the radiative forcing from ~~global cropland expansion between the 1850s and 2000s, with a focus on~~ the change in tropospheric ozone at the LGM may be comparable to that of the present day. However, most climate simulations of the LGM still use preindustrial ozone values as boundary conditions, including this study and the Paleoclimate Modelling Intercomparison Project 2 (PMIP2, Braconnot et al., 2012). Accurate quantification of the tropospheric ozone forcing at the LGM relative to the preindustrial requires the use of an online radiative transfer model that convolves changes in the ozone distribution with other radiatively active climate processes.

Besides SOA, changes in biogenic VOC emissions ~~, which influence preindustrial-to-present day changes in~~ also affect the atmospheric concentrations of other climate forcing agents. Recent studies have demonstrated the importance of considering the net effect of human-induced changes in biogenic VOC emissions on global climate forcing over the industrial period (e.g., Unger, 2014a, b; Heald et al., 2014; Heald and Spracklen, 2015). Unger (2014a) quantified the global radiative impact of changes to the atmospheric concentrations of ozone, methane, and ~~biogenic SOA burdens. She found~~ SOA due to a reduction in the emission of biogenic VOCs resulting from global cropland expansion between the 1850s and 2000s. She estimated a net cooling of $-0.11 \pm 0.17\,\mathrm{W\,m^{-2}}$~~due to changing biogenic VOC emissions from global land use changes~~, which is comparable in magnitude but opposite in sign to the net forcing from the changes in surface albedo and land carbon release associated with cropland expansion. ~~Our work demonstrates that besides changes in land use, changes in environmental factors controlling~~ When other known anthropogenic influences on biogenic VOC emissions ~~should also be included in calculations of the net radiative forcing . For example, Unger (2014)reported a decrease in biogenic VOC emissions of 37due to expanding cropland, but did not include the effects of meteorological variables or~~ are also considered, the net global climate forcing is estimated to be $-0.17\,\mathrm{W\,m^{-2}}$ (Unger 2014b). Our work demonstrates that reducing the uncertainties on such an estimate will require improvements in our knowledge of isoprene photochemistry and CO_2-sensitivity~~on such emissions. In our study,~~ , as well as reconciling model estimates of land cover change over the industrial period.

We find that biogenic VOC emissions decrease by ~~just~~ 8 % in the present day relative to the preindustrial due to changing meteorology~~and land use change~~, redistribution of natural vegetation, and cropland expansion, and by 25 % when the CO_2-sensitivity of isoprene emissions is also considered. The larger reduction is comparable to results from previous studies that have estimated a 20-26 % reduction in biogenic VOC emissions from the late 19th century to the present day (Lathiere et al., 2010; Pacifico et al., 2012; Unger, 2013). Consistent with our study, Lathiere et al. (2010) determined that the CO_2-sensitivity effect dominates the change in isoprene emissions between 1901-2002, with the impact of land use change about half that of CO_2-sensitivity. In contrast, Pacifico et al. (2012) and Unger (2013) found cropland expansion to be the dominant driver of the reduction. This discrepancy likely arises for two reasons. First, our study applied an increase of approximately 10 % in global cropland expansion (Guenther et al., 2012), which is smaller than the 22 % change estimated by Unger (2013). Second, we apply a CO_2-sensitivity algorithm that most likely provides an upper limit of this effect for past climates (Possell and Hewitt, 2011).

The primary goal of this model study is to explore the sensitivity of the oxidative capacity of present and past atmospheres to assumptions about isoprene emissions and the fate of its oxidation products. We ~~do not attempt~~ are reluctant to offer “best guess” estimates ~~for the following reasons. First, the parameterization of the~~ in large part because the uncertainty in the CO_2-isoprene interaction ~~used in this study is based on a limited number of plant taxa (Possell and Hewitt, 2011), and differs substantially from another proposed form of the response curve at sub-ambient~~ is substantial and our knowledge of the isoprene photo-oxidation mechanism is still evolving. Some studies have suggested that canopy-scale processes may complement or offset the leaf-scale response to atmospheric CO_2 levels (~~Wilkinson~~ e.g., Sun et al., ~~2009). Models of biogenic VOC emissions, such as the one employed in this study, remain uncertain as they rely on a limited number of measurements (Barkley~~ 2013). Also, it is likely that the application of the same CO_2-sensitivity parameterization to all PFTs leads to an overestimate of this effect. As discussed below, observations of the relevant chemical species that could constrain the oxidative capacity of past atmospheres are sparse. Laboratory and field measurements, however, strongly suggest that the C1 chemistry scheme is an inadequate representation of the isoprene photo-oxidation mechanism (Paulot et al., ~~2011). Until we have a better understanding of why plants emit isoprene,uncertainties in estimates of past and future biogenic isoprene emissions will likely persist (Pacifico~~ 2009a, b; Mao et al., ~~2009). Second, knowledge of the photochemical cascade of~~ 2013c). Therefore, model studies that depend on a simple, C1-like isoprene ~~oxidation is still evolving. Updated mechanisms are still unable to fully reconcile measured and modeled OH concentrations (Mao~~ photo-oxidation scheme are likely outdated, particularly with respect to their ability to accurately simulate the tropospheric oxidative capacity. All of the models participating in the ACCMIP study in support of the IPCC AR5 used a C1-like isoprene photo-oxidation mechanism (Naik et al., ~~2012). The reactivity of isoprene nitrates, which could significantly affect the efficiency of ozone production, is not well understood (e.g., Lee~~ 2013). Our results demonstrate that even under identical emission scenarios, the original and new isoprene photo-oxidation mechanisms yield different interpretations of various parameters such as changes in global mean OH and methane lifetime across the preindustrial-present day transition.

Quantifying the oxidative capacity of past atmospheres remains an ongoing challenge because the oxidants are not directly preserved in the ice-core record, and paleo-proxies that can provide a simple and robust constraint have not been readily identified (Levine et al.,~~2014; Mller et al., 2014). Rohrer et al. (2014) reported a linear dependence of OH on local ozone photolysis rates at two sites with vastly different NO$_x$ concentrations in China, a result at odds with our current understanding of the theoretical dependence of OH on NO$_x$. Third, considerable uncertainties still exist in mechanisms of SOA formation from VOC precursors (Henze and Seinfeld, 2006) . Formation of SOA in the GEOS-Chem CTM is predicted based upon rate constants and aerosol yield parameters determined from laboratory chamber studies, which may not be representative of atmospheric conditions (Karambelas~~ 2011; Alexander and Mickley, 2015). Our results call for greater attention and research efforts in the following measurements to help constrain model estimates of the oxidative capacity of past atmospheres: (1) Ice-core CO. Quantifying the amount of CO produced in situ from organic substrates trapped within the ice would facilitate the use of ice-core CO measurements as constraints for model results; (2) Ice-core $\Delta^{17}O(NO_3^-)$.

Because of its greater sensitivity to oxidant abundances, ice-core measurements of $\Delta^{17}O(NO_3^-)$ may in fact provide a more robust proxy than $\Delta^{17}O(SO_4^{2-})$ for reconstructing the oxidation capacity of past atmospheres. For example, cloud amount and pH do not influence the isotopic composition of nitrate as they do for sulfate (Levine et al., ~~2014). We also do not consider cloud processing of isoprene oxidation products and condensation onto inorganic aerosol species, which could increase the predicted SOA yields from isoprene oxidation (Liao~~ 2011). In particular, measurements of $\Delta^{17}O(NO_3^-)$ in tropical ice cores, which are so far sparse, may be highly valuable given that the dominant natural sources of NO_x and production of OH are most prevalent in the tropics (Buffen et al., ~~2007)~~2014); (3) Field campaigns focused on measurements of oxidant cycling in high-isoprene, low-NO_x environments. Such a suite of observations will help constrain the modeled sensitivity of tropospheric oxidants to past climate changes. ~~Such processes are beyond the scope of this study but warrants further investigation. Lastly, the limited availability of direct observations of past oxidant levels hinders our ability to quantitatively assess results from our model sensitivity experiments.~~

~~This study highlights~~ The main scientific value of our study lies in its demonstration of the importance of biogenic VOC emissions and the fate of their oxidation products in influencing chemistry-climate interactions across the last glacial-interglacial time interval and the industrial era. ~~The range of uncertainties in our results demonstrates how current understanding of~~ Because of existing uncertainties in isoprene emissions and photochemistry~~remains inadequate, thereby impeding our ability to constrain the oxidative capacities of the present and past atmospheres~~ , ~~its controlling factors, and the radiative forcing of trends~~ there are larger uncertainties in model estimates of the oxidative capacity of past atmospheres than previously acknowledged. These uncertainties, in turn, limit our confidence in estimating radiative forcing due to changes in short-lived species such as SOA over time~~. All of our present-day sensitivity experiments underestimate methane and methyl chloroform lifetimes inferred from observations. Our findings corroborate those of the recent Atmospheric Chemistry and Climate Model Intercomparison Project that uncertainties in our understanding of the long-term trends in OH and methane lifetime will~~

~~persist unless natural precursor emissions and chemical mechanisms are well constrained (Naik~~ , as well as our ability to identify the factors controlling global mean OH levels between the LGM and the present day.

