Response to Reviewers

Reviewer Comments in Blue, Responses in Black.

We thank both reviewers for their positive and constructive assessments of our work.

Anonymous Referee #2

Summary. This paper describes an assessment of the oxidizing capacity of the troposphere using a modeling framework for current, pre-industrial and last-glacial-maximum conditions. Using sets of specific assumptions about tropospheric composition in the present, pre-industrial, and last-glacial- maximum, the distributions of four oxidants and other model parameters are presented. The modeling framework accounts for subtle changes to the earth system such as temperature effects on tropical upwelling and stratospheric circulation. Given some parameters that have significant uncertainties (e.g. LGM mean temperature, fire emissions, lightning), runs at the limits of the values were performed to establish their effects on oxidant levels. The model results were compared with the limited available data from ice cores and other sources.

Assessment and general comments.

This is a useful addition to the assessment of historic values of tropospheric oxidation capacity. Many important issues were carefully considered in their roles controlling the abundance of oxidants. I think that the paper should be published. I have a few issues that the authors should consider in preparation of the final version of the paper.

Four oxidants were selected for evaluation. Should explicit presentation of concentrations of peroxy radicals and Criegee radical intermediates also be presented (since they are presumably available in the model runs already performed, and can be important for some oxidative processes)?

In the interest of length, we explicitly describe only the four most important tropospheric oxidants. The GEOS-Chem chemical mechanism at present does not include the Criegee radical. There is some discussion of RO_2 in the H_2O_2 section, and in interpretation of the ice-core record.

Throughout the paper, ranges of various input parameters are presented, qualitative terms like “highly uncertain” are used, and 1 sigma estimates of output parameters are given. What seems to be missing is a propagation of errors analysis that shows quantitatively how uncertainties in input parameters (including the other models that provide input to the CTM) affect the model-derived values. Perhaps a brief discussion could be given, with reference to other papers. Are trends in the abundance of oxidants statistically significant given the input uncertainties and, if possible, uncertainties in the model representations of the controlling factors.

Given the complexity and computational cost of the forward function of the model, the sheer number of variables involved, each with their own uncertainties (many unknown), there is simply no practical way to perform a propagation of errors analysis, which are typically done with box models.

Our strategy for dealing with the large uncertainties — e.g., the order of magnitude difference in fire emission estimates at the LGM — is to test the response of the oxidants to the upper and lower bounds of estimates available from the literature. Our simulations are intended to bound the truth for three key areas of uncertainty (SST, fires, lightning), and to identify the parameters to which OH is very sensitive to motivate future research aimed at reducing uncertainties in those areas.

Does the coarse resolution of the GCM and GTM affect the results, especially given that OH depends very specifically on local conditions (solar flux, O3, water vapor, etc.)?

It is true that there can be considerable small-scale spatial and temporal variability in local OH concentrations given its extremely short lifetime. However, there is also substantial large-scale structure in the key parameters that govern OH on spatiotemporal scales representable by global models, which may dominate the mean response. From personal experience, we find relatively small changes in global mean OH in GEOS-Chem driven by GEOS meteorology at 4° x 5° resolution vs. 2° x 2.5°. However, it is possible the response would become larger at finer resolutions. This is not something we can test in this study, due to the coarse resolution of the standard GISS climate model. To our knowledge there is no study looking specifically at the impact of model resolution on global mean OH. Wild and Prather (JGR, 2006) examined the effect of resolution on the global ozone budget, and found boundary layer ozone production sensitive, but not the free troposphere (where most OH is produced). We now acknowledge the relatively coarse resolution in Section 2.1.

Specific comments.

Page 1. Line 51-52. I agree that changes in the tropospheric oxidative capacity could perturb ecosystems via oxidative stress (e.g. ozone damage to vegetation), but I don't agree that changes in the oxidative capacity will change the deposition of oxidized nutrients such as nitrate. The rate of deposition of nitrate is determined by the source strength of NOx, not by the rate of oxidation.

