Author response to reviews for "Evaluating Simplified Chemical Mechanisms within Present-Day Simulations of CESM Version 1.2 CAM-chem (CAM4): MOZART-4 vs. Reduced Hydrocarbon vs. Super-Fast Chemistry"
By Benjamin Brown-Steiner et al.

We first want thank the reviewers for their valuable and insightful comments, and for taking the time to review our manuscript.

We now respond to the reviewer comments, which are reproduced in black text below. Our responses follow immediately in red text, and any additions to the manuscript are included in italic red text, along with Line references, which refer to their locations in the revised manuscript.

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Editor, F. O'Connor:

Dear Benjamin and co-authors,
As the topical editor for your manuscript, may I remind you that I'm requesting that the data be made available on a suitable repository with a digital object identifier (DOI) before final publication of your manuscript in GMD. Reference to this repository can then be included in your final manuscript. I trust that this will be acceptable to you.
Regards, Fiona O'Connor

We have uploaded the relevant data to a repository hosted on the MIT domain (http://dspace.mit.edu/handle/1721.1/114993). The Data/Code availability sections have been updated to direct readers to this repository, as is discussed in the comments below.

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Anonymous Referee #1
Received and published: 13 March 2018

Brown-Steiner et al present a study of how two reduced chemical mechanisms perform in a number of comparisons against the more comprehensive MOZART scheme (MO). The Reduced Hydrocarbon mechanism (RH) contains around half the number of MOZART reactions, whilst the Super-Fast mechanism (SF) is about 1/6 of MO. The work has been done to explore how much of a compromise it is by choosing one of these simple mechanisms over the more comprehensive scheme, when considering computational time gains versus accuracy of the chemical predictions.

The model runs have been conducted on a global scale for 25 years. This has enabled the authors to pull out modelled data to compare with each other, and for the time periods and locations of ozonesonde, aircraft and CASTNET observations. Given how small SF is, it performs unexpectedly well, particularly against the CASTNET data, and in some cases better than the

other two schemes. The RH scheme often tracks MO quite well, but with some exceptions, particularly for CO.

The Super-Fast mechanism could be used to explore chemical sensitivity studies in a fraction of the time it would take to run MOZART in locations of low biogenic activity.

I think the manuscript fits within the GMD journal remit and should be published. I have a few minor comments and queries.

General comments:

Please check throughout for the consistency about the length of the run. Page 6 line 1. 'we use MERRA.. for 25 years (1990 – 2014)'. However figure 1 plots maps for the year 2015, and figure 4 shows vertical distributions for 2015? Figure 6 also looks like it starts at 1991, not 1990 and carries on beyond 2014. Same applies to the statement on page 9, end of line 13 about the run being 1990-2014. Also figure 7 'for the full 1990-2015 time series', which is 26 years.

We ran the simulations for 26 years (1990 – 2015) and used the first year as spin up, so the analyses are for 25 years (1991 – 2015). We have corrected the descriptions and added a line indicating the 1990 year as spin up:

Page 6, Line 2: "…for 2*6* years (1990 – 201*5*)…"
Page 6, Lines 3-4: "*The year 1990 is dropped to allow for spin-up.*"
Page 9, Line 24-25: "…sites throughout the *1991 – 2015* period…"
Figure 7, Caption: "…the full *1991* – 2015…"

Section 2.2.1 MOZART-4. This section is very short and doesn't give the reader much information about MOZART other than to go searching through the suggested literature. I think a bit more information on what the scheme includes (e.g. how many alkanes/aromatics/biogenic species are considered explicitly) and omits would be useful, particularly as it is being used as the benchmark scheme.

We have added additional details and point again to Emmons et al. (2010) for a complete description.

