

We sincerely thank Alexander for his valuable feedback that will help to improve our manuscript. Below we provide point-by-point responses (in red) to Alexander's comments (reproduced in black italics), with modifications to the manuscript indicated in **bold**.

*Stanton and Tandon present numerical model calculations, which aim to attribute the role of Volatile Organic Compounds (VOC) on climate. This is a worthwhile question and progress on the topic is needed in light of efforts like the WCRPs Lighthouse Activity on "Explaining and Predicting Earth System Change". However, this study falls significantly far from being able to answer the question. I think the authors should be commended for their attempt with the modelling but significant flaws in the model design mean that they are unable to answer the problem they have set out to. I would suggest a significant revision, including a change of the title of the manuscript if the present results are to be used as the underpinning data for a revision.*

*Good points:*

*Overall the manuscript is well written. The climate analyses are excellent and the team are clearly experts in this area.*

Thank you for this positive feedback.

*Bad points:*

*The experiment design is very much flawed in being able to answer the question of VOCs impacts on climate. We have known for a long time that the effect of VOCs is non-linear on key climate forcings (e.g., O<sub>3</sub>, CH<sub>4</sub>, aerosols). By removing the VOCs one is significantly perturbing the system into a state which does not allow the role of VOCs to be teased out. The study answers the question: "What are the impacts of removing VOC chemistry on pre-industrial climate simulated by CESM2". This is a useful question but far from the grander question raised by the title. I think this point is a critical one that can not be addressed without addressing the core of the study/revising the aims and scope.*

Thank you for this feedback. We agree that the influence of VOC chemistry would depend on levels of other atmospheric constituents like ozone, methane and aerosols. For this reason, we do not think it would be feasible in one paper to answer the general question of how VOC chemistry influences climate across all possible climate states. For the question to be well-posed, the base climate state needs to be specified. We make clear in the abstract and text that we focus only on preindustrial simulations, which is such a standard assumption for a base climate state that we didn't think it was necessary to specify that in the title as well. But prompted by your feedback, we will modify our title to be "How Does Tropospheric VOC Chemistry Affect Climate? An Investigation of **Pre-Industrial Control Simulations** Using the Community Earth System Model Version 2." This hopefully makes it absolutely clear that we are looking at just preindustrial climates.

As for your comment that "By removing the VOCs one is significantly perturbing the system into a state which does not allow the role of VOCs to be teased out." We agree that removing VOCs entirely would be a potentially extreme perturbation to the chemistry-climate system, with a whole chain of possible effects that would likely be hard to disentangle. But it would be

misleading to say that VOCs are absent in our MACtl simulation. Rather, in MACtl, the chemical reactions involving VOCs are absent, and they are replaced by the SOAG scheme (Liu et al., 2012; Emmons et al., 2010). So the difference between WACtl and MACtl is not the presence of VOCs but rather the presence of VOC *chemistry*. We will add text to Section 2 of the manuscript to make this clear.

*As someone who has looked at aspects of the title problem I am very surprised by the large changes in surface temperature that the authors show in Figure 1. The small difference in Global Mean Surface Temperature (GMST) suggests that the surface response is really not that significant. How does that compare to the spread of PI GMST simulated by CMIP6 models or even ensemble members of CESM2? Are these changes really significantly different from the uncertainty in the literature? The model we use in the group, UKESM-1-LL, shows significant variance across ensemble members (even under PI conditions). As it currently stands, I don't think the results suggest that there is a significant impact of VOC chemistry on climate; BUT as I said I am not sure that the experiment design allows one to answer this question.*

Thank you for this feedback. Hopefully, our response to your previous comment clarifies our experimental setup's relevance to the scientific question. Given that SOA effects can be highly regional, we should not necessarily expect a large GMST response to VOC chemistry. While our statistical significance tests provide some confidence that our surface temperature responses are significant, we can show some additional results to increase confidence in the robustness of our results. First, we have extended our simulations by 70 years so that the averaging period is now 211 years. Our revised manuscript will show results from these extended simulations, and the updated Fig. 1 is reproduced below as Fig. R2-1. All of the key features in these results are the same as in the submitted manuscript, indicating that internal variability was not strongly influencing our results.