Constraining the anthropogenic radiative forcing over the industrial period inherently depends on our ability to quantify the chemical composition of the preindustrial atmosphere. In particular, assessing the radiative forcing from changes involving biogenic processes is an ongoing challenge in the modeling community, but has importance in the coming decades as policymakers face decisions that depend critically on accurate knowledge of the atmospheric oxidative capacity. For example, recent studies have demonstrated the importance of considering the net effect of human-induced changes in biogenic VOC emissions on global climate forcing over the industrial period (e.g., Unger, 2014a, b; Heald et al., 2014; Heald and Spracklen, 2015). Tackling the long-standing issue of the dynamics of future global methane sources and sinks is also crucial for the next generation of climate projections (Quiquet et al., 2015; Kirschke et al., 2013). ~~In addition, our results call for greater attention and research efforts in improving model representations of SOA formation from VOC precursors and heterogeneous reactions that act as HO_x and NO_x sinks – such processes may influence the present-day sensitivity of OH to NO_x emissions. We recommend that as knowledge of the environmental factors controlling biogenic isoprene emissions and of~~ However, including detailed photochemical mechanisms in chemistry-climate models is computationally expensive. In the ACCMIP models involved in the IPCC assessments of the preindustrial and present day, the tropospheric chemical mechanisms of non-methane hydrocarbons were represented in varying degrees of complexity (Lamarque et al., 2013), and the isoprene photo-oxidation ~~mechanism evolves,re-evaluating model estimates of the oxidative capacities of past atmospheres should be a priority for future research.In particular, our ability to reconcile the discrepancies between measured and modeled HO~~mechanisms did not consider HO_x~~concentrations in regions with~~ -recycling under low-NO_x ~~and high-VOC concentrations will be of particular importance for improving model estimates of the oxidative capacities of present and past atmospheres~~conditions (Naik et al., 2013). Chemistry-climate models attempting to explain methane trends since the Last Glacial Maximum have also historically depended on relatively simple schemes for isoprene photo-oxidation (e.g., Valdes et al., 2005; Kaplan et al., 2006). Our work points to the value of incorporating into such models both current knowledge and the associated uncertainties regarding biogenic isoprene emissions and photochemistry.

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References

Alexander, B., Savarino, J., Barkov, N. I., Delmas, R. J., and Thiemens, M. H.: Climate driven changes in the oxidation pathways of atmospheric sulfur, Geophys. Res. Lett., 29, 30-1–30-4, doi:10.1029/2002GL014879, 2002.

Alexander, B., Savarino, J., Kreutz, K. J., and Thiemens, M. H.: Impact of preindustrial biomass-burning emissions on the oxidation pathways of tropospheric sulfur and nitrogen, J. Geophys. Res., 109, D08303, doi:10.1029/2003JD004218, 2004.

~~Barkley, M.P., Palmer, P.~~ Alexander, B., Mickley, L. J.: Paleo-perspectives on potential future changes in the oxidative capacity of the atmosphere due to climate change and anthropogenic emissions, Current Pollution Reports, in review.

Bartlein, P. J., Harrison, S. P., Brewer, S., Connor, S., Davis, B. A. S., Gajewski, K., Guiot, J., Harrison-Prentice, T. I., ~~Ganzeveld, L., Arneth, A.~~Hender- son, A., Peyron, O., Prentice, I. C., Scholze, M., ~~Hagberg, D., Karl, T.~~Seppa, H., ~~and Yantosca, R.M.: Can a "state of the art" chemistry transport model simulate Amazonian tropospheric chemistry?, J.Geophys.Res., 116, D16302, ,~~ Shu- man, B., Sugita, S., Thompson, R. S., Viau, A. E., Williams, J., and Wu, H.: Pollen-based continental climate reconstructions at 6 and 21 ka: a global synthesis, Clim. Dynam., 37, 775–802, 2011.

Beerling, D. J., Nicholas Hewitt, C., Pyle, J. A., and Raven, J. A.: Critical issues in trace gas biogeochemistry and global change, Philosophical Transactions Series A, Mathematical, Physical, and Engineering Sciences, 365, 1629–1642, doi:10.1098/rsta.2007.2037, 2007.

Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B. D., Fiore, A. M., and Schultz, M. G.: Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, J. Geophys. Res., 106, 23073, doi:10.1029/2001JD000807, 2001.

Bousquet, P., Hauglustaine, D. A., Peylin, P., Carouge, C., and Ciais, P.: Two decades of OH variability as inferred by an inversion of atmospheric transport and chemistry of methyl chloroform, Atmos. Chem. Phys., 5, 2635–2656, doi:10.5194/acp-5- 2635-2005, 2005.

Braconnot, P., Harrison, S. P., Kageyama, M., Bartlein, P. J., Masson-Delmotte, V., Abe-Ouchi, A., Otto-Bliesner, B., and Zhao, Y.: Evaluation of climate models using palaeoclimatic data, Nature Clim. Change, 2, 417–424, 2012.

Brook, E. J., Harder, S., Severinghaus, J., Steig, E. J., and Sucher, C. M.: On the origin and timing of rapid changes in atmospheric methane during the last glacial period, Global. Biogeochem. Cy., 14, 559–572, 2000.

Buffen, A. M., Hastings, M. G., Thompson L. G., and Mosley-Thompson, E.: Investigating the preservation of nitrate isotopic composition in a tropical ice core from the Quelccaya Ice Cap, Peru, J. Geophys. Res. Atmos., 119, 2674–2697, doi:10.1002/2013JD020715, 2014.

Carslaw, K. S., Lee, L. A., Reddington, C. L., Pringle, K. J., Rap, A., Forster, P. M., Mann, G. W., Spracklen, D. V, Woodhouse, M. T., Regayre, L. A. and Pierce, J. R.: Large contribution of natural aerosols to uncertainty in indirect forcing., Nature, 503, 67–71, doi:10.1038/nature12674, 2013.

CLIMAP: The Surface of the Ice-Age Earth, Science (New York, N.Y.), 191, 1131–1137, 1976.

de Reus, M., Fischer, H., Sander, R., Gros, V., Kormann, R., Salisbury, G., Van Dingenen, R., Williams, J., Zöllner, M., and Lelieveld, J.: Observations and model calculations of trace gas scavenging in a dense Saharan dust plume during MINATROC, Atmos. Chem. Phys., 5, 1787–1803, doi:10.5194/acp-5-1787-2005, 2005.

Faïn, X., Chappellaz, J., Rhodes, R. H., Stowasser, C., Blunier, T., McConnell, J. R., Brook, E. J., Preunkert, S., Legrand, M., Debois, T., and Romanini, D.: High resolution measurements of carbon monoxide along a late Holocene Greenland ice core: evidence for in situ production, Clim. Past., 10, 987–1000, doi:10.5194/cp-10-987-2014, 2014.

Fiore, A. M., Dentener, F. J., Wild, O., Cuvelier, C., Schultz, M. G., Hess, P., and Zuber, A.: Multimodel estimates of intercontinental source-receptor relationships for ozone pollution, J. Geophys. Res., 114, D04301, doi:10.1029/2008JD010816, 2009.

Fiore, A. M., Naik, V., Spracklen, D. V, Steiner, A., Unger, N., Prather, M., and Zeng, G.: Global air quality and climate, Chem. Soc. Rev., 41, 6663–6683, doi:10.1039/c2cs35095e, 2012.

Gildor, H., Ashkenazy, Y., Tziperman, E., Lev, I.: The role of sea ice in the temperature-precipitation feedback of glacial cycles, Clim. Dyn., 43, 1001–1010, doi:10.1007/s00382-013-1990-7, 2014.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model. Dev., 5, 1471–1492, doi:10.5194/gmd-5-1471-2012, 2012.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.