Section 2.2.1: "*As described in detail in Emmons et al. (2010), MOZART-4 mechanism is a tropospheric mechanism that contains 85 gas-phase species and 12 bulk aerosol species, with 39 photolysis and 157 gas-phase reactions. Large alkanes, alkenes, and aromatics are lumped together (BIGALK, BIGENE, and TOLUENE, respectively), and monoterpenes are lumped together as C10H16 and treated as α-pinene.*"

Page 9 line 1. Please describe what 'BAM' means

Page 9, Line 10: "…the *Bulk Aerosol Model* (BAM) *(see Tilmes et al., 2015)*…"

Page 10. Line 20. There is a single line describing figure 6 and I then didn't fully understand the results drawn from it. My assumption is that the range of ozone at each time step in the model has been extracted for the region and the differences in the percentiles plotted here (although the

figure caption says the CASTNET observations are only for JJA?). The results say it takes 5-10 years for the models to stabilise, but the plots also show that the CASTNET observations themselves need 5-10 years to stabilize? If the models are behaving similarly to the observations, why would we need the spin up? There's a bit of a leap of understanding, so I think a bit more description is needed. I can see why you would expect the range in predicted ozone to settle as times goes on using constant emissions – but why also in the observations?

In a concurrent paper under review in ACPD (Brown-Steiner et al., in review) we expand on the implications of this figure. We add additional clarifications of Figure 6 and point to reader to the concurrent paper for additional discussion. We also add this paper to the references.

Page 11, Line 5: "*Brown-Steiner et al. (in review, ACPD) examines these implications, and also concludes that it takes approximately 10-years for long-term signals to emerge from meteorological variability. These results demonstrate the challenge in examining chemical signals in highly variable data, particularly if there are trends or changes to the ozone distribution, as is seen in the CASTNET data for the Southeastern US.*"

Page 14 line 16 spelling. 'mechanism', not 'mechanisms'.

Corrected.

Figures:

Figure 5, panels g,h and i. what does the 1x1 refer to?

They are individual grid cells within each region. This has been added to the caption.

Figure 5, caption: "*Plots g, h, and i are individual grid cells from within each region*."

Figure 7. Titles overlap with plots.

The figure has been updated to correct this.

Figure 8. I'm struggling to see the orange N_2O_5 line in any of these plots. It could be that the line is hidden under the PAN+N_2O_5 line, but given the variation between PAN+N_2O_5 and N_2O_5 in the global ozone plot, I expected to see it?

The figure has been updated so that each line is more easily discernable.

Figure 8. Which single year are these seasonal cycles for? Why was this particular year chosen? How much variability is there between the first year run (1990) and the last (2014)?

Year 2015 was selected as a representative year, and we find some variability year-to-year due to meteorology, but all models tend to demonstrate the same year-to-year variability. For the sensitivity tests with PAN and N_2O_5, we only ran 2 years and selected the 2nd year (1991). We

also discovered a bug in the plotting code in the sensitivity tests which has been corrected. Some of the seasonal cycles were offset by 2 months, and but does not impact our conclusions.

Figure 8, Caption: "…single year *(2015)*, averaged…"

Figure 9, Caption: "…SF mechanism *(which were ran only for 2 years, 1990 – 1991, with 1991 being plotted here)*…"

Figure 9. Please give the location of the grid cell, (lon, lat).

This has been added to the caption of Figure 9.

Figure 9, Caption: "*(100˚ west and 47˚ north)*"

Figure 10. please add units.

Added.

Figures, general comment:
About half way through the figures the colour scheme changes. In figures 2,3,5 and 6 MO is red, RH blue and SF is green. Later in figures 8 and 9, MO is black, RH is still blue but SF is now red. For the quick skimming reader, the assumption is that red is the benchmark scheme. It's a bit confusing.

All figures have been updated to remain consistent with the color schemes (MO red, RH blue, SF green).

