

Review of “Factors controlling variability in the oxidative capacity of the troposphere since the Last Glacial Maximum” by Murray et al.

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)?

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.

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.)?

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 NO_x, not by the rate of oxidation.

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 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...”.

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.

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.

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

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

Page 5. Line 437. It would be helpful to explicitly define ΔSST . I think it is $\text{SST}_{\text{LGM}} - \text{SST}_{\text{pre-industrial}}$, 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.

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.

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).

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.

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

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.

Figure 3. Does it make sense that areas with no trend (ΔT or $\Delta\text{Precip rate} = 0$, white) can have statistically significant changes?

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

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.