Response to Referee #1 for comments on "Preindustrial to present day changes in tropospheric hydroxyl radical and methane lifetime from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP)" by Naik et al.

We are grateful for the reviewer's comments on our paper. Below, our responses in plain text follow the reviewer's comments shown in *italics*.

1. *The authors present an analysis of multi-model simulations to gain insight into the drivers of OH and methane. Overall, I believe that this manuscript has significant deficiencies. Therefore I do not recommend that it be published without major additional analysis.*

We appreciate the reviewer for indicating the deficiencies in our manuscript. We have addressed some of these in the revised manuscript (see below). The primary concern the reviewer has is that we have not performed a thorough evaluation of OH and its drivers simulated by the models against measurements. Detailed model versus observation comparison may best be done in single model studies where the complexities of accounting for differences in sampling patterns, resolutions, averaging kernels etc. can be properly accounted for. Together with model evaluations performed by Lamarque et al. (2013) (temperature and humidity) and Young et al. (2012) (tropospheric ozone), one can get a picture of the skill of models in representing the atmospheric oxidizing capacity.

2. *The title and abstract are not clear in that I was led to believe that the entire 1850-2000 period was simulated. I recommend that it be explicitly stated in the abstract that the simulations are time slices. For the same reason, the first sentence of Section 2.1 is misleading – "investigate the historical evolution (1850-2000).."*

We have revised the abstract and Section 2.1 to clarify that we investigate the preindustrial to present day changes in OH and methane lifetime using time slice simulations. We feel that the title is appropriate as it states "preindustrial to present-day changes", which is consistent with the proposed revision. Further, the title is aligned with the titles of other ACCMIP papers that explore preindustrial to present/future trends (http://www.atmos-chem-phys-discuss.net/special_issue176.html).

3. *Major Concern: Unfortunately, I did not learn anything new about the drivers of OH and methane from this manuscript. I recommend that the authors explicitly say what new results are presented and how the analysis contributes to the scientific under-standing of methane and OH.*

To the best of our knowledge, this work is the first multi-model analysis of historical OH changes, though individual modeling studies have been conducted previously (as noted in 2nd paragraph, page 30760 of the manuscript). Our study is an analysis of the current generation of chemistry-climate models (CCMs) and demonstrates our current level of understanding of the historical OH trends. We have revised the manuscript to highlight the following key results of this work:

- All models overestimate OH abundance in the Northern Hemisphere.
- All models simulate a small increase in OH from 1980 to 2000 consistent with recent observation-derived estimates.

- There are significant uncertainties in our understanding of the long-term trends in OH and methane lifetime as indicated by the large inter-model diversity in the sign and magnitude of preindustrial to present-day OH/methane lifetime changes.

- Through the use of ΔCO/ΔNOx ratios simulated by the models (section 4.1 in the manuscript), we emphasize the need for better constrained natural precursor emissions and a concerted effort to evaluate chemical schemes implemented in the models.

The CCMs are becoming increasingly complex with the inclusion of several atmospheric processes that influence atmospheric radical chemistry. Our study probably does not provide a definitive answer on the long-term trends in OH, but by generating a hypothesis, we have confirmed the need for a coordinated process-oriented evaluation of CCMs, similar to that conducted for stratospheric processes (Eyring et al., 2005), to gain a better understanding of the drivers of atmospheric oxidation capacity.

4. *Major Concern: Most methane is lost in the lower (>600 mb) tropical/subtropical troposphere (so is methylchloroform), so why not focus the analysis of the model output in this region. There are a number of factors not discussed that drive OH, which do have observational constraints.*

While we agree that much of methane is lost in the lower tropical/subtropical troposphere, however, the models do vary in the vertical distribution of methane loss (see Figure 1 on page 11 of this document). Therefore, as suggested by Lawrence et al. (2001), we wanted to provide a full picture of tropospheric OH in our analysis rather than limit to a smaller subdomain. We also wanted to adhere to the definition of the tropospheric chemical methane lifetime (calculated as the total atmospheric burden divided by the tropospheric loss flux) in our analysis so that our results could be compared with previous modeling/measurement studies.

a. The overhead ozone column is a major driver of OH. Why didn't the authors compare the model output to the three decades of observations of the overhead ozone column?