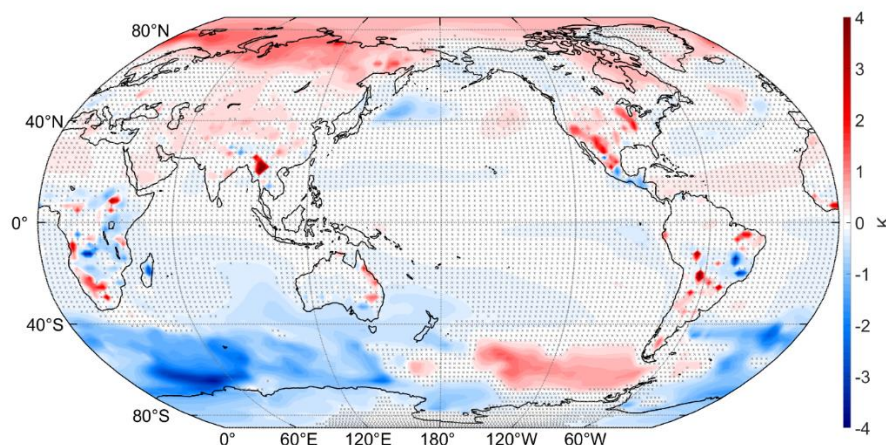


Figure R2-1: Annual mean difference (WACtl – MACtl) in surface temperature (K) from 211 years of model output. Gray crosses indicate regions that are not statistically significant, with uncrossed regions being statistically significant at the 95% level.

We do not think it would be particularly helpful to look at the spread among different CMIP6 models, as that spread can be due to intermodel differences in climate states, not just internal

climate variability. Furthermore, in the CESM2 large ensemble, the atmospheric component was the Community Atmospheric Model (CAM), not WACCM, so it would not cleanly compare with our simulations. The CMIP6 archive does include a preindustrial control simulation using the same configuration as our WACtl simulation, but it is only 250 years long, which is not long enough to be helpful for this discussion. However, the CMIP6 archive also includes a 500-year preindustrial control simulation using the same configuration as our MACtl simulation. This is long enough to give an indication of internal variability when averaging over time periods comparable to the lengths of our simulations.

Below is the difference in surface temperature when averaging over non-overlapping 211-year time slices in this CMIP6 control run of CESM2-WACCM6. Each of the panels shows a different choice of averaging period, and they are plotted on the same shading scale as used in Fig. 1 of our manuscript and Fig. R2-1 above. None of these calculations shows temperature differences comparable to the significant temperature differences shown in Fig. R2-1. This analysis further establishes that the responses shown in our simulations are not due to internal climate variability, and the responses represent the preindustrial climate effects of VOC chemistry. We will add this analysis to the manuscript.