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Anonymous Referee #2
Received and published: 21 March 2018

Brown-Steiner et al. have performed an evaluation of the performance of a model of atmospheric chemistry run with three different chemical mechanisms to understand how big an impact there is by choosing a different chemical mechanism (network). This is an interesting paper, an important bit of science, and one of only a few examples in the literature to do this sort of work in a 3D sense. Evaluating the performance of these different mechanisms enables sound conclusions to be drawn about their utility. The aim is to see if a very simple mechanism, which would enable much longer (or many more) integrations as solving the coupled ODEs in the chemical network is computationally very expensive, is suitable. This is a very well written paper and I could hardly spot any typos or grammatical errors above those spotted by reviewer #1. However, I would like to see further experiments performed before I would recommend that this be published. As it stands, I don't think the suitability of the Super Fast (SF – simple chemistry) scheme to be used beyond a present day set up has been demonstrated.

And I think this is key for the argument that the SF scheme is suitable. The present work focuses on fairly long integrations (25 years or so), where anthropogenic emissions are fixed but

interactive biogenic emissions can change as the meteorology in the model changes. Some very nice analysis is then performed against surface observations of O3 which emphasises that for these conditions, the SF scheme performs well – in accord with the other more complex schemes.

But, to be convinced that the SF scheme is suitable for long simulations of transient forcing, I would like to see simulations that test the response of the chemical schemes to the sorts of changes that have happened over the Anthropocene and for which the SF scheme may well end up being used for within CEMS (i.e. CMIP/AerChemMIP type experiments). For example, I would like to see, as a minimum, a set of simulations using ACCMIP pre-industrial emissions (you could keep the meteorology fixed as it is if that makes things easier) so that we can see what happens between these different schemes when they are perturbed with significant changes in NOx and VOC (CH4).

The Super-Fast mechanism was included in ACCMIP studies in both historical and future conditions (as reviewed in the Supplemental Material), although a full description is not in the scientific literature. We hope this manuscript allows other researchers to more easily find and utilize the SF mechanism and that this manuscript can serve as a baseline for future simulations and testing.

As this study is intended as a demonstration of the Super-Fast mechanism's utility, rather than a comprehensive evaluation, and as we have only analyzed present-day, we have added "Present-Day" to the manuscript title "Evaluating Simplified Chemical Mechanisms within *Present-Day* Simulations of CESM …"

Demonstrating the capabilities of the Super-Fast mechanism for long-term transient forcing was beyond our scope and capabilities, and we agree that more work needs to be done with the Super-Fast mechanism (as well as the Reduced Hydrocarbon mechanism), and that care should always be taken when any model component is utilized outside of previously demonstrated periods and conditions. As such, we have made sure that the mechanism files are available (see reproducibility comment below), and we are in discussion as how to best integrate these mechanisms into available forms at the NCAR/CESM website.

In light of this, we have added language that makes clear the limitations of this manuscript and future research directions which will be needed to further study the utility and capabilities of the Super-Fast and Reduced Hydrocarbon mechanisms, as well as made clear where the code can be accessed (see comment below).

Abstract: "Here we present and compare three 25-year *present-day* offline simulations…"

Page 14, Lines 27-28: "…we have compared three chemical mechanisms of different levels of complexity within the CESM CAM-chem framework *for present-day chemical and climatological conditions.*"

We have also added language in the conclusions highlighting that this study is only for present-day conditions:

Page 14, Lines 36-40: "*We examine present-day chemistry with MO, RH, and SF. Both MO and SF have been compared in other model intercomparisons, including for preindustrial conditions (see the Supplemental Material for additional information). We hope that the analysis presented in this paper, and the availability of the mechanism files (Supplemental Material) will provide a baseline for continuing research of both the RH and SF mechanisms.*"

I also am a bit concerned with the reproducibility of these experiments outside of the team working on this. There are no mentions of compsets (is that the word used within the CESM model set ups? I'm going from here http://www.cesm.ucar.edu/models/cesm1.2/casename_conventions_cesm.html) that have been used. Citing some rather old papers as the sources of the rate constants and reactions used, for example in the Reduced Hydrocarbon scheme, makes it difficult for others to test the schemes without large potential for making translational errors (I know, I have made many myself!). I would propose that the mechanism data files be made available (perhaps in a simple scv format?) or at least the compsets for these experiments be made available so that others can perform their own tests. GMD is a journal dedicated to holding high standards with code and I think that the mechanisms should be treated as a bit of complex code that should be archived in order to be more easily tested. This would be desirable but I can appreciate that this may not be top priority.