Thanks for the suggestion. We have included a comparison of the late twentieth century trends in total column ozone simulated by ACCMIP models against measurements from the merged Total Ozone Mapping Spectrometer/solar backscatter ultraviolet (TOMS/SBUV).

b. Water vapor is another important driver, but there is no comparison of the model output to AIRS or MLS water vapor.

Water vapor/specific humidity simulated by ACCMIP models has been evaluated against AIRS data in Lamarque et al. (2013). We now summarize results from that analysis in our revised manuscript. MLS measures upper tropospheric water vapor and, as noted by the reviewer, this region is not relevant for CH_4 loss.

c. Clouds are another important driver and there are several datasets available for model evaluation.

We agree that clouds (and aerosols) impact photolysis rates and, therefore, drive OH changes. Clouds have been previously shown to have a relatively small influence on global scale but may play a more significant role on regional scales (Voulgarakis et al., 2009; Liu et al., 2006). Models differ in how they parameterize cloud effects on chemistry and the diurnal cycle of clouds is also critical in assessing the effects on gas-phase radical chemistry. A systematic evaluation of clouds to assess their role on OH in the models requires relevant cloud diagnostics from the models. Since only limited number of ACCMIP models provided cloud diagnostics, we are unable to perform a thorough evaluation at this time. Parent climate models of many of these ACCMIP models have been evaluated against "A-Train" satellite observations in an effort to assess the skill in simulating clouds by Jiang et al. (2012), who find that the models simulate water vapor and clouds better in the lower and middle troposphere than in the upper troposphere.

d. *There is now nearly a decade of observations of the tropospheric NOx column, another important driver of OH.*

We agree that a significant amount of satellite data (http://www.temis.nl/airpollution/no2.html) is now available to evaluate tropospheric NO_2 column from models. These, unfortunately, cannot be used to evaluate ACCMIP models as the model output was not sampled along sun-synchronous satellite orbits and local times. This is one of the endeavors of the Chemistry Climate Modeling Initiative (CCMI, http://www.pa.op.dlr.de/CCMI/CCMI_Obs4CCMI.html).

e. *Why not compare model tropospheric ozone with MOZAIC aircraft data? Possibly Young et al. (2012) discusses this, so please summarize their findings.*

Evaluation of model tropospheric ozone is beyond the scope of this paper. Young et al. (2012) evaluate ACCMIP model ozone against satellite (TES, OMI and MLS) and ozonesonde data. We use their analysis to inform our discussion of the simulated present-day inter-hemispheric OH asymmetry in the models (page 30768, lines 19-22).

5. *Section 3: The authors state that the "Models can be categorized into two groups…" Why these two groups? In the context of individual model uncertainty, what model trends in OH are statistically significant?*

We divided the models into these two categories because of the OH trends they simulate. However, we understand that this can be confusing as the models simulate a wide range of trends from increases to decreases. Therefore, we have revised the manuscript to remove this grouping and present the trends as a range of responses simulated by the models.

The large spread in the preindustrial to present day OH/methane lifetime changes simulated by models indicates large uncertainties in our understanding of their long-term changes. As discussed in section 4.1, we find that models that simulate strong increases in tropospheric CO burden compared with NOx burden, simulate decreases in present day global mean OH relative to preindustrial (except HadGEM2), while models that have larger relative increases in NOx compared with CO burdens simulate increases in OH (except GISS-E2-R and GISS-E2-R-TOMAS) (see Figure 3 in manuscript).

In section 4.1, we conjecture that the intermodel diversity in the simulated ΔCO/ΔNOx (and OH) trends is driven in part due to differences in emissions, particularly natural emissions (since models used the same anthropogenic emissions), arising from the different underlying chemical schemes (that dictate the amount of VOC emissions in the models) implemented in the models. Differences in stratospheric O_3 column and its influence on tropospheric O_3 photolysis, photolysis schemes, tropospheric dynamics, and interactions with aerosols could be playing a role. It is difficult to assess the individual model uncertainty without multi-member ensemble simulations.