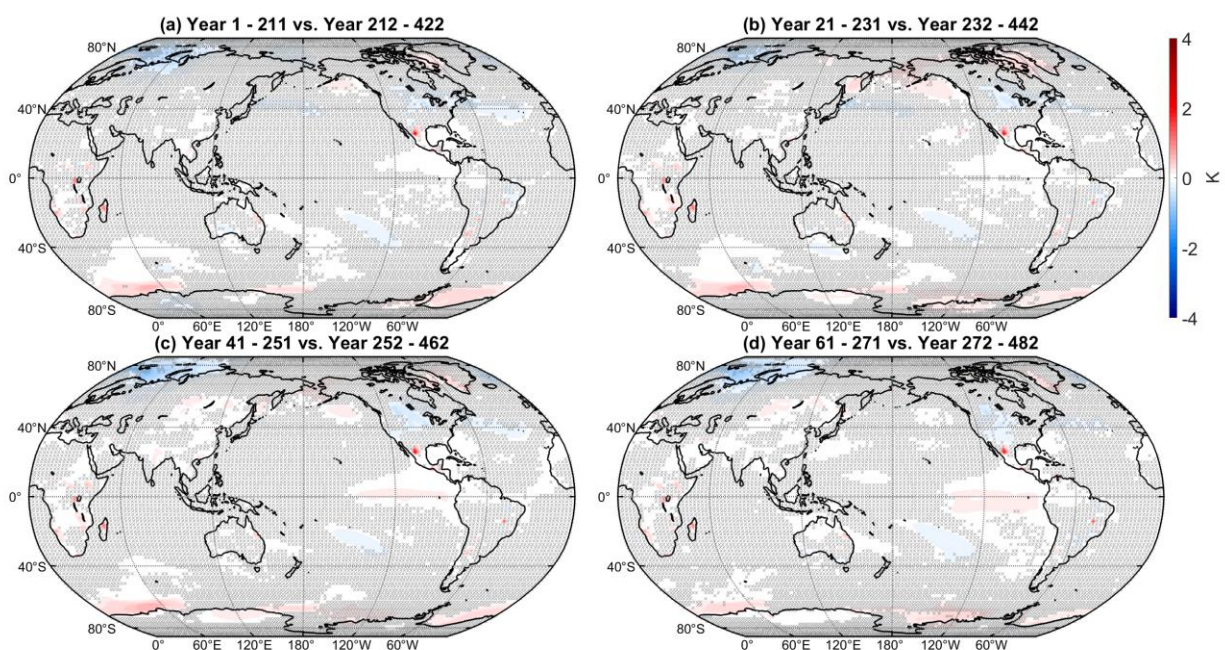


Figure R2-2: Difference of time-averaged surface temperature between non-overlapping 211-year time slices of the CMIP6 preindustrial control simulation of CESM2-WACCM6-FV2 (variant label r1i1p1f1). This simulation uses the same configuration as our MACtl simulation. The precise simulation years that were averaged are indicated in the title over each panel.

*What was also lacking for me was more of a focus on the causal links between tropospheric composition changes and their impacts on radiative forcings. There is clearly a very large response in OH. Why? I would guess the removal of isoprene, which has been addressed before, many times (see e.g., Bates and Jacob, 2019; Squire et al., 2015; von Kuhlmann et al., 2004). I was surprised not to see mention of isoprene at all in any analyses. Moving from OH one can*

*then identify the impacts of changes in oxidising capacity on aerosols and aerosol precursors. What happens to SO<sub>2</sub>? Why does Sulfate change the way it does? Some of this can only be understood by constructing budgets of the variables (production and loss) and analysing them. Like I said the climate analysis is good but the attribution to composition changes leaves a lot to be desired and can be thoroughly improved to provide insight into causality (but not attribution of it!).*

Thank you for this feedback. Just to clarify, isoprene chemistry is included in WACtl but not in MACtl. Yes, the addition of isoprene chemistry in WACtl likely explains the large decrease in OH relative to MACtl. We will add details of the impacts of isoprene chemistry in the results section under figure 10 along with references to the earlier studies you mention (Bates and Jacob, 2019; Squire et al., 2015; von Kuhlman et al., 2004). For example, L485 **“The reduction of tropospheric concentration of OH due to the inclusion of isoprene chemistry has been well documented in the literature (e.g., Bates and Jacob, 2019; Squire et al., 2015; von Kuhlman et al., 2004). To illustrate this link in the chain, ...”**. The influence of OH versus precipitation on SO<sub>2</sub> and sulfate changes will be addressed in a comment below.

*In additio to these minor comments I have more minor comments:*

*L26: The abstract is missing a conclusive statement at the end.*

The following statement will be added to the end of the abstract: **“Some of these responses are quantitatively large enough in some regions to motivate investigation of possible influences of VOC chemistry on anthropogenic climate change.”**

*L38: I don't think oxidization is a word. Change to oxidation.*

Thank you for catching this, we will correct this to **“oxidation.”**

*L41: Not clear how RO<sub>2</sub> makes NO<sub>3</sub>. Add a reaction or reference. Need to define HO<sub>2</sub> and RO<sub>2</sub>.*

Sorry for the confusion here. We should have said RONO<sub>2</sub> instead of NO<sub>3</sub> here. The manuscript will be modified here as follows: **“These peroxy radicals (RO<sub>2</sub>) can participate in further oxidation reactions, producing a range of products, such as organic nitrates (RONO<sub>2</sub>) and hydroperoxyl radicals (HO<sub>2</sub>).”**

*L45: Not only "typically". Actually. That's the nature of a CTM. See Young et al (2018) for an overview of the types of models and feedbacks/couplings and adopt that nomenclature.*

Thank you, we will change “is typically” to **“by design is”** and we will insert the CTM acronym here in order to adopt standard nomenclature.