The reviewer makes a good point that the total deposition flux is determined by the total source of fixed nitrogen to the atmosphere. However, the distribution of the deposition will reflect changes in oxidants and meteorological parameters, which can have consequences for biogeochemical cycles. For example, the remote equatorial Pacific Ocean is generally N-limited, and therefore, a decrease in the oxidation rate of NO_x to HNO_3 could lead to an increase of nitrate deposited there.

We clarify the text to read "and by altering the deposition **patterns** of oxidized nutrients such as nitrate".

Page 2. Line 132. The effect of stratospheric ozone on some photolysis rates (e.g. O3 to O(1D)) is well known, thus I think the use of "potentially" to the describe the impact is misleading. I suggest eliminating the words "...potentially large..." and just say "...in particular the effect of stratospheric ozone on photolysis rate coefficients...".

We have amended the text to read:

"in particular the ~~potentially large~~ effect of the stratospheric ozone burden on photolysis rates in the troposphere, **to which OH is especially sensitive** (e.g., Holmes et al., 2013).

Page 3. Lines 142-144. I agree that it is more efficient to use offline coupling to determine sensitivities. However, it would be interesting to take your best estimate values and do a fully coupled run with an earth system model.

Such a study is beyond the scope of this analysis. It would also be not directly comparable to the current results, as earth system models at present lack the detailed complexity of the GEOS-Chem chemical mechanism and physical processes. However, the recent development of several coupled chemistry-climate models — including ModelE2 — will enable future studies of reactive chemical feedbacks onto the climate of past atmospheres, which ICECAP cannot do.

We add the following to the Conclusion the potential of fully coupled models in the Conclusion:
"**Offline-coupling allows for rapid sensitivity tests and identification of first-order effects of changing climate on composition. However, it does not enable the examination of chemical feedbacks on climate, which would require a fully integrated earth system model, such as ModelE2 (Shindell et al., 2013).**"

Page 3. Lines 151-152. Some discussion as to whether an equilibrium terrestrial biosphere is appropriate. How does such an approximation compare with reality? I could see that perhaps it could be reasonable for the LGM part of the simulation, but it could be a poor approximation for pre-industrial and likely completely wrong for present-day.

We already discuss this issue in Section 2.2. BIOME4-TG has been extensively used for simulating changes in land cover in past climates relative to the present (e.g., Kaplan, 2002; Kaplan et al., 2003, 2006; Harrison and Prentice, 2003). We account for the present-day impact of humans on the natural land cover product as simulated by BIOME4 by prescribing land-use fractions on top of the simulated present-day vegetation distribution. We feel it is most robust for our experimental design to be as consistent as possible in how we simulated each different climate scenario, rather than introducing additional levels of uncertainty, e.g., by using satellite landcover products to drive MEGAN for the present (as normal for GEOS-Chem) but modeled landcover products for the past. And we demonstrate that ICECAP does a reasonable job in reproducing present-day chemistry related to the biosphere and oxidants (e.g., VOC emissions, deposition fluxes). We amend Section 2.2 to

"**We elect to represent present-day land cover with BIOME4-TG rather than prescribe it from satellite products (as normal for GEOS-Chem) for consistency between simulations. However, to represent anthropogenic land use, we superimpose a present-day crop fraction mask from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.1 (Guenther et al., 2012).**"

Page 3. Line 174. Appears that the word "method" is missing and should be "...and the method that we employ to test...".

The line now reads:
"Section 4 describes the response of natural emissions to changing climate **as well as** the **scenarios** we employ to test the sensitivity to uncertainties in past lightning and fire emissions."

Page 3. Line 252. Appears to be a word missing in ".... cloud cover fraction, surface ??? and wind speed...".

The line is corrected to read "cloud cover fraction, **and surface** wind speed".

Page 5. Line 437. It would be helpful to explicitly define ΔSST. I think it is $SST_{LGM} - SST_{preindustrial}$, but the text is not clear on this. I guess it can be inferred from Figure 2, but I still think an explicit definition is called for.

