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 the reviewer for his/her valuable comments and suggestions. His/her 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 #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 We also make clear the C1 photochemical scheme is likely outdated.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 ($\Delta \mathrm{SST}_{15^{\circ}\mathrm{S}-^{\circ}\mathrm{N}}$) of -1.2°C. The "cold LGM" uses SSTs from Webb et al. (1997) who found $\Delta \mathrm{SST}_{15^{\circ}\mathrm{S}-^{\circ}\mathrm{N}}$ 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 $\Delta \mathrm{SST}_{15^{\circ}\mathrm{S}-^{\circ}\mathrm{N}}$ 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: $\int_{\text{surface}}^{\text{tropopause}} k_{CH_4+OH}(T)[OH][CH_4]\,dx\,dy\,dz$. 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 $J_{O_3} q\, S_N / \left({S_C}^{3/2}\right)$ 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 $J_{O_3} q\, S_N / \left({S_C}^{3/2}\right)$ 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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