6. *Section 3.1: Why not discuss the findings of Lawrence et al. (2001) here concerning the limitations of constraining tropospheric OH?*

Thanks for the suggestion. Following the recommendation of Lawrence et al. (2001), we have included a comparison of the regional OH distributions simulated by the models for the 2000 time slice in our revised manuscript. This would provide more information about the degree to which the OH distributions simulated by models agree or disagree and highlight the limitations of constraining tropospheric OH.

7. *In the last sentence of this subsection, the last word "observations" is not appropriate as there are very few direct observations of OH.*

In the last sentence of section 3.1 ("We test if OH sinks may also be too low in the NH compared with the SH, by evaluating the distribution of CO simulated in the ACCMIP models against observations in the following section."), we are referring to the observations of CO, i.e., we evaluate the simulated CO distributions against surface and satellite measurements in section 3.2 to test if OH sinks may be too low in the NH compared with the SH. We have rephrased this sentence in the revised manuscript for clarity.

8. *Why aren't the model distributions of methane compared to GMD and SCIAMACHY data?*

We did not compare the model methane distributions with GMD and SCIAMACHY data because all models, except LMDzORINCA, prescribe methane values either from historical reconstruction or from observations.

Response to Referee #2 for comments on "Preindustrial to present day changes in tropospheric hydroxyl radical and methane lifetime from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP)" by Naik et al.

We appreciate the reviewer's constructive comments on our paper.

Major comment

1. *One of the major findings of the work is that there are considerable differences between models in both the sign and the magnitude of changes in OH concentration and methane lifetime in the period 1850-2000. In several instances it is stated that these differences arise from the 'unique ways in which the chemical and physical drivers of OH interact within each model'. Given the aims of the paper, there needs to be a more in-depth discussion of these drivers and an attempt to establish which processes are the dominant factors in determining the reported changes.*

The large spread in the magnitude and sign of preindustrial to present day OH/methane lifetime changes simulated by models indicates large uncertainties in our understanding of their long-term changes. As discussed in section 4.1, we find that models that simulate strong increases in tropospheric CO burden compared with NOx burden, simulate decreases in present day global mean OH relative to preindustrial (except HadGEM2), while models that have larger relative increases in NOx compared with CO burdens simulate increases in OH (except GISS-E2-R and GISS-E2-R-TOMAS) (see Figure 3 in manuscript). We conjecture here that the intermodel diversity in the simulated ΔCO/ΔNOx (and OH) trends is driven in part due to differences in emissions, particularly natural emissions (since models used the same anthropogenic emissions), arising from the different underlying chemical schemes (that dictate the amount of VOC emissions in the models) implemented in the models.

Through the use of attribution experiments performed by a subset of models, we find that methane and NOx emissions are the dominant drivers of changes in OH/methane lifetime followed by CO and NMVOCs as discussed in sections 6 and 7 in the manuscript. The large intermodel diversity in the response of OH to NOx and NMVOC emissions reflects the differences in chemistry schemes implemented in the models and uncertainties in natural emissions.

Furthermore, differences in stratospheric O_3 column and its influence on tropospheric O_3 photolysis, photolysis schemes, tropospheric dynamics, and interactions with aerosols could be playing a role. We have added a stronger statement to the conclusions that summarizes these drivers.

Minor comments

2. *Pg 30759, line 21: Please consider changing 'O(1D) radicals' to 'O(1D) atoms'. Pg 30759, line 22: Please state that the reaction is with water vapor.*

Done.

3. *Pg 30759, line 23: The production rates of OH are highest in the tropical lower to middle troposphere for the reasons stated, it does not necessarily follow that the concentrations will* *be highest in this region.*

We have replaced “OH concentration” to “production of OH” in this sentence.

4. *Pg 30759, line 26: Please amend to 'OH has a tropospheric lifetime on the order of seconds.*

Done.