Guilderson, T. P., Fairbanks, R. G., and Rubenstone, J. L.: Tropical Temperature Variations Since 20,000 Years Ago: Modulating Interhemispheric Climate Change, Science, 253, 663–665, doi:10.1126/science.263.5147.663, 1994.

Guzmán, M. I., Hoffmann, M. R., and Colussi, A. J.: Photolysis of pyruvic acid in ice: Possible relevance to CO and CO_2 ice core record anomalies, J. Geophys. Res., 112, D10123, doi:10.1029/2006JD007886, 2007.

Haan, D., and Raynaud, D.: Ice core record of CO variations during the last two millennia: atmospheric implications and chemical interactions within the Greenland ice, Tellus, 50B, 253–262, 1998.

Harder, S. L., Shindell, D. T., Schmidt, G. A., and Brook, E. J.: A global climate model study of ~~CH4~~ CH_4 emissions during the Holocene and glacial-interglacial transitions constrained by ice core data, Global. Biogeochem. Cy., 21, GB1011, doi:10.1029/2005GB002680, 2007.

Heald, C. L., Ridley, D. A., Kroll, J. H., Barrett, S. R. H., Cady-Pereira, K. E., Alvarado, M. J., and Holmes, C. H.: Contrasting the direct radiative effect and direct radiative forcing of aerosols, Atmos. Chem. Phys., 14, 5513–5527, doi:10.5194/acp-14-5513-2014, 2014

Heald, C. L., Spracklen, D. V.: Land use change impacts on air quality and climate, Chem. Rev., doi:10.1021/cr500446g, 2015.

Henze, D. K. and Seinfeld, J. H.: Global secondary organic aerosol from isoprene oxidation, Geophys. Res. Lett., 33, L09812, doi:10.1029/2006GL025976,2006.

Hewitt, C. N., Lee, J. D., MacKenzie, A. R., Barkley, M. P., Carslaw, N., Carver, G. D., Chappell, N. A., Coe, H., Collier, C., Commane, R., Davies, F., Davison, B., DiCarlo, P., Di Marco, C. F., Dorsey, J. R., Edwards, P. M., Evans, M. J., Fowler, D., Furneaux, K. L., Gallagher, M., Guenther, A., Heard, D. E., Helfter, C., Hopkins, J., Ingham, T., Irwin, M., Jones, C., Karunaharan, A., Langford, B., Lewis, A. C., Lim, S. F., MacDonald, S. M., Mahajan, A. S., Malpass, S., McFiggans, G., Mills, G., Misztal, P., Moller, S., Monks, P. S., Nemitz, E., Nicolas-Perea, V., Oetjen, H., Oram, D. E., Palmer, P. I., Phillips, G. J., Pike, R., Plane, J. M. C., Pugh, T., Pyle, J. A., Reeves, C. E., Robinson, N. H., Stewart, D., Stone, D., Whalley, L. K., and Yin, X.: Overview: oxidant and particle photochemical processes above a south-east Asian tropical rainforest (the OP3 project): introduction, rationale, location characteristics and tools, Atmos. Chem. Phys., 10, 169–199, doi:10.5194/acp-10-169-2010, 2010.

Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.-C., and Zhang, Y.: Amplified trace gas removal in the troposphere, Science (New York, N.Y.), 324, 1702–1704, doi:10.1126/science.1164566, 2009.

Holden, P. B., Edwards, N. R., Wolff, E. W., Lang, N. J., Singarayer, J. S., Valdes, P. J., and Stocker, T. F.: Interhemispheric coupling, the West Antarctic Ice Sheet and warm Antarctic interglacials, Clim. Past, 6, 431–443, doi:10.5194/cp-6-431-2010, 2010.

Holmes, C. D., Prather, M. J., Søvde, O. A., and Myhre, G.: Future methane, hydroxyl, and their uncertainties: key climate and emission parameters for future predictions, Atmos. Chem. Phys., 13, 285–302, doi:10.5194/acp-13-285-2013, 2013.

Horowitz, L. W., Liang, J., Gardner, G. M., and Jacob, D. J.: Export of reactive nitrogen from North America during summertime: Sensitivity to hydrocarbon chemistry, J. Geophys. Res., 103, 13451–13476, 1998.

Hutterli, M. A., Bales, R. C., Mcconnell, J. R., and Stewart, R. W.: HCHO in Antarctic snow: Preservation in ice cores and air-snow exchange, Geophys. Res. Lett., 29, 1235, doi:10.1029/2001GL014256, 2002.

Isaksen, I. S. and Dalsøren, S. B.: Atmospheric science. Getting a better estimate of an atmospheric radical, Science (New York, N.Y.), 331, 38–39, doi:10.1126/science.1199773, 2011.

~~Khalil, M. A. K. and Rasmussen, R. A.: Atmospheric methane: Trends over the last 10000 years, Atmos. Environ., 21, 2445–2452, 1987.~~

Kaplan, J. O.: Wetlands at the Last Glacial Maximum: Distribution and methane emissions, Geophys. Res. Lett., 29, 1079, doi:10.1029/2001GL013366, 2002.

Kaplan, J. O., Folberth, G., and Hauglustaine, D. A.: Role of methane and biogenic volatile organic compound sources in late glacial and Holocene fluctuations of atmospheric methane concentrations, Global Biogeochem. Cy., 20, GB2016, doi:10.1029/2005GB002590, 2006.

~~Karambelas, A.~~Khalil, M. A. K. and Rasmussen, R. A.: Atmospheric methane: Trends over the last 10 000 years, Atmos. Environ., ~~Pye, H. O.T., Budisulistiorini, S. H., Surratt, J.~~ 21, 2445–2452, 1987.

Kirschke, S., Bousquet, P., Ciais, P., Saunois, M., Canadell, J. G., Dlugokencky, E. J., Bergamaschi, P., Bergmann, D., Blake, D. R., Bruhwiler, L., Cameron-Smith, P., Castaldi, S., Chevallier, F., Feng, L., Fraser, A., Heimann, M., Hodson, E. L., Houweling, S., Josse, B., Fraser, P. J., Krummel, P. B., Lamarque, J.-F., Langenfelds, R. L., Le Quere, C., Naik, V., O'Doherty, S., Palmer, P. I., Pison, I., Plummer, D., ~~and Pinder, R. W.: Contribution of Isoprene Epoxydiol to Urban Organic Aerosol: Evidence from Modeling and Measurements,Environ. Sci. Technol.Lett.~~Poulter, B., Prinn, R. G., Rigby, M., Ringeval, B., Santini, M., Schmidt, M., Shindell, D. T., Simpson, I. J., Spahni, R., Steele, L. P., Strode, S. A., Sudo, K., Szopa, S., van der Werf, G. R., Voulgarakis, A., van Weele, M., Weiss, R. F., Williams, J. E. and Zeng, G.: Three decades of global methane sources and sinks, Nat. Geosci, 6, 813–823, doi:10.1038/ngeo1955, 2013.

Krol, M. and Lelieveld, J.: Can the variability in tropospheric OH be deduced from measurements of 1,~~278–283, , 2014.~~ 1,1-trichloroethane (methyl chloroform)?, J. Geophys. Res., 108, 4125, doi:10.1029/2002JD002423, 2003.

Lamarque, J.-F., Shindell, D. T., Josse, B., Young, P. J., Cionni, I., Eyring, V., Bergmann, D., Cameron-Smith, P., Collins, W. J., Do- herty, R., Dalsoren, S., Faluvegi, G., Folberth, G., Ghan, S. J., Horowitz, L. W., Lee, Y. H., MacKenzie, I. A., Nagashima, T., Naik, V., Plummer, D., Righi, M., Rumbold, S. T., Schulz, M., Skeie, R. B., Stevenson, D. S., Strode, S., Sudo, K., Szopa, S., Voulgarakis, A., and Zeng, G.: The Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP): overview and description of models, simulations and climate diagnostics, Geosci. Model Dev., 6, 179–206, doi:10.5194/gmd-6-179-2013, 2013.

Lathière, J., Hauglustaine, D. A., De Noblet-Ducoudré, N., Krinner, G., and Folberth, G. A.: Past and future changes in biogenic volatile organic compound emissions simulated with a global dynamic vegetation model, Geophys. Res. Lett., 32, L20818, doi:10.1029/2005GL024164, 2005.