We have amended the text to read:
"For our "*warm-LGM*" simulation, we use the SST reconstruction from Climate: Long range Investigation, Mapping, and Prediction (CLIMAP, 1976), with an average change in SST within 15° of the equator ($\Delta SST_{15°S-15°N}$) of –1.2° C, **relative to the preindustrial**."

Page 5. Section 3.1. It would be good to see a brief discussion of the relative change in SSTs from preindustrial to present day that are being used in this work. An average parameter such as the tropical ΔSST used for the LGM in this section would be instructive.

We have added the following text to Section 3.1:
"**These changes at the LGM are all greater in magnitude than the present-day $\Delta SST_{15°S-15°N}$ of +0.4°C, relative to the preindustrial.**"

Page 7. Line 664-669. The inclusion of bromine chemistry is interesting and apparently very important. It would be useful to provide some indication of the level of reactive bromine that the model produces, and comparisons with observations (in situ and remote).

The bromine implementation is described at length and compared to present-day observations by Parrella et al. (2012), which we have cited several times in the paper. We consciously omit lengthy discussion of halogen chemistry, as it had little impact in explaining the changes between oxidants in each simulation, as discussed in the fifth paragraph of Section 5.2. The nature of the present implementation of reactive bromine in GEOS-Chem — fixed boundary conditions at the surface and tropopause — led to relatively small changes in tropospheric Br_y between climates.

Page 9. Lines 823 and 862. The concept of OH "buffering" should be defined and explained at least qualitatively, and preferable quantitatively. The answer is implied in lines 864-866, but should be more explicit.

We have changed the sentences to read:

"In general, oxidant burdens decrease with decreasing surface temperature, and changes in OH are ~~well-buffered~~ **relatively small** compared to the other oxidants."

"However, the response of mean OH as seen in Fig. 8 is ~~more buffered than~~ **relatively small compared to the changes in** the overall rates of its production and loss reactions."

The quantitative values are provided in Fig. 8 and Fig. 9.

Page 14, Lines 1372-1374. Suggest slightly changing to make the meaning clearer: "...to present, despite the large change in the mean concentration."

We have incorporated this suggestion.

Page 15, Line 1494-1497. There are other studies (e.g. Thompson and Stewart, JGR, 1991; Stewart and Thompson, JGR, 1996) that describe the factors to which OH is most sensitive. These (and perhaps others) should be referenced here or earlier in the paper.

We now include Thompson and Stewart in the second paragraph of the Introduction, where we acknowledge other studies examining the parameters to which OH is most sensitive.

The goal of this work and the sentence in question identifies the factors to which OH is most sensitive *across glacial-interglacial time scales*. This reflects both the relative sensitivity of OH to a comparable percent change — which as the reviewer points out have been well studied for decades (we amend the introduction to emphasize this) — but also how those parameters change across glacial-interglacial time scales, the latter being what we took great care to try to most appropriately represent in this work.

Figure 3. Does it make sense that areas with no trend (ΔT or ΔPrecip rate = 0, white) can have statistically significant changes?

Yes, small absolute changes — which only appear to be zero because of the global color bar — can be locally significant if the model's internal variability is even smaller at that location.

Figure 6. I couldn't see this figure in the pdf version I downloaded.

The version on the ACPD website includes Fig. 6.

Figure 11. It is worth mentioning that the Antarctic ozone hole is not reproduced in the model (or ΔSCO would be much more negative for Pre-industrial to present, correct?). This is mentioned in the text, but in places, but it might be good to reiterate it in this figure caption.

We have changed the caption to read:
"Preindustrial simulated zonal mean stratospheric ozone columns [DU], and the change in ozone in the present day relative to the preindustrial (top panels). **The model does not include the heterogeneous chemistry of the Antarctic ozone hole**. Also shown are the changes during the "warm" and "cold" simulations of the LGM, relative to the preindustrial (bottom panels). The difference plots share a common color bar."