*L56: They didn't have to prescribe SSTs. They chose to. there are still elements of climate response with fixed SSTs and the use of fixed SSTs is the defacto method for calculating key climate metrics like ERF.*

Thank you, we agree. The text here will be changed to the following: **“Climate simulations with more comprehensive chemistry typically prescribed sea surface temperatures (SSTs) (e.g.,**

**Tilmes et al., 2019), which facilitates calculating some climate metrics like effective radiative forcing (ERF) (e.g., Forster et al., 2016), but this approach limits the ability...”.**

*L61: Define NO<sub>x</sub>.*

On L61 the following will be added after NO<sub>x</sub>: “(NO<sub>x</sub> = NO + NO<sub>2</sub>)”.

*L73: ...limits the model’s ability to produce a "full" climate response. Add "full".*

Thanks, we will add “**full**” here.

*L84-85: Absolute temperature variations across climate models is way larger than this. Anyway, what is key to climate change is the difference between simulations under different forcings within a model. This statement can be misconstrued and so needs to be toned down, alot. I still don't see the surface temperature response as being at all significant so would like to be convinced more on this point.*

Our response to your earlier comment hopefully provides reassurance about the robustness of our results within the framework of CESM2-WACCM. (And we agree, the spread across CMIP6 models isn’t the key consideration here.) We see that our statement here could be misconstrued to challenge the role of greenhouse gases in future climate change. So, we will modify the text here as follows: “When the effects of tropospheric VOC chemistry are isolated, our simulations show significant impacts on climate, comparable in some regions to the temperature changes **expected from greenhouse gas increases** over a century in future climate change scenarios.”

*L87: Typically RONO<sub>2</sub> are formed from RO<sub>2</sub>+NO too. Should be made clear if BVOC+NO<sub>3</sub> is the only route to RONO<sub>2</sub> or if there are other routes, too. And what Organic Nitartes are comprised of in the model. PAN?*

BVOC + NO<sub>3</sub> is not the only route for RONO<sub>2</sub> in the WACtl case. RO<sub>2</sub> + NO is also included. PAN is included in WACtl, but not in MACtl. In WACtl, organic nitrates consists of PAN and a number of other species (Emmons et al., 2020). We will update the manuscript here to clarify this.

Based on further investigation of how NO<sub>y</sub> is treated in the model, we will be updating much of this section. For example, we recently learned that, while gas phase NO<sub>y</sub> is included in the model, the condensed phase (which impacts radiation) is lumped with sulfate aerosols. This matter will also be addressed in a comment below.

*Table 1: It’s unclear how key reactions, like the CH<sub>4</sub> oxidation, varies between experiments. Neither is it clear what the emissions of NO<sub>x</sub> and VOCs are.*

The CH<sub>4</sub> oxidation reactions are the same in WACtl and MACtl, with the only difference being a CH<sub>4</sub> production term in the WACtl case. This production term enters into the reaction of propene with ozone (O<sub>3</sub> + C<sub>3</sub>H<sub>6</sub> → C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> + HCHO, C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> → CH<sub>4</sub> + CO<sub>2</sub>).

The emissions of VOCs are addressed further down in the manuscript (see L189 to L193). NO<sub>x</sub> emissions are addressed on L184 and L193-194. This will be clarified in the revised manuscript.

*L143: So there is no methane? No CO? Why? NB I am not saying CO is a VOC.*

CH<sub>4</sub> and CO are solution species in both MACtl and WACtl. The manuscript will be updated here to make this clear: “any explicit **non-methane VOC (NMVOC)** chemistry in the troposphere,…”

*L175: I agree HONO is important but many things are missing that are important for ozone (see for example my review paper on tropospheric ozone, Archibald et al. 2020). The focus on HONO seems quite parochial.*

Thank you for this comment. A large majority of the species present in Table 1 of Archibald et al. (2020) are present in WACtl except HONO, CH<sub>3</sub>CH(OO)CH<sub>3</sub>, CH<sub>3</sub>CH(OOH)CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>CO, C<sub>2</sub>H<sub>5</sub>C(O)OO, PPAN, MeONO<sub>2</sub> (assuming this is CH<sub>3</sub>ONO<sub>2</sub>), MSA, and DMSO. To our knowledge, besides HONO, none of these additional species are expected to be important for ozone. Note that in Table 1 of Archibald et al. (2020) there may be a typo. The variable named MGLY has the formula (CH<sub>3</sub>COCHHO), but it appears this is meant to be methyl glyoxal, which has the formula (CH<sub>3</sub>COCHO).