Lathière, J., Hewitt, C. N., Beerling, D. J.: Sensitivity of isoprene emissions from the terrestrial biosphere to 20th century changes in atmospheric CO_2 concentration, climate, and land use, Global Biogeochem. Cycles, 24, GB1004, doi:10.1029/2009GB003548, 2010.

Lee, H.-M., Henze, D. K., Alexander, B., and Murray, L. T.: Investigating the sensitivity of surface-level nitrate seasonality in Antarctica to primary sources using a global model, Atmos. Environ., 89, 757–767, doi:10.1016/j.atmosenv.2014.03.003, 2014.

Lee, ~~L., Teng, A. P., Wennberg, P. O., Crounse, J. D., and Cohen, R. C. : On Rates and Mechanisms of OH and O3 Reactions with Isoprene-Derived Hydroxy Nitrates, J. Phys. Chem-A., 118, 1622–1637, 2014.~~
~~Lee, C. C.~~ C. C. W.,Savarino, J., and Thiemsen, M. H.: Mass independent oxygen isotopic composition of atmospheric sulfate: Origin and implications for the present and past atmospheres of Earth and Mars, Geophys. Res. Lett., 28, 1783–1786, 2001.

LeGrande, A. N., Schmidt, G. A., Shindell, D. T., Field, C. V, Miller, R. L., Koch, D. M., and Hoffmann, G.: Consistent simulations of multiple proxy responses to an abrupt climate change event, P. Natl. Acad. Sci. USA, 103, 837–842, 2006.

Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737–740, doi:10.1038/nature06870, 2008.

Levine, J. G., Wolff, E. W., Jones, A. E., Hutterli, M. A., Wild, O., Carver, G. D., and Pyle, J. A.: In search of an ice core signal to differentiate between source-driven and sink-driven changes in atmospheric methane, J. Geophys. Res., 116, D05305, doi:10.1029/2010JD014878, 2011.

~~Liao, H., Henze, D. K., Seinfeld, J. H., Wu, S., and Mickley, L. J.: Biogenic secondary organic aerosol over the United States?: Comparison of climatological simulations with observations, J. Geophys. Res., 112, 1–19, , 2007.~~
Liu, S. C., Trainer, M., Fehsenfeld, F. C., Parrish, D. D., Williams, E. J., Fahey, D. W., and Murphy, P. C.: Ozone production in the rural troposphere and the implications for regional and global ozone distributions, J. Geophys. Res., 92, 4191–4207, 1987.

Liu, Y. J., Herdlinger-Blatt, I., McKinney, K. A., and Martin, S. T.: Production of methyl vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation, Atmos. Chem. Phys., 13, 5715–5730, doi:10.5194/acp-13-5715-2013, 2013.

~~Mao, J. , Fan, S., Jacob, D.~~ Mahowald, N. M., Yoshioka, M., Collins, W. D., Conley, A. J., ~~and Travis, K. R.: Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols , Atmos. Chem. Phys., 13, 509–519, , 2013.~~ Fill- more, D. W., and Coleman, D. B.: Climate response and radiative forcing from mineral aerosols during the last glacial maximum, pre-industrial, current and doubled-carbon dioxide climates, Geophys. Res. Lett., 33, L20705, doi:10.1029/2006GL026126, 2006.

Mao, J., Jacob, D. J., Evans, M. J., Olson, J. R., Ren, X., Brune, W. H., Clair, J. M. St., Crounse, J. D., Spencer, K. M., Beaver, M. R., Wennberg, P. O., Cubison, M. J., Jimenez, J. L., Fried, A., Weibring, P., Walega, J. G., Hall, S. R., Weinheimer, A. J., Cohen, R. C., Chen, G., Crawford, J. H., McNaughton, C., Clarke, A. D., Jaeglé, L., Fisher, J. A., Yantosca, R. M., Le Sager, P., and Carouge, C.: Chemistry of hydrogen oxide radicals (HO_x) in the Arctic troposphere in spring, Atmos. Chem. Phys., 10, 5823–5838, doi:10.5194/acp-10-5823-2010, 2010.

Mao, J., ~~Paulot, F., Jacob, D. J., Cohen, R. C., Crounse, J. D., Wennberg, P. O., and Horowitz, L. W.: Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry, J. Geophys. Res.-Atmos., 118, 11256–11268, , 2013.~~

~~Mao, J.,~~ Ren, X., Zhang, L., Van Duin, D. M., Cohen, R. C., Park, J.-H., Goldstein, A. H., Paulot, F., Beaver, M. R., Crounse, J. D., Wennberg, P. O., DiGangi, J. P., Henry, S. B., Keutsch, F. N., Park, C., Schade, G. W., Wolfe, G. M., Thornton, J. A., and Brune, W. H.: Insights into hydroxyl measurements and atmospheric oxidation in a California forest, Atmos. Chem. Phys., 12, 8009–8020, doi:10.5194/acp-12-8009-2012, 2012.

Mao, J., Fan, S., Jacob, D. J., and Travis, K. R.: Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols, Atmos. Chem. Phys., 13, 509–519, doi:10.5194/acp-13-509-2013, 2013.

Mao, J., Paulot, F., Jacob, D. J., Cohen, R. C., Crounse, J. D., Wennberg, P. O., and Horowitz, L. W.: Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry, J. Geophys. Res.-Atmos., 118, 11256–11268, doi:10.1002/jgrd.50817, 2013.

Michalski, G.: First measurements and modeling of ~~Δ 17~~ Δ^{17}O in atmospheric nitrate, Geophys. Res. Lett., 30, 1870, doi:10.1029/2003GL017015, 2003.

McLinden, C. A., Olsen, S. C., Hannegan, B. ., Wild, O., and Prather, M. J.: Stratospheric ozone in 3D models: A simple chemistry and the cross-tropopause flux, J. Geophys. Res., 14653–14665, 2000.

~~Mller, J.-F., Peeters~~Montzka, S. A., Spivakovsky, C. M., Butler, J. H., Elkins, J. W., Lock, L. T., ~~and Stavrakou, T.: Fast photolysis of carbonyl nitrates from isoprene, Atmos. Chem.Phys., 14, 2497–2508, , 2014.~~ and Mondeel, D. J.: New observational constraints, for atmospheric hydroxyl on global and hemispheric scales, Science, 288, 500–503, 2000.

Murray, L. T., Mickley, L. J., Kaplan, J. O., Sofen, E. D., Pfeiffer, M., and Alexander, B.: Factors controlling variability in the oxidative capacity of the troposphere since the Last Glacial Maximum, Atmos. Chem. Phys., 14, 3589–3622, doi:10.5194/acp-14-3589-2014, 2014.

Murray, L. T., Fiore, A. M., Shindell, D. T., Naik, V., Horowitz, L. W., and Evans, M. J.: Uncertainties in global atmospheric hydroxyl projections tied to fate of reactive nitrogen and carbon, in preparation, 2015.

Naik, V., Voulgarakis, A., Fiore, A. M., Horowitz, L. W., Lamarque, J.-F., Lin, M., Prather, M. J., Young, P. J., Bergmann, D., Cameron-Smith, P. J., Cionni, I., Collins, W. J., Dalsøren, S. B., Doherty, R., Eyring, V., Faluvegi, G., Folberth, G. A., Josse, B., Lee, Y. H., MacKenzie, I. A., Nagashima, T., van Noije, T. P. C., Plummer, D. A., Righi, M., Rumbold, S. T., Skeie, R., Shindell, D. T., Stevenson, D. S., Strode, S., Sudo, K., Szopa, S., and Zeng, G.: Preindustrial to present-day changes in tropospheric hydroxyl radical and methane lifetime from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), Atmos. Chem. Phys., 13, 5277–5298, doi:10.5194/acp-13-5277-2013, 2013.

Novelli, P. C., Masarie, K. A., and Lang, P. M.: Distributions and recent changes of carbon monoxide in the lower troposphere, J. Geophys. Res., 103, 19015–19033, doi:10.1029/98JD01366, 1998.

Oyarzun, R., Lillo, J., Sánchez-Hernández, J. C., and Higueras, P.: Pre-industrial Metal Anomalies in Ice Cores: A Simplified Reassessment of Windborne Soil Dust Contribution and Volcanic Activity during the Last Glaciation, International Geology Review, 47, 1120–1130, doi:0.2747/0020-6814.47.11.1120, 2005.

