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 #1

This article presents an offline coupled GCM-Vegetation-Chemistry model study of the atmospheric oxidation capacity in the present-day, pre-industrial and Last Glacial Maximum atmospheres. It specifically investigates the roles of lightning and fire emissions as well as stratospheric chemistry. The focus on the effect of NO is especially valuable in my view as it has not attracted a lot of attention in previous studies. Presenting a complex multi-model setup and several sensitivity tests on 3 different time slices is challenging. I think the manuscript could be improved in order to allow a non specialized audience (e.g. from the paleo-climate community) to better grasp the overall main controlling factors and uncertainties, and major points of agreement versus differences with previous studies. The reliability of the main conclusions is currently difficult assess although this could be improved. Suggestions are provided below.

General comments:

p24521 l6-9, p24543 l6-8 and p24556 l11: at least Crutzen and Brül, 1993, Karol et al., 1995 and Martinerie et al., 1995 have considered changes in the stratospheric ozone burden.

We have clarified the text to read:
“However, no LGM model study to date has considered the full suite of changes in the key variables for controlling tropospheric oxidants **in a 3-D framework**, in particular the potentially large effect of the stratospheric ozone burden on photolysis rates in the troposphere.”

p24521 l28 - p24522 l3, p24551 l4 - p24552 l14 and p24557 l9-10: the discussions of $\Delta^{17}O$ to be published in Soften et al. in prep should be suppressed as no result is shown. Moreover the reasons why this study might lead to a different conclusion than Levine et al., JGR, 2011 regarding its utility as a proxy for oxidant variability are not explained.

We remove the references to the manuscript in prep. The statement p24557 l9-10 stands on already published results, as described in p24551 lines 4-17.

p24524 l21 - p24525 l4, p24534 l22-28, p24535 l5-12, p24538 l3-21, and Figure 6: a detailed description of sulfur chemistry and aerosols treatment is provided, however their impact is only briefly and partially analysed (Section 6). Aerosol related perspectives could be provided in Section 8 (e.g. coupled climate-chemistry simulations).

In consideration of article length, changes in the aerosol burdens and their expected impact on climate — including radiative forcing calculations — is the subject of a separate paper currently in preparation (which we now state in the Introduction). However, we felt it necessary to include aerosols in Section 4 for completeness of the model description, and in Section 6 as they afford some of the few observational constraints for evaluating the model in past climates.

p24527 l20 - p24528 l8; p24530 l5 - p24531 l2; p24541 l10 - p24542 l13; p24544 l24 - p24545 l2: The potential impact of the large O3 biases for present-day atmosphere on the reliability of LGM results (especially ozone photolysis rates) should be commented. For example, would the conclusion on the strong effect of JO3 be the same if ozone fields from Rind et al., 2009 were used?

As described in Sections 2.5 of both the main text and the supplement, there is little bias in the present-day tropical stratosphere ozone columns, which is the location of most importance for determination of photolysis rates in the troposphere. The ozone biases in the extratropical stratosphere and troposphere have little impact on the global OH budget, as the burden of OH is primarily in the tropical lower free troposphere (e.g., Spivakovsky et al., 2000), which we now emphasize in section 3.3. Global mean OH is well represented in the model, as supported by comparison with the methyl chloroform and methane lifetimes versus their observational constraints. (Note: we have also corrected a small error in our calculation of the methyl chloroform lifetime).

Section 2.5 and Supplement: the modelled NOx levels in present-day atmosphere are not evaluated although NOx are a focus of this study. For example satellite data could be used as in e.g. Schindell et al., ACP, 2013 (www.atmos-chem-phys.net/13/2653/2013/) or van Noije, ACP, 2006 (www.atmos-chem-phys.net/6/2943/2006/).

The anthropogenic emission inventories used in GEOS-Chem have been extensively evaluated (e.g., Hudman et al., JGR, 2007; van Donkelaar et al., ACP, 2008; Lamsal et al., GRL, 2011), and we feel that comparison to the ozone columns is a more sensitive test. However, we have added a section to the Supplement in which we compare GOME NO_2 columns from the 1990s to the present-day ICECAP simulation.

p24536 l14 - p24537 l6 and Section 6: I was surprised to see no mention of methane isotopes ice core records in the discussions of fire emissions and comparison with ice core-record (see e.g. Sapart et al., Nature, 2012, doi:10.1038/nature11461; Fischer et al., Nature, 2008, Levine et al., JGR, 2011 and references therein).