*L198: I think this is a major weakness of the study. I would welcome comments on the limitations that this imposes and whether 39 years is really long enough for a fully coupled model to "spin-up".*

Neither of our model simulations was “spun-up” from a rest state. Rather the WACtl case was initialized from a climatological ocean and sea ice state, and the MACtl run was initialized from a reference case of the same model configuration that was already spun up. As we showed in our response to the Anonymous Reviewer (see Fig. R1-1), the difference between the initial SST states appears to be a shift in the phase of internal variability (specifically El Nino-Southern Oscillation, ENSO), rather than a fundamental difference in the long-term climate state. So 39 years is a reasonable time period to allow for WACtl to adjust from its initial state, as that adjustment would mostly involve an adjustment to VOC chemistry. We will update the manuscript to make these points.

*Figure 1: This is rather puzzling a result. For a start the largest changes are over the oceans. This is where some fixed SST runs would help to remove any noise caused by changes in ocean circulation which will have a long time signal (and require more than 140 years of run). The main changes in temperature seem associated with sea ice zones. Is that correct? What could cause such large and significant ~ grid-box level changes in surface temperature over land? I can't think of a mechanism associated with chemistry.*

We thank you for this feedback. While running fixed SST simulations would reduce noise, it would greatly limit the full climate response, which is what we are interested in. Hopefully our response to your earlier comment addresses any concern that our responses are strongly influenced by internal variability. While the most significant surface temperature changes are in the extratropics, these changes are not confined to sea ice zones.

We are not sure of the mechanisms driving the localized surface temperature changes over land. Most of our investigation of mechanisms was focused on the zonal mean changes, and we plan to investigate more localized changes in future studies. We will update the manuscript to this effect.

*Figure 1-Figure 6 and results and discussion. How large are these changes compared to for example the spread of CMIP6 models and or the spread of LENS/2 simulations with CESM/2.*

Please refer to our earlier response and Figure R2-1 regarding the comparison of the surface temperature response to internal variability. As we stated before, comparisons to the spread of CMIP6 models and LENS simulations would not be especially conclusive here, but we provided comparison to a longer CMIP6 control simulation using CESM2-WACCM6.

*L445: Are RONO2 coupled to the radiation scheme?*

Thank you for this question. As we stated above, we investigated further and found out (through correspondence with the modelling centre) that gas phase RONO<sub>2</sub> is not coupled to the radiation scheme, and condensed phase RONO<sub>2</sub> is lumped with sulfate aerosol (which does impact radiation). So the radiative effects of condensed organic nitrates are not treated separately from those of sulfate aerosols. This updated understanding requires updates to our results sections, as we can now be more confident that the widespread cooling in the extratropical troposphere is likely due to increased sulfate aerosols in the stratosphere combined with reduced sulfate aerosols in the troposphere.

*Figure 9-12: % changes would be much more helpful. Please also express species in units that are more widely used in the literature. pptw for example is not used in atmospheric chemistry circles. Instead use mass per unit volume (g/m<sup>3</sup> for example).*

Thank you for these suggestions. We did experiment with showing % changes, and we found that % changes can potentially be misleading in the results. This is because, in regions where the climatological value of a species is very low, then a very small absolute change can produce a huge percent change. We will update the manuscript in a few places where percent changes may be suitable (i.e., Figure 10, and 11). Any figures in pptw units will be updated to be in units of g m<sup>-3</sup> or mg m<sup>-3</sup>. For gas-phase species, the usage of ppm still seems appropriate.