Pacifico, F., Folberth, G. A., Jones, C. D., Harrison, S. P., and Collins, W. J. Sensitivity of biogenic isoprene emissions to past, present, and future environmental conditions and implications for atmospheric chemistry, J. Geophys. Res.-Atmos., 117, D22303, doi:10.1029/2012JD018276, 2012.

~~Pacifico, F., Harrison, S. P., Jones, C. D., and Sitch, S.: Isoprene emissions and climate, Atmos. Environ., 43, 6121–6135, , 2009.~~

Park, R. J.: Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: Implications for policy, J. Geophys. Res., 109, D15204, doi:10.1029/2003JD004473, 2004.

Parrella, J. P., Jacob, D. J., Liang, Q., Zhang, Y., Mickley, L. J., Miller, B., Evans, M. J., Yang, X., Pyle, J. A., Theys, N., and Van Roozendael, M.: Tropospheric bromine chemistry: implications for present and pre-industrial ozone and mercury, Atmos. Chem. Phys., 12, 6723–6740, doi:10.5194/acp-12-6723-2012, 2012.

~~Patra, P. K., Krol, M. C., Montzka, S. a, Arnold, T., Atlas, E. L., Lintner, B. R., and Young, D.: Observational evidence for interhemispheric hydroxyl-radical parity, Nature., 513, 219–223, , 2014.~~

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates, Atmos. Chem. Phys., 9, 1479–1501, doi:10.5194/acp-9-1479-2009, 2009.

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kürten, A., Clair, J. M. S., Seinfeld, J. H., and Wennberg, P. O.: Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, Science (New York, N.Y.), 325, 730–733, 2009.

Paulot, F., Henze, D. K., and Wennberg, P. O.: Impact of the isoprene photochemical cascade on tropical ozone, Atmos. Chem. Phys., 12, 1307–1325, doi:10.5194/acp-12-1307-2012, 2012.

Paulot, F., Jacob, D. J., and Henze, D. K.: Sources and Processes Contributing to Nitrogen Deposition: An Adjoint Model Analysis Applied to Biodiversity Hotspots Worldwide, Environ. Sci. Technol., 47, 3226–3233, 2013.

Pavelin, E. G., Johnson, C. E., Rughooputh, S., and Toumi, R.: Evaluation of pre-industrial surface ozone measurements made using Schönbein's method, Atmos. Environ., 33, 919–929, 1999.

Peñuelas, J., and Staudt, M.: BVOCs and global change, Trends Plant Sci., 15, 133–144, doi:10.1016/j.tplants.2009.12.005, 2010.

Pfeiffer, M., Spessa, A., and Kaplan, J. O.: A model for global biomass burning in preindustrial time: LPJ-LMfire (v1.0), Geosci. Model Dev., 6, 643–685, doi:10.5194/gmd-6-643-2013, 2013.

Pike, R. C. and Young, P. J.: How plants can influence tropospheric chemistry?: the role of isoprene emissions from the biosphere, Weather, 64, 332–336, 2009.

Possell, M. and Hewitt, C. N.: Isoprene emissions from plants are mediated by atmospheric CO_2 concentrations, Glob. Change. Biol., 17, 1595–1610, doi:10.1111/j.1365-2486.2010.02306.x, 2011.

Power, M. J., Marlon, J., Ortiz, N., Bartlein, P. J., Harrison, S. P., Mayle, F. E., and Zhang, J. H.: Changes in fire regimes since the Last Glacial Maximum: an assessment based on a global synthesis and analysis of charcoal data, Clim. Dynam., 30, 887–907, doi:10.1007/s00382-007-0334-x, 2007.

Power, M. J., Marlon, J. R., Bartlein, P. J., and Harrison, S. P.: Fire history and the Global Charcoal Database: A new tool for hypothesis testing and data exploration, Palaeogeogr. Palaeocl., 291, 52–59, doi:10.1016/j.palaeo.2009.09.014, 2010.

Prather, M. J., Holmes, C. D., and Hsu, J.: Reactive greenhouse gas scenarios: Systematic exploration of uncertainties and the role of atmospheric chemistry, Geophys. Res. Lett., 39, L09803, doi:10.1029/2012GL051440, 2012.

Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G., ~~and~~ McCulloch, A., Harth, C., Salameh, P., O?Doherty, S., Wang, R. H. J., Porter, L, and Miller, B. R.: Evi- dence for substantial variations of atmospheric hydroxyl radicals over the past two decades, Science, 292, 1882–1888, 2001.

Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G., and Krummel, P. B.: Evidence for variability of atmospheric hydroxyl radicals over the past quarter century, Geophys. Res. Lett., 32, L07809, doi:10.1029/2004GL022228, 2005.

Quiquet, A., Archibald, A. T., Friend, A. D., Chappellaz, J., Levine, J. G., Stone, E. J., Telford, P. J. and Pyle, J. A.: The relative importance of methane sources and sinks over the Last Interglacial period and into the last glaciation, Quat. Sci. Rev., 112, 1–16, doi:10.1016/j.quascirev.2015.01.004, 2015.

Rind, D., Chandler, M., Lonergan, P., and Lerner, J.: Climate change and the middle atmosphere: 5. Paleostratosphere in cold and warm climates, J. Geophys. Res., 106, 20195, doi:10.1029/2000JD900548, 2001.

Rind, D., Lerner, J., McLinden, C., and Perlwitz, J.: Stratospheric ozone during the Last Glacial Maximum, Geophys. Res. Lett., 36, L09712, doi:10.1029/2009GL037617, 2009.

Rohrer, F., Lu, K., Hofzumahaus, A., Bohn, B., Brauers, T., Chang, C.-C., and Wahner, A.: Maximum efficiency in the hydroxyl-radical-based self-cleansing of the troposphere, Nat. Geosci., 7, 559–563, doi:10.1038/ngeo2199, 2014.

Savarino, J., Lee, C. C. W., and Thiemens, M. H.: Laboratory oxygen isotopic study of sulfur(IV) oxidation: Origin of the mass-independent oxygen isotopic anomaly in atmospheric sulfates and sulfate mineral deposits on Earth, J. Geophys. Res., 105, 29079–29088, 2000.

Scott, C. E., Rap, A., Spracklen, D. V., Forster, P. M., Carslaw, K. S., Mann, G. W., Pringle, K. J., Kivekäs, N., Kulmala, M., Lihavainen, H., and Tunved, P.: The direct and indirect radiative effects of biogenic secondary organic aerosol, Atmos. Chem. Phys., 14, 447–470, doi:10.5194/acp-14-447-2014, 2014.

Sitch, S., Cox, P. M., Collins, W. J., and Huntingford, C.: Indirect radiative forcing of climate change through ozone effects on the land-carbon sink, Nature, 448, 791–794, doi:10.1038/nature06059, 2007.

Sofen, E. D., Alexander, B., and Kunasek, S. A.: The impact of anthropogenic emissions on atmospheric sulfate production pathways, oxidants, and ice core $\Delta^{17}O(SO_4^{2-})$, Atmos. Chem. Phys., 11, 3565–3578, doi:10.5194/acp-11-3565-2011, 2011.

Sofen, E. D., Alexander, B., Steig, E. J., Thiemens, M. H., Kunasek, S. A., Amos, H. M., Schauer, A. J., Hastings, M. G., Bautista, J., Jackson, T. L., Vogel, L. E., McConnell, J. R., Pasteris, D. R., and Saltzman, E. S.: WAIS Divide ice core suggests sustained changes in the atmospheric formation pathways of sulfate and nitrate since the 19th century in the extratropical Southern Hemisphere, Atmos. Chem. Phys., 14, 5749–5769, doi:10.5194/acp-14-5749-2014, 2014.

Spolaor, A., Vallelonga, P., Cozzi, G., Gabrieli, J., Varin, C., Kehrwald, N., Zennaro, P., Boutron, C., and Barbante, C.: Iron speciation in aerosol dust influences iron bioavailability over glacial-interglacial timescales, Geophys. Res. Lett., 40, 1–6, doi:10.1002/grl.50296, 2013.