5. *Pg 30760, lines 7-9: It should be stated that OH rapidly cycles with the HO2 radical, and that H2O2 is formed from HO2 and not OH.*

Thanks. We have revised this sentence to:

“Conversely, in clean air the reaction chain can be terminated by the loss of HO2 and RO2 radicals (R3 and R4) via

$$HO2 + HO2 \rightarrow H2O2 + O2 \quad (R9)$$

$$RO2 + HO2 \rightarrow ROOH + O2 \quad (R10).”$$

Further, we now include chemical reactions (R1 – R11) in the manuscript to better clarify the tropospheric OH oxidation chemistry.

6. *Pg 30760, line 10: It should be made clear that the sources of OH in unpolluted forested low NOx environments are still uncertain. There are several papers now published which demonstrate this uncertainty and indicate that the mechanisms proposed by Lelieveld et al. (2008) and Peeters et al. (2009) cannot fully explain the observations.*

Thanks for the suggestion. We have revised the text as follows:

“Recent laboratory studies have indicated that reaction of selected RO_2 radicals with HO_2 can produce OH at significant yields (Dillon and Crowley, 2008 and references therein):

$$RO2 + HO2 \rightarrow RO + OH + O2 \quad (R11)$$

This has implications for NOx poor, VOC rich forested environments where radical recycling via (R5) and (R6) is suppressed. Several chemical mechanisms, proposed for the cycling of HO_2 to OH under low-NOx, high NMVOC conditions, are yet to satisfactorily reconcile discrepancies between models and OH observations indicating large uncertainties in our understanding of the atmospheric oxidation chemistry (Stone et al., 2012 and references therein).”

7. *Pg 30761: It should be noted that relatively long-term observations of OH do exist (Rohrer & Berresheim, 2006). There is also little mention in the manuscript of comparisons between observations of OH and model calculations which provide insight to the key drivers of OH concentrations.*

Thanks for bringing this reference to our attention. We have revised the text on this page as follows:

“Much effort has been placed on understanding the long-term trends and interannual variability in atmospheric OH concentrations over the past two to three decades. Long-term measurements of OH concentrations provide insight on its trend/variability over specific chemical regimes (Rohrer and Berresheim, 2006; Stone et al. 2012, and references therein). For an understanding of the changes in global mean OH in the absence of global scale observations, however, one must rely on measurements of trace gases whose emissions are well known and whose primary sink is OH."

We agree that comparisons between modeled and observed OH concentrations provide insight into the budget of OH and an understanding of the underlying chemistry (e.g. Stone et al. 2012 and references therein). However, a thorough evaluation of models against OH measurements (ground-based, aircraft) requires that we also compare model data with relevant co-measured species (e.g. HO2, H2O2, NO_x, VOCs and their oxidation products) sampled at the times and locations of the measurements since OH concentrations are highly variable in space and time. Because our simulations represent average climatological conditions, the interpretation of the differences in observed and modeled OH is problematic. A full evaluation is further hampered as all relevant species were not requested in the model output. Hence we do not compare modeled OH concentrations with observations in this study. In the revised manuscript, we have highlighted the importance of evaluating models against measurements of OH and relevant species.

8. **8.** *Pg 30763: A table summarising some of the key characteristics of the model would be helpful here in addition to the references provided.*

We would prefer not to add additional model summary here as this would be repetitive. Model characteristics important for OH and CH_4 lifetime are summarized in Table A1 of Voulgarakis et al. (2012) and detailed model description is provided by Lamarque et al. (2013). Both these manuscripts, in addition to others that use ACCMIP data, are accessible from http://www.atmos-chem-phys-discuss.net/special_issue176.html and http://www.atmos-chem-phys.net/special_issue296.html.

9. *Pg 39764, lines 3-5: What is the value for kOH+CH4 for those models not using the recommendation by Sander et al. (2011)? What is the range in the different values used between models and how much is this likely to influence the modelled OH and CH4 concentrations?*

Global mean k_{OH+CH4} for the 2000 time slice ranges from 2.99 to 3.14 x 10^{-15} cm^3 $molec^{-1}$ s^{-1} with a multi-model mean value of 3.07±0.04 x 10^{-15} cm^3 $molec^{-1}$ s^{-1}. Given that the relative standard deviation in global mean k_{OH+CH4} is less than 2%, this is unlikely to contribute significantly to the intermodel diversity in the simulated OH and CH_4 lifetimes. We have included a table with k_{OH+CH4} values in the supplementary information.