The model did not simulate online methane (or methane isotopes), so we cannot directly compare to the ice-core $\delta^{13}CH_4$ record, which we now make clear. However, we have included the discussion of these measurements in Section 4.6

"Fischer et al. (2008) interpreted ice-core measurements of $\delta^{13}CH_4$ in a box model, and determined the pyrogenic source of methane to be roughly constant between the LGM and the preindustrial at 45 Tg CH_4 yr^{-1}, a value higher than most estimates of the present-day biomass burning methane source (29-48 Tg CH_4 yr^{-1}; Bousquet et al., 2011; Chen and Prinn, 2006; Pison et al., 2009; van der Werf et al., 2010), but not taking into account the potential large influence of atomic chlorine (a minor oxidation pathway) on $\delta^{13}CH_4$ (Levine et al., 2011b)."

Specific Comments

p24518 l26 and Section 5.4: I guess that NO3 is used here as a night time proxy for NOx (NO+NO2+NO3), this should be clarified as the term NOx is used when speaking of emissions.

Our interest is the nitrate radical itself, which is a major oxidant and often overlooked. It is the dominant oxidant at nighttime, reacting with many of the species that OH does during the daytime (OH and NO_3 have opposite diel cycles, as described in Section 5.4 and references therein, e.g., Wayne et al., 1991). We therefore discuss NO_3, of which NO_x emissions are a precursor (as for the other oxidants). We amend Section 5.4 to emphasize this fact.

"The chemistry of the nighttime troposphere is dominated by the **gas-phase** nitrate radical NO_3**, acting as the major dark oxidant for VOCs that would otherwise react during daytime to form ozone** (Wayne et al., 1991)."

p24520 l11-12, l18-19, l27-29 and Table 1: the modelling studies agreement on ozone changes does not seem much better to me than for OH results in Table 1. Please rephrase.

The models agree in the signs of the ozone changes between the different climate scenarios, which is objectively a better agreement than OH, in which they do not. We have modified the text to make this more explicit.

p24520 l29 - 24521 l5: The discussion of previous results on LGM OH should also mention the study of Levine et al., GRL, 2011 which concludes that methane concentration changes are essentially source driven as in this study.

We reference the Levine et al. GRL 2011 study elsewhere in this section (p24520 l4-10) and in other sections when we discuss the methane lifetime (e.g., p24554 l23-p24554 l3 explicitly states the reviewer's comment). The paragraph the reviewer cites here is limited to a discussion of models that reported OH directly, which the Levine et al. (2011) study does not.

p24528 l10 - 24529 l4: Different ice sheet topography and SST from the reference datasets in PMIP3-CMIP5 are used at LGM. The major differences between these boundary conditions should be better commented (especially for ice sheet topography), and the impact of these differences on the climate results should be commented.

We have revised the text as follows.
"~~We use here the reconstruction of ice sheet thickness and extent from Licciardi et al. 1998~~. At the LGM, large permanent land ice sheets 3-4 km thick existed over northern North America (Laurentide and Cordilleran), Greenland, and northwestern Eurasia (Fennoscandian). **We use here the reconstruction of ice sheet thickness and extent from Licciardi et al. (1998), which has a lower maximum Laurentide ice sheet (LIS) elevation than those in the Paleoclimate Modelling Intercomparison Project (PMIP) studies (Braconnet et al., 2007a; Braconnet et al., 2012). Ullman et al. (2013) evaluated the sensitivity of the resulting LGM climate in ModelE to two different ice-sheet reconstructions, including Licciardi et al. (1998). They concluded that the lower maximum LIS elevation led to cooler temperatures in the northern latitudes.** The accumulation of water in terrestrial ice sheets caused sea levels to drop 120 m, exposing an additional 3% of the Earth's surface as land, particularly in Southeast Asia and Oceania, the Bering Strait, and the southeastern continental shelf of South America (Clark and Mix, 2002)."

p24534 l5-8 and p24535 l14 - p24536 l12: the study of Steinkamp and Lawrence, ACP, 2011 (www.atmos-chem-phys.net/11/6063/2011/) should be mentioned in the discussion of soil NOx emissions, as well as the ACCMIP intercomparison for present day and pre-industrial soil and lightning NOx emissions (Stevenson et al., ACP, 2013, www.atmos-chem-phys.net/13/3063/2013/).