Stevenson, D. S., Young, P. J., Naik, V., Lamarque, J.-F., Shindell, D. T., Voulgarakis, A., Skeie, R. B., Dalsoren, S. B., Myhre, G., Berntsen, T. K., Folberth, G. A., Rumbold, S. T., Collins, W. J., MacKenzie, I. A., Doherty, R. M., Zeng, G., van Noije, T. P. C., Strunk, A., Bergmann, D., Cameron-Smith, P., Plummer, D. A., Strode, S. A., Horowitz, L., Lee, Y. H., Szopa, S., Sudo, K., Na- gashima, T., Josse, B., Cionni, I., Righi, M., Eyring, V., Conley, A., Bowman, K. W., Wild, O., and Archibald, A.: Tropospheric ozone changes, radiative forcing and attribution to emissions in the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), Atmos. Chem. Phys., 13, 3063–3085, doi:10.5194/acp-13-3063-2013, 2013.

Stute, M., Forster, M., Frischkorn, H., Serejo, A., Clark, J. F., Schlosser, P., Broecker, W. S., and Bonani, G.: Cooling of Tropical Brazil (5 °C) During the Last Glacial Maximum, Science, 269, 379–383, doi:10.1126/science.269.5222.379, 1995.

Sun, Z., Niinemets, Ü., Hüve, K., Rasulov, B., and Noe, S. M.: Elevated atmospheric CO_2 concentration leads to increased whole-plant isoprene emission in hybrid aspen (Populus tremula ? Populus tremuloides), New Phytol., 198, 788–800, doi:10.1111/nph.12200, 2013.

Tai, A. P. K., Mickley, L. J., Heald, C. L., and Wu, S.: Effect of ~~CO2~~ CO_2 inhibition on biogenic isoprene emission: Implications for air quality under 2000 to 2050 changes in climate, vegetation, and land use, Geophys. Res. Lett., 40, 3479–3483, doi:10.1002/grl.50650, 2013.

Thornton, J. A., Jaeglé, L. and McNeill, V. F.: Assessing known pathways for HO_2 loss in aqueous atmospheric aerosols: Regional and global impacts on tropospheric oxidants, J. Geophys. Res.-Atmos., 113, D05303, doi:10.1029/2007JD009236, 2008.

Trowbridge, A. M., Asensio, D., Eller, A. S. D., Way, D. A., Wilkinson, M. J., Schnitzler, J.-P., and Monson, R. K.: Contribution of various carbon sources toward isoprene biosynthesis in poplar leaves mediated by altered atmospheric ~~CO2~~ CO_2 concentrations, PloS One, 7, e32387, doi:10.1371/journal.pone.0032387, 2012.

Unger, N.: Isoprene emission variability through the twentieth century, J. Geophys. Res.-Atmos., 118, 13606–13613, doi:10.1002/2013JD020978, 2013.

Unger, N.: Human land-use-driven reduction of forest volatiles cools global climate, Nature Climate Change, 4, 1–4, doi:10.1038/nclimate2347, 2014.

Unger, N.: On the role of plant volatiles in anthropogenic global climate change, Geophys. Res. Lett., 41, 8563–8569, doi:10.1002/2014GL061616, 2014.

Unger, N. and Yue, X.: Strong chemistry-climate feedbacks in the Pliocene, Geophys. Res. Lett., 41, 527–533, doi:10.1002/2013GL058773, 2014.

Valdes, P. J.: The ice age methane budget, Geophys. Res. Lett., 32, L02704, doi:10.1029/2004GL021004, 2005.

van der Werf, G. R., Peters, W., van Leeuwen, T. T., and Giglio, L.: What could have caused pre-industrial biomass burning emissions to exceed current rates?, Clim. Past., 9, 289–306, doi:10.5194/cp-9-289-2013, 2013.

van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009), Atmos. Chem. Phys., 10, 11707–11735, doi:10.5194/acp-10-11707-2010, 2010.

Voulgarakis, A., Naik, V., Lamarque, J.-F., Shindell, D. T., Young, P. J., Prather, M. J., Wild, O., Field, R. D., Bergmann, D., Cameron-Smith, P., Cionni, I., Collins, W. J., Dalsøren, S. B., Doherty, R. M., Eyring, V., Faluvegi, G., Folberth, G. A., Horowitz, L. W., Josse, B., MacKenzie, I. A., Nagashima, T., Plummer, D. A., Righi, M., Rumbold, S. T., Stevenson, D. S., Strode, S. A., Sudo, K., Szopa, S., and Zeng, G.: Analysis of present day and future OH and methane lifetime in the ACCMIP simulations, Atmos. Chem. Phys., 13, 2563–2587, doi:10.5194/acp-13-2563-2013, 2013.

Waelbroeck, C., Paul, A., Kucera, M., Rosell-Melé, A., Weinelt, M., Schneider, R., and Turon, J.-L.: Constraints on the magnitude and patterns of ocean cooling at the Last Glacial Maximum, Nature Geosci., 2, 127–132, doi:10.1038/ngeo411, 2009.

Wang, Y. and Jacob, D. J.: Anthropogenic forcing on tropospheric ozone and OH since preindustrial times, J. Geophys. Res.-Atmos., 103, 31123–31135, doi:10.1029/1998JD100004, 1998.

Wang, Z., Chappellaz, J., Park, K., and Mak, J. E.: Large variations in Southern Hemisphere biomass burning during the last 650 years, Science (New York, N.Y.), 330, 1663–1666, doi:10.1126/science.1197257, 2010.

Webb, R. S., Rind, D. H., Lehman, S. J., Healy, R. J., and Sigman, D.: Influence of ocean heat transport on the climate of the Last Glacial Maximum, Nature, 385, 695–699, 1997.

Weber, S. L., Drury, A. J., Toonen, W. H. J., and van Weele, M.: Wetland methane emissions during the Last Glacial Maximum estimated from PMIP2 simulations: Climate, vegetation, and geographic controls, J. Geophys. Res., 115, D06111, doi:10.1029/2009JD012110, 2010.

Wilkinson, M. J., Monson, R. K., Trahan, N., Lee, S., Brown, E., Jackson, R. B., and Fall, R.: Leaf isoprene emission rate as a function of atmospheric ~~CO2~~ CO_2 concentration. Glob. Change. Biol., 15, 1189–1200, doi:10.1111/j.1365-2486.2008.01803.x, 2009.

Table 1. Atmospheric CO_2 concentrations and global annual terrestrial plant isoprene emissions for each climate scenario.

Climate Scenario	$[CO_2]$ (ppmv)	Global Annual Terrestrial Plant Isoprene Emissions		
		without CO_2-sensitivity ($\mathrm{Tg\,C\,yr^{-1}}$)	with[a] CO_2-sensitivity ($\mathrm{Tg\,C\,yr^{-1}}$)	Percent change with CO_2-sensitivity relative to without (%)
Present day	354	536	557	$+3.9$
Preindustrial	280	580	740	$+28$
Warm LGM	188	478	849	$+78$
Cold LGM	188	261	463	$+77$

* This study uses the empirical relationship from Possell and Hewitt (2011) to test the sensitivity of plant isoprene emissions to atmospheric CO_2 concentrations.

Table 2. Summary of the different climate, chemistry and plant isoprene emission scenarios tested in this model study. For each climate scenario except for the present day, all possible combinations of chemistry and emission schemes are tested (for the present day, only the "with" CO_2-sensitivity scheme is used). We perform 21 simulations in total.

Climate	Notes
Present day	ca. 1990s
Preindustrial	ca. 1770s
Warm LGM	19-23 ka; SSTs from CLIMAP Project Members(1967) with $\Delta SST^{a}_{15^\circ S-^\circ N}$ of $-1.2\,^\circ C$
Cold LGM	19–23 ka; SSTs from Webb et al. (1997) with $\Delta SST^{a}_{15^\circ S-^\circ N}$ of $-6.1\,^\circ C$
Chemistry	**Notes (color scheme used in figures)**
C1[b]	Original isoprene chemistry and original HO_2 uptake (orange)
C2	New isoprene chemistry and original HO_2 uptake (green)
C3	New isoprene chemistry and new HO_2 uptake (blue)
CO_2-sensitivity of plant isoprene emission	**Notes**
Without (wo)[b]	Controlling factors include temperature, light availability, leaf age, and leaf area index (LAI)
With (w)	Controlling factors include the above and atmospheric CO_2 concentrations

[a] The average change in sea surface temperature (SST) within 15 ° of the equator relative to the preindustrial.
[b] The "C1-wo" combination corresponds to the schemes used by Murray et al. (2014) in their "best estimate" scenarios.

Table 3. Calculated present-day methyl chloroform (MCF) and methane lifetimes against tropospheric oxidation by OH ($\tau_{\mathrm{MCF,OH}}$, $\tau_{\mathrm{CH_4,OH}}$), with consideration of CO_2-sensitivity of plant isoprene emissions.