*L465: What matters more is how SOA are dealt with in the model, not what the literature says. Can you please expand on the coupling of SOA to radiation (through direct and indirect effects).*

We appreciate this feedback. SOA is indeed coupled to the radiation scheme (RRTMG) in CESM2-WACCM6 in both the WACtl and MACtl cases. This coupling is through both the direct effect (influencing aerosol optical depth) and the indirect effect (SOA acting as cloud condensation nuclei). Clouds are also coupled to RRTMG. This will be clarified in the methods and results sections.

*L483: This causality is not possible to determine. One would need to isolate ONLY the VBS to assert this.*

Thank you for pointing this out. The language of causality will be removed here. The manuscript will be changed as follows: “**Although causality cannot truly be determined**, the VBS

mechanism for SOA formation would be expected to act as a sink for various radical species (OH, NO<sub>3</sub>, NO, NO<sub>2</sub> and Cl). To verify this point, a sensitivity analysis of only the VBS mechanism is required, which is left for future work.”

L523: This can be because: 1) you have less OH so less SO<sub>2</sub> forms sulfate 2) you have more clouds and rain so more SO<sub>4</sub> is wet deposited. Which is it? I think you need to examine the SO<sub>4</sub> budget.

We greatly appreciate these points as they have helped to strengthen our analysis. It appears that OH changes have a stronger influence compared to wet deposition changes. To provide evidence for this, a new figure will be included in the results section, reproduced below.

