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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Uncertainties in isoprene photochemistry and emissions: implications for the oxidative capacity of past and present atmospheres and for trends in climate forcing agents" *by* P. Achakulwisut et al.

Anonymous Referee #2

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General Comments The work presented in this manuscript builds on the model study from Murray et al (2014) to explore the model space around the tropospheric oxidative capacity of the atmosphere using modeled conditions during specific time slices from the LGM, preindustrial, and present day. The authors apply three chemistry schemes and two CO2 sensitivities based on recent advances in our understanding of isoprene emissions and photochemistry.

The modeling work and subsequent analysis appears to have been a lot of work. How-

ever, it is not clear to me that this work has advanced scientific knowledge. The experimental setup includes new parameterizations for isoprene emissions, photochemistry, and CO2 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?

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)?

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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.

Specific Comments

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.

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.

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'.

Pg 2201 ln 3: the word 'but' seems out of place. Was this supposed to be 'and'?

Pg 2203 ln 9: missing a space between H2O and uptake.

Pg 2204 ln 9: Trends again.

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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 . . .".

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 CH4 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.

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.

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

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it probably should not be included in those regression lines.

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.

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.

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 $\sim$10 years, are sources and sinks in equilibrium at the end of 10 years? Does CH4 change with time in the model? Regardless, the authors should have a statement addressing equilibrium conditions in the model here.

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)

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.

Pg 2212 ln 7: What year does the CH4 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

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weighted to account for unequally spaced stations?

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?

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.

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.

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.

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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.

Pg 2214 ln 28: ". . .values ranging from 3 to 42%" this should be ". . .values ranging from 35 to 42%"

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?

Pg 2214 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.

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.

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.

Pg 2216 discussion of CH4 lifetimes: Something that I find to be curious about this

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discussion is that they are showing a fairly large range of CH4 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 CH4 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 CO2 sensitivity and C2 without CO2 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 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 CH4 emissions in the LGM. Is this the message that the authors wish to convey with this figure?

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.

Pg 2217 ln 11: Doesn't the C1 with CO2 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?

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.

Pg 2218 ln 3-6: I got really confused in this for example case, but eventually I think I

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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."

Pg 2219 ln 18: It would be useful if the authors reported the Rˆ2 values for C2 and C3, even (especially) if they are not statistically significant.

Pg 2220 ln 4: Technically speaking, they show n=3 in Fig 7 since Present Day is run only WITH the CO2 sensitivity. Granted it should be nearly the same, but I think they should explicitly say this.

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.

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.

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?

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Pg 2221 ln 21: Did the authors leave out a word at the end of this sentence? "...a new photo-oxidation PATHWAY"?

Pg 2221 ln 23-25: Again this claim of novelty seems out of place. See earlier comment.

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?

Pg 2223 ln 12: Same question as on Pg 2217 ln 11, see above.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 2197, 2015.