	Model Chemistry Scheme[a]			
Lifetime	C1	C2	C3	Lifetimes inferred from observations
$\tau_{\mathrm{MCF,OH}}$ [yr]	4.8	4.1	4.5	$6.0^{+0.5}_{-0.4}$[b]
$\tau_{\mathrm{CH_4,OH}}$ [yr]	10.3	8.9	9.6	11.2 ± 1.3[c]

[a] See Table 2 for a full description of the different chemistry schemes tested in this study.

[b] Inferred from observations (Prinn et al., 2005).

[c] Inferred from observations (Prather et al., 2012).

Table 4. Modeled percent changes in the surface $[O_3]/[OH]$ and $[O_3]/[RO_2]$ ratios for the present day relative to the preindustrial, and in the surface [OH] concentration for the warm and cold LGM relative to the preindustrial, for different model sensitivity experiments. Surface $[O_3]/[OH]$ and [OH] values are averaged over the 46–66° S latitude band to compare with values inferred from ice-core measurements of $\Delta^{17}O(SO_4^{2-})$ by Sofen et al. (2014) and Alexanderet al. (2002). Surface $[O_3]/[RO_2]$ are averaged over the 34–54° S and 62.5–72.5° W (extratropical South America) to compare with values inferred from ice-core measurements of $\Delta^{17}O(NO_3^-)$ by Sofen et al. (2014), as described in Sect. 3.2.

Chemistry[a] Scheme	CO_2 -sensitivity of plant isoprene emissions	Present day – Preindustrial	Present day – Preindustrial	Warm LGM – Preindustrial	Cold LGM – Preindustrial
		Percent change in surface $[O_3]/[OH]$ over 46–66° S (%)	Percent change in surface $[O_3]/[RO_2]$ over S. America (%)	Percent change in surface [OH] over 46–66° S (%)	Percent change in surface [OH] over 46–66° S (%)
C1	without	35	2.3	68	87
	with	39	−0.3	105	106
C2	without	42	5.1	93	95
	with	42	2.8	105	101
C3	without	38	2.5	102	109
	with	40	−0.4	120	117
Observation-derived estimates		260	−60 to −90	40[b]	40[b]

[a] See Table 2 for a full description of the different chemistry schemes tested in this study.

[b] Percent increase in sulfate formed from gas-phase oxidation by OH

Table 5. Global methane burden and lifetime against tropospheric oxidation by OH ($\tau_{CH_4,OH}$).

Climate	Chemistry	CO_2 -sensitivity	CH_4 burden (Tg)*	Loss by OH in troposphere (Tg y^{-1})	$\tau_{CH_4,OH}$ (y)
Present day	C1	w	4790	465	10.3
	C2	w	4790	539	8.9
	C3	w	4790	497	9.6
Preindustrial	C1	wo	2010	184	11.0
		w	2010	165	12.2
	C2	wo	2010	238	8.4
		w	2010	230	8.7
	C3	wo	2010	223	9.0
		w	2010	214	9.4
warm LGM	C1	wo	1040	91	11.5
		w	1040	62	16.8
	C2	wo	1040	127	8.2
		w	1040	112	9.3
	C3	wo	1040	120	8.7
		w	1040	102	10.2
cold LGM	C1	wo	1040	66	15.8
		w	1040	48	21.7
	C2	wo	1040	87	11.9
		w	1040	79	13.1
	C3	wo	1040	81	12.9
		w	1040	72	14.5

* Global burden calculated from mean surface concentration using a conversion factor of 2.75 Tg CH_4 ppbv^{-1} (Prather et al., 2012).

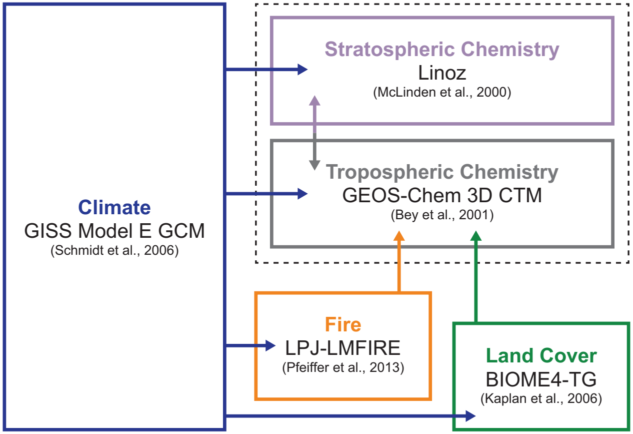

Figure 1. The ICE age Chemistry And Proxies (ICECAP) model framework consists of four global models, represented here by boxes with solid lines. The stratospheric and tropospheric chemistry schemes are coupled online in the GEOS-Chem Chemical Transport Model (CTM). Arrows indicate the flow of model output. The ICECAP model framework was especially designed for simulating the oxidative capacity of past atmospheres. (Adapted from Murray et al., 2014, Fig. 1.)

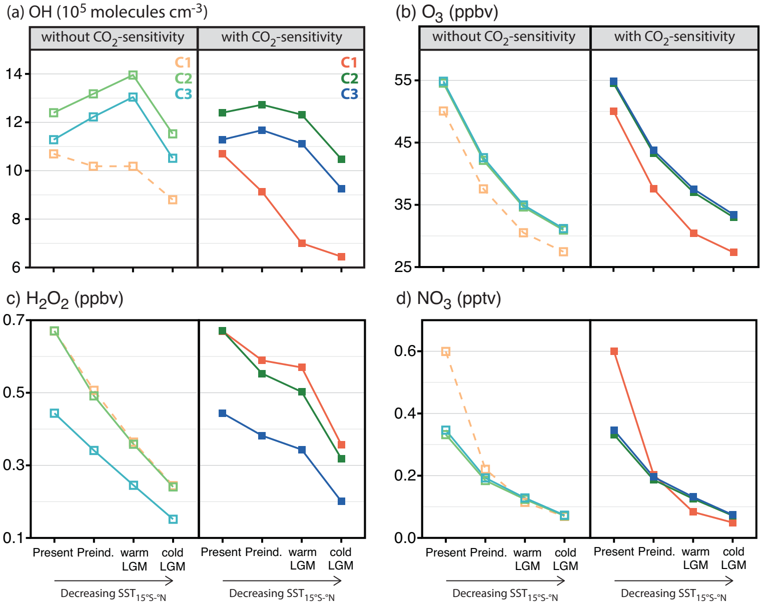

Figure 2. Simulated sensitivity of the tropospheric mean mass-weighted oxidant burdens of OH, O_3, H_2O_2, and NO_3 to each combination of climate, chemistry, and plant isoprene emission scheme. Simulations are as described in Table 2. The climate scenarios are present day, preindustrial, warm LGM, and cold LGM, with decreasing sea surface temperatures within 15° of the equator (SST$_{15^\circ S-^\circ N}$), going from left to right along the abscissa. The chemistry schemes are C1 (orange curves), C2 (green), and C3 (blue). Plant isoprene emissions are modeled without (light-shaded) or with (dark-shaded) sensitivity to atmospheric CO_2 concentrations. The tropospheric burdens are calculated with the tropopause determined from the thermal lapse rate. The dotted light-orange line represents the results reported in Murray et al. (2014) for their “best estimate” lightning and fire emissions scenarios.

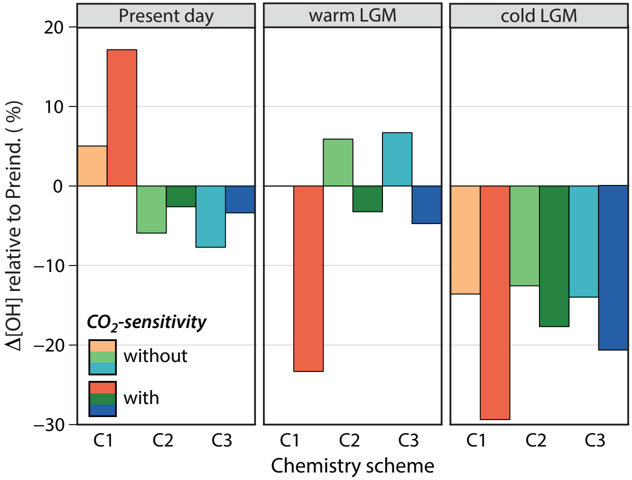

Figure 3. Percent changes (%) in the tropospheric mean mass-weighted OH burden for a range of scenarios relative to their respective preindustrial scenarios (e.g., C1-w Present day relative to C1-w Preindustrial). Simulations are as described in Table 2. The climate scenarios are present day, preindustrial, warm LGM, and cold LGM. The chemistry schemes are C1 (orange bars), C2 (green), and C3 (blue). Plant isoprene emissions are modeled without (light-shaded) or with (dark-shaded) sensitivity to atmospheric CO_2 concentrations. For the present day, test simulations with and without CO_2-sensitivity yield nearly identical isoprene emissions. We therefore perform all present-day simulations with CO_2-sensitivity turned on and assume that these model results apply to the respective present-day "without" scenarios. (Note: The percent change at the warm LGM relative to the preindustrial is very small when the C1 chemistry scheme is used without consideration of the CO_2-sensitivity (C1-wo), and so no light orange bar is apparent in the middle panel.)