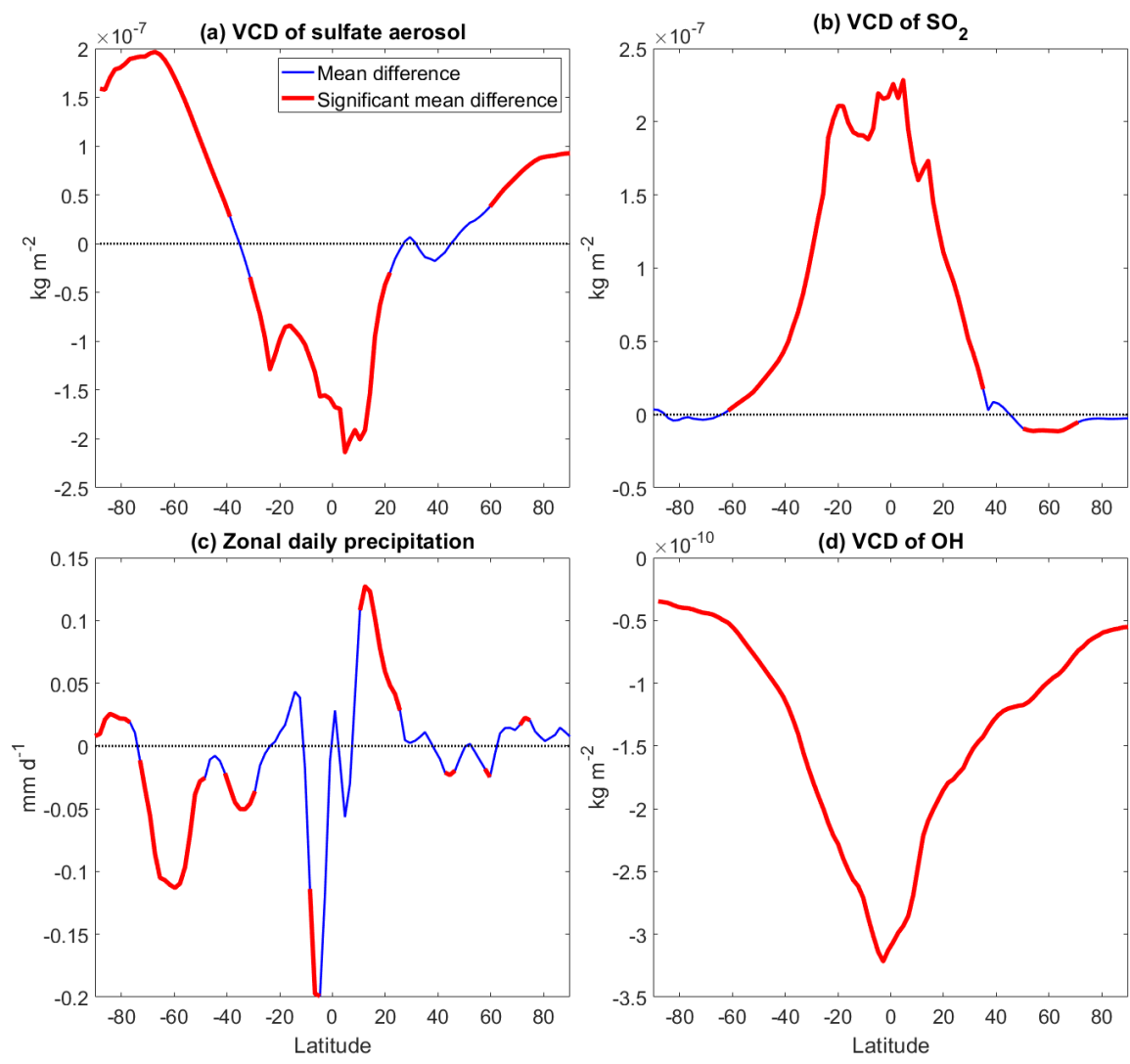


Figure R2-3: (a) Annual mean difference (WACTl – MACTl) in vertical column density (VCD) of sulfate aerosol (kg m<sup>-2</sup>), (b) VCD of SO<sub>2</sub> (kg m<sup>-2</sup>), (c) zonal mean precipitation (mm d<sup>-1</sup>), and (d) VCD of OH (kg m<sup>-2</sup>). The differences that are statistically significant at the 95% level are colored red.

Panel (a) indicates a decrease in sulfate aerosol over the tropics, where OH decreases, but there is no widespread increase in precipitation in the tropics. This suggests that the tropical decreases in



sulfate are driven primarily by changes in OH rather than changes in wet deposition of SO<sub>4</sub>. It is notable, however, that over approximately 2-25°N, there is a precipitation increase that aligns with a local minimum in the sulfate aerosol change. This suggests that increased wet deposition of SO<sub>4</sub> is also contributing to the sulfate aerosol decrease in particular regions.

#### References:

Bates, K.H, and Jacob, D.J.: A new model mechanism for atmospheric oxidation of isoprene: global effects on oxidants, nitrogen oxides, organic products, and secondary organic aerosol, *Atmospheric Chemistry and Physics*, 19, 9613-9640, <https://doi.org/10.5194/acp-19-9613-2019>, 2019.

Emmons, L.K., Walters, S., Hess, P.G., Lamarque J.-F., Pfister, G.G., Filmore, D., Granier, C., Guenther, A., Kinnison, D., Laepple, T, et al.: Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), *Geoscientific Model Development*, 3(1), 43-67, <https://doi.org/10.5194/gmd-3-42-2010>, 2010.

Emmons, L. K., Schwantes, R. H., Orlando, J. J., Tyndall, G., Kinnison, D., Lamarque, J.-F., et al.: The Chemistry Mechanism in the Community Earth System Model version 2 (CESM2). *Journal of Advances in Modeling Earth Systems*, 12, e2019MS001882. <https://doi.org/10.1029/2019MS001882>, 2020.

Forster, P.M., Richardson, T., Maycock, A.C., Smith, C.J., Samset, B.H., Myhre, G., Andrews, T., Pincus, R., and Schulz, M.: Recommendations for diagnosing effective radiative forcing from climate models for CMIP6, *Journal of Geophysical Research: Atmospheres*, 121(20), 12460-12475, <https://doi.org/10.1002/2016JD025320>, 2016.

Squire, O.J., Archibald, A.T., Griffiths, P.T., Jenkin, M.E., Smith, D., and Pyle, J.A.: Influence of isoprene chemical mechanism on modelled changes in tropospheric ozone due to climate and land use over 21<sup>st</sup> century, *Atmospheric Chemistry and Physics*, 15, 5123-5143, <https://doi.org/10.5194/acp-15-5123-2015>, 2015.

von Kuhlmann, R., Lawrence, M.G., Pöschl, U., and Crutzen, P.J.: Sensitivities in global scale modeling of isoprene, *Atmospheric Chemistry and Physics*, 4, 1-17, 2004.