We have added to the data uploaded to the archive (http://dspace.mit.edu/handle/1721.1/114993) the chemical mechanism input files (reduced_hydrocarbon.in and superfast.in) and add additional text to the methods section and code availability section to direct readers to various CESM/NCAR resources. We clarify that we use the FMOZSOA compset for the MO simulation and make modifications to the chemical mechanism input file and speciation of species, as described in the text.

Page 6, Lines 22-25: "*The chemical mechanism input files for MO is available in the standard CESM release (http://www.cesm.ucar.edu/models/cesm1.2/) and the chemical mechanism input files used for RH and SF are archived (see section on Code Availability)*"

Page 6, Lines 36-39: "*We use the FMOZSOA compset (see http://www.cesm.ucar.edu/models/cesm1.2/cesm/doc/modelnl/compsets.html) and make modifications to the chemical mechanism input files (see section on Coda Availability) and emission files for the following mechanisms.*"

Code Availability: "*The chemical mechanism files for both RH (reduced_hydrocarbon.in) and SF (superfast.in) are included in the Supplemental Material.*"

Supplemental Material: "*The SF mechanism is in the CESM code archive as an unsupported chemical mechanism, which can be activated using the option '-chem super_fast_llnl'.*"

Minor corrections/comments:

Page 8, line 23: A key conclusion of Squire et al. was that sign of the response to changes in emissions of isoprene was different in SF compared to more complex schemes traceable to our best understanding of the chemistry of isoprene (ie. The MCM). I think this needs to be acknowledged here in addition to current acknowledgement that "there are biases in regions of high biogenic chemistry".

We have added language to this section to highlight this Squire et al. (2015) conclusion:

Page 8, Lines 37-40: "*Schnell et al. (2015) also conclude that the SF mechanism responds differently than other more complex mechanisms, particular under different O_x production regimes (e.g. SF shows a net increase in O_x production when isoprene emissions increase in NO_x-limited regions, which the other mechanisms show a net decrease, or little change).*"

I note from Table S2 and from the discussion in Squire et al., that the SF scheme does not include NO3. Presumably the bias in isoprene at night (Figure 9) could be solved by simulating NO3 in the SF scheme? Have the authors considered this? It was not clear from the manuscript if that was tested in addition to the nice tests looking at the impacts of adding in PAN and N2O5.

The authors did not test the addition of NO3 to the Super-Fast scheme. The addition of the PAN and N2O5 sensitivity tests are intended primarily as a demonstration of the type of simulations and sensitivity studies that the Super-Fast mechanism allows for.

To this point, we have added language in the manuscript that speculates about the addition of NO3 to the Super-Fast mechanism:

Page 15, Lines 16-18: "<u>*The SF mechanism does not include NO_3, which may also explain some of the nighttime biases. Future simulations in which NO_3 chemistry is added to the SF mechanism may correct some of these biases.*</u>"

Table S2, reaction 14: "idential" should be "identical".

Corrected.

Figure 8: Axis labels are way too small. Please make bigger. As above for Figure 9.

Figure 8 font sizes have been increased, and we will work with the editors to see if this plot can be included as a full page. If not, we will work with the editors to make sure they are readable. Figure 9 font sizes have been increased.

How are the VOC emissions dealt with between the different schemes? I presume that there are different amounts of VOC that go into the simulations? Please can you clarify the magnitude and distribution amongst molecules of the VOC emissions. Emissions are a key part of the chemical mechanism in my opinion.

Supplemental Table S1 includes the mapping of VOC species from MO to RH (which is discussed in section 2.2.2). For SF, we mapped only the MO ISOP species directly to the SF ISOP species. We have also added some text discussing this point:

Page 8, Line 9: "*We map the MO isoprene directly to the single SF isoprene species (ISOP).*"