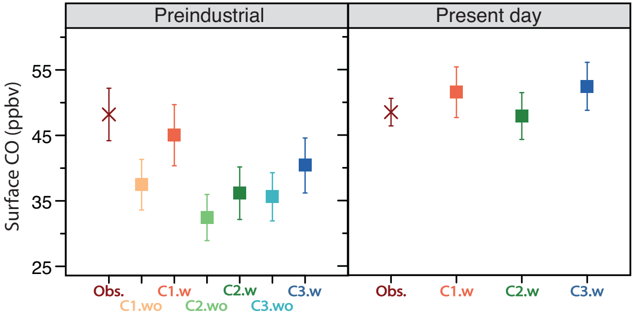

Figure 4. Comparison of model results with observations of CO surface concentrations (ppbv) over Antarctica for the preindustrial (1770s) and present-day (1990s) simulations. Simulations are as described in Table 2; colors are as in Fig. 2. The maroon crosses represent observations from different sources for each time slice. Wang et al. (2010) measured ice-core CO concentrations at the South Pole of 48 ± 4 ppbv for the year 1777 (±110 years); the associated errors represent analytical uncertainties. The mean CO surface concentration measured at the South Pole by the NOAA Global Monitoring Division for the 1990s is 49 ± 2 ppbv; the associated errors represent inter-annual variability. The squares represent values averaged over Antarctica from our model simulations tested with different chemistry and isoprene emission schemes for the preindustrial and present-day scenarios. Simulations are as described in Table 2; colors are as in Fig. 2. Error bars associated with the model results represent ±1 standard deviation of the spatially-averaged mean value.

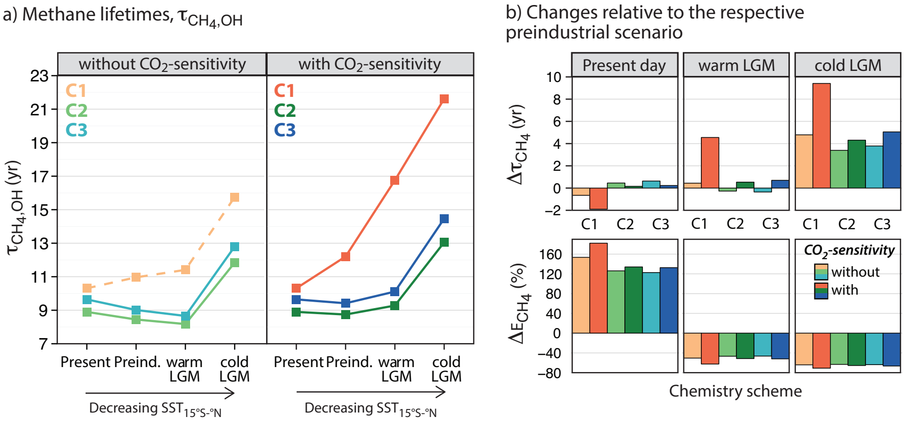

Figure 5. Left Panel: calculated global methane lifetime against oxidation by tropospheric OH for each combination of climate, chemistry and plant isoprene emission scenarios. Simulations are as described in Table 2; colors are as in Fig. 2. The dotted light-orange line represents the results reported in Murray et al. (2014) for their "best estimate" lightning and fire emissions scenarios. Right Panels: Changes in the global methane lifetimes (yr) and emissions (%) relative to their respective preindustrial scenarios (e.g., C1-w Present day relative to C1-w Preindustrial). Colors are as in Fig. 3. Changes in methane emissions are calculated by assuming that they scale with changes in methane loss by OH in the troposphere.

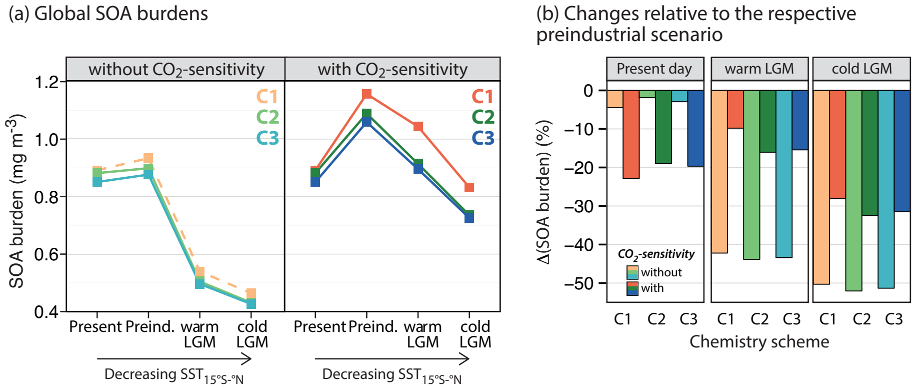

Figure 6. Left Panel: tropospheric mean mass-weighted secondary organic aerosol (SOA) burdens for each combination of climate, chemistry and plant isoprene emission scenarios. Simulations are as described in Table 2; colors are as in Fig. 2. The dotted light-orange line represents the results reported in Murray et al. (2014) for their "best estimate" lightning and fire emissions scenarios. Right Panel: Percent changes in tropospheric mean SOA burdens relative to their respective preindustrial scenarios (e.g., C1-w Present day relative to C1-w Preindustrial). Colors are as in Fig. 3.

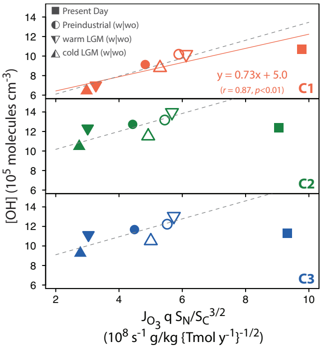

Figure 7. Tropospheric mean mass-weighted OH burden in each simulation as a function of $J_{O_3} q\, S_N / \left(S_C^{3/2}\right)$, where J_{O_3} is the tropospheric mean mass-weighted ozone photolysis frequency (s^{-1}), q is the tropospheric mean mass-weighted specific humidity ($g\,kg^{-1}$), and S_N and S_C are the tropospheric sources of reactive nitrogen ($Tmol\,N\,a^{-1}$) and of reactive carbon ($Tmol\,C\,a^{-1}$), respectively. S_C is calculated as the sum of emissions of CO, NMVOCs, and an implied source of methane equal to its loss rate by OH. Model results for different chemistry schemes are separated into three subsets as follows. Top panel: original isoprene chemistry and original HO_2 uptake (C1). Middle panel: new isoprene chemistry and original HO_2 uptake (C2). Bottom panel: new isoprene chemistry and new HO_2 uptake (C3). Different symbols denote different climate scenarios (present day, preindustrial, warm LGM, cold LGM). Filled symbols represent simulations in which the CO_2-sensitivity of plant isoprene emission is considered (w); unfilled symbols are those without (wo). All present-day simulations were performed with CO_2-sensitivity turned on. The orange line shows a reduced major axis regression fit for the C1 subset, with the regression equation and correlation coefficient ~~of determination~~ (~~R^2)~~ $r = 0.87$, $p < 0.01$) inset. We do not find a statistically significant correlation between OH and $J_{O_3} q S_N / \left(S_C^{3/2}\right)$ for the C2 ($r = 0.36$) and C3 ($r = 0.34$) subsets. When the present-day values are excluded and a multiple regression model is fitted to the remaining ensemble, we find that the three different chemistry schemes possess the same values for the slopes of the linear correlation but different values for the intercepts, as shown by the dashed grey lines (see text for details).