We add the following text to Section 4.2:
"Emissions of NO_x from soil microbial activity follow the parameterization of Yienger and Levy (1995) as implemented by Wang et al. (1998) and are dependent on land cover type, precipitation, and temperature. **The parameterization yields 7.2 Tg N yr^{-1} in the present day, which is higher than GEOS-Chem driven by GEOS4 meteorology (5.6 Tg N yr^{-1}), but lower than recently developed parameterizations (8.6-10.7 Tg N yr^{-1}; Steinkamp and Lawrence, 2011; Hudman et al., 2012).**"

We add the following text to Section 4.5:
"We assume a uniform production rate of 310 mol N per all flash types (corresponding to 6.3 Tg N yr^{-1} in the present day), and distribute emissions vertically following Ott et al. (2010). **This falls within the range of current global models (5.5 ± 2.0 Tg N yr^{-1}; Stevenson et al., 2013), and matches a recent top-down estimate of 6.3 ± 1.4 Tg N yr^{-1} from multiple satellite constraints (Miyazaki et al., 2013).**"

p24534 l26-28: DMS results should be compared with Castebrunet et al., GRL, 2006 (doi: 10.1029/2006GL027681).

We add the following text to Section 4.3:
"**Our 84% reduction in DMS emitted from the Southern Ocean in the *warm-LGM* scenario is somewhat greater than the 55% reduction simulated by Castebrunet et al. (2006), who also used the CLIMAP SST/sea-ice reconstruction and held constant the Kettle et al. (1999) distribution, but used a different transfer velocity scheme and a different climate model.**"

p24537 l8-10 and p24542 l14-18: The uncertainties on fire emission types and emission factors in the context of changing climate (e.g. humidity) and their possible impact on the reliability of the conclusion that OH is insensitive to variations in fire emissions should be introduced. The uncertainty analysis in van der Werf et al., 2010 could be used.

We add the following text to Section 4.6:
"For all simulations, we use distributions of dry matter consumed per PFT from the LPJ-LMfire model (Pfeiffer et al., 2013) coupled with emission factors from the Global Fire Emissions Database version 3 (GFED3) (van der Werf et al., 2010) for NOx, CO, SO2, black carbon, OC, and 17 additional gas-phase species. **We assume emission factors per PFT remain constant in all climates, and do not test their sensitivity to changes in meteorological or geographical conditions. Such sensitivity is still poorly understood on global scales (Van Leeuwen and van der Werf, 2010).**"

We add the following text to Section 5.1:
"Fire emissions of NO, CO, and VOCs in the model assume fixed emission factors per dry matter consumed (van der Werf et al., 2010), so large absolute differences in burning yield relatively small changes in $S_N/(S_C^{3/2})$. **However, we note that if fire emission factors per species were to vary independently of one another in response to climate, then the fire influence on OH could be greater.**"

p24553 l9-11: the reliability of the LGM methane maximum shift should be commented. For example, is it consistent with bottom-up studies such as Weber et al., 2010?

We amend the text in Section 2.4 to read:
"We therefore assume tropical methane to be 4% higher than recorded at Antarctica. This is similar to the present-day gradient, and consistent with earlier model studies of LGM methane (Kaplan, 2006) **and wetland emissions (Weber et al., 2010)**."

Table 1: ΔOH results from Bock et al., Earth Planet. Sci. Lett., 2012 (http://dx.doi.org/10.1016/j.epsl.2012.06.052) using a similar design as Martinerie et al., 1995 but updated chemical reaction rates could be mentioned together with Martinerie et al., 1995.

We have added Bock et al. (2012) to Table 1.

Section 2.4 of the Supplement could be suppressed as it mostly repeats the article main text, or changed into a "Carbon monoxide" Section commenting better Figure 8.

We prefer to keep the OH section in the supplement, for completeness in the evaluation of the model. CO is used here as a constraint on the meridional distribution of OH, as is common in global model validation (e.g., Naik et al., 2013; Shindell et al., 2006).

Technical corrections:

p24519 l14: what is meant by "a new model framework"?

We have changed the text to read "a new **offline-coupled** model framework".

p24519 l23: “most oxidants are highly volatile” - unclear. Do you mean very short lived?

We have changed the text to read “most oxidants are highly **reactive**.”

p24554 l16: “a Bolivian ice core” - please provide the reference.

The reference (*Campen,* 2000) is given in Sect. 2.4 to which p24554 l16 references. We have also added the reference here.

“However, we note that if the tropical fraction of total methane in LGM were to increase by 33% as implied by a Bolivian ice core **(*Campen*, 2000)** — an extremely unlikely scenario (Sect. 2.4)”

The title of the Supplement is slightly different from the article title.

The titles have been synchronized.

p7 of Supplement: “Liu et al.” - incomplete reference

The reference has been corrected.