10. *Pg 30765: The authors state that the methane lifetime calculated using different definitions of the tropopause height vary by less than 3 %, and thus that the definition of the tropopause height has minimal effect on the methane lifetime. However, the paper concludes that in the period 1980-2000 the methane lifetime decreases by ~ 4 %. Are the 3 % changes in methane lifetime using the different definitions of tropopause height truly insignificant to the conclusions?*

It turns out that we made a mistake in our calculation of the differences in the methane lifetime using different definitions of the tropopause. The difference between methane lifetime for the 2000 time slice calculated with the tropopause at 200 hPa and that with the tropopause defined as air with ozone concentrations less than or equal to 150 ppb in the 1850 time-slice simulation is less than 1% as opposed to 3% in the manuscript. Furthermore, we calculate the percent change in 1980 to 2000 methane lifetime using the 150 ppb O_3 tropopause and find it to be -4.3±1.9%, which is exactly the same as that obtained using 200 hPa tropopause. Hence, we conclude that the definition of the tropopause height has minimal effect on the methane lifetime. We have revised the text to reflect this correction and included a table of methane lifetime calculated using the 150 ppb O_3 tropopause for the three time slices in the supplementary information.

11. *Pg 30766, line 10: Increased NOx concentrations increase the rate of cycling between OH and HO2. It is not strictly a source of OH since it is most likely that the HO2 will have been produced via OH in the first instance.*

We stand corrected. We have revised the sentence to:

"Despite similar imposed changes in emissions, specifically increases in the emissions of NO_x (contributing to secondary OH production), CO and NMVOCs (OH sinks) …"

12. *Pg 30766: The classification of models into two groups requires further discussion. Why do the models behave differently?*

We classified the models into these two categories because of the OH trends they simulate. However, we understand that this can be confusing as the models simulate a wide spectrum of trends from increases to decrease. Therefore, we have revised the manuscript to remove this grouping and present the trends as a range of responses simulated by the models. Models behave differently in part due to differences in emissions, particularly natural emissions (since models used the same anthropogenic emissions), arising from the different underlying chemical schemes (that dictate the amount of NMVOC emissions in the models) implemented in the models. Please see response to reviewer #1 comment 5 for more information.

13. *Pg 30767, line 18: There should be some further discussion here of OH observations in the atmosphere. Aircraft measurements in particular offer information regarding OH concentrations over large spatial and temporal domains.*

Please see our response to comment #7.

14. *Pg 30771, line 28: Why does the HadGEM2 model show no change in OH?*

Without additional sensitivity simulations, it is difficult to ascertain why HadGEM2 shows no preindustrial to present-day OH change despite ΔCO/ΔNOx implying a large positive change. It would appear that the positive and negative influences on global OH in HadGEM2 are cancelling out. It is not odd in itself that HadGEM2 shows no OH response since there is a wide spectrum from increases to decreases - so it is not surprising that a model happens to be on the border by chance.

15. *Pg 30772, line 18: There are a number of other papers which have attempted to assess the validity of tropospheric chemistry schemes used in models which ought to be referenced.*

We have included the following references to highlight previous work on the comparison of tropospheric chemistry schemes: Luecken et al. (2008), Emmerson and Evans (2009), and Chen et al. (2010).

16. *Pg 30776, line 14 and pg 30778 line 6: There are a number of other important papers which address the response of OH to biogenic NMVOCs which ought to be discussed/referenced.*

In addition to the studies already cited, we have included the following references to emphasize that the response of OH to biogenic NMVOCs is an area of active research: Hofzumahaus et al. (2009), Whalley et al. (2011), Lu et al. (2011), Elshorbany et al. (2012) and Mao et al. (2012).

References:

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Figures

Figure 1. Percentage of methane oxidized in various subdomains of the atmosphere simulated by the ACCMIP models for the 2000 time slice. Red and blue indicate regions where percentage of methane oxidized is greater and lesser than the multimodel mean value, respectively.