

Response to reviewer comments for manuscript: **Tropospheric ozone radiative forcing uncertainty due to pre-industrial fire and biogenic emissions** by Rowlinson et al.

We thank the two reviewers for their detailed feedback on our manuscript. We have now carefully revised the manuscript according to all the comments provided. To guide the review process, we have copied the reviewer comments below (in black) and provided our responses (in blue).

**Responses to reviewer #1:**

**Reviewer Summary:**

In this study, the authors use a chemistry transport and different inventories of preindustrial fire and biogenic emissions to argue that the uncertainty range of ozone radiative forcing has been overestimated in past multi-model studies and assessments. The paper is the ozone counterpart to Hamilton et al. (2018), which made a similar point about biomass-burning aerosols.

The paper is very well written and structured in a straightforward way. The changes in simulated tropospheric ozone are well understood from differences in precursor emissions, so the question is whether the alternative sets of preindustrial emissions are a good guide to the overall uncertainty. This is where my concerns are, as detailed below. Addressing my comments may involve new simulations, so may represent major revisions.

**Authors' response:** We would like to thank the reviewer for the positive and constructive comments on our manuscript. We have now revised the manuscript to address the reviewer's concerns and added further information to clarify why certain decisions were made.

**Main Comments:**

1. My main concern with the study is that the PD/PI pairs used to estimate radiative forcing are not consistent. There is only one PD simulation, using the CMIP6 inventory. But shouldn't the SIMFIRE-BLAZE PI simulation be coupled with a SIMFIRE-BLAZE PD simulation? Shouldn't the LMfire PI simulation be coupled with an LMfire PD simulation? If the PD simulations differ from CMIP6 in the same way as the PI simulations, then the impact on radiative forcing would be small. I acknowledge that fire models (including those used to provide the CMIP6 inventory) are typically overfitted to present-day observations, so their PD simulations should share common patterns, but at least the PD and PI distributions would always be consistent in terms of the internal physics of the fire emissions.

**Authors' response:** Our experimental design with a single PD anchor point is driven by the research question addressed. The focus of our study is tropospheric ozone radiative forcing uncertainty due to PI fire and biogenic emissions. Changing the PD inventory adds an additional uncertainty from the PD dataset.

However, to address the reviewer's concern we have now performed a new model simulation, PD SIMFIRE-BLAZE, to explore the impact of the uncertainty in PD fire inventories on tropospheric ozone radiative forcing (RF). A PD simulation is not available for LMfire, a PI fire model not designed to undertake a PD simulation. We find that this additional uncertainty is very small. This agrees well with the fact that the PD tropospheric ozone (RE) has been shown to be well constrained by satellite observations (Rap et al., 2015), implying that the uncertainty in tropospheric ozone RF (i.e. PD RE - PI RE) caused by uncertainties in PD emission inventories is small.

We therefore now compare PD vs. PI simulations with both PD CMIP6 and PD SIMFIRE-BLAZE inventories. We find very similar PD tropospheric ozone burdens (31.0 DU for PD CMIP6 and 31.2 DU for PD SIMFIRE-BLAZE) and similar PI to PD RF when coupled to each PI inventory, see table below.

Comparison of O<sub>3</sub> RF from each PI emissions inventory relative to the two PD inventories, CMIP6 and SIMFIRE-BLAZE.

	Tropospheric O <sub>3</sub> RF (Wm <sup>-2</sup> )
PD CMIP6 – PI CMIP6	0.38
PD CMIP6 – PI SIMFIRE-BLAZE	0.35
PD CMIP6 – PI LMfire	0.27
PD SIMFIRE-BLAZE – PI CMIP6	0.38
PD SIMFIRE-BLAZE – PI SIMFIRE-BLAZE	0.36
PD SIMFIRE-BLAZE – PI LMfire	0.26

This is now discussed in the text and a comparison of the two PD simulations is included in Table 2 of the manuscript.

**Changes in manuscript:**

**L129-137**

“The PD simulations used anthropogenic emissions from the MACCity emissions dataset (from EU projects MACC/CityZEN; Lamarque et al. (2010)) and CCMI biogenic emissions (Sindelarova et al., 2014). Two PD simulations were performed, namely the primary PD simulation (PD CMIP) driven by the Global Fire Emissions Database version 4 with small fires (GFED v4s) inventory as employed in CMIP6 (Randerson et al., 2017; van Marle et al., 2017), and PD SIMFIRE-BLAZE (Knorr et al., 2014). A PD simulation is not available for LMfire, a PI fire model not designed to undertake a PD simulation. To isolate the effect of revised natural PI emissions on PI-to-PD tropospheric ozone RF, we compare the 6 PI simulations against the main PD CMIP6 simulation. The other PD simulation, i.e. PD SIMFIRE-BLAZE, was also included in our analysis in order to explore the additional uncertainty in RF introduced by PD emission inventories uncertainties. However, as PD tropospheric ozone RE was shown to be well constrained by satellite observation (Rap et al., 2015), this additional uncertainty is known to be small.”

And clarified in the results section 3.4:

**Changes in manuscript:**

**L393-398**

“The estimated tropospheric O<sub>3</sub> RF, based on the CMIP6 PI and PD control simulations, is 0.38 Wm<sup>-2</sup> (Fig. 4 and Table 2), comparing well with the IPCC AR5 estimate of 0.4 ± 0.2 Wm<sup>-2</sup> (Myhre et al., 2013; Stevenson et al., 2013). We obtain the same 0.38 Wm<sup>-2</sup> RF value when contrasting the PI CMIP6 simulation against the other the other PD simulation (PD SIMFIRE-BLAZE). This is consistent with the fact that PD tropospheric O<sub>3</sub> is well constrained by satellite observations (Rap et al., 2015). Given the similarity of the PD simulations, the main PD CMIP6 simulation is used here as the PD for RF calculations in this section.”

2. In a related concern, I note that section 2.6 implies that CCMI is a reasonable biogenic emission inventory for present-day because it compares well to flux measurements and other models. Then LPJ-GUESS is said to be similar to CCMI for present-day, implying it is also a reasonable inventory. Those are weak arguments, but there is at least an attempt at looking at performance of inventories. In contrast, section 2.4 on fire emission inventories does not discuss present-day performance. This is a problem because if SIMFIRE-BLAZE and/or LPJ-LMfire happen to be biased in an era where they can be constrained by observations, then the authors overstate the case for preindustrial emission uncertainty.

**Authors' response:** To address this concern, we have now conducted a comparison of PD emissions for the CMIP6 and SIMFIRE-BLAZE inventories and included this analysis in the manuscript (within the text, figures 1 and 2, and in Table 2). We believe this adds confidence in the reliability and relevance of the inventories.

#### **Changes in manuscript:**

##### **L164-171**

"The fire emissions in the PD SIMFIRE-BLAZE model are very similar to the PD CMIP6 inventory, with only slightly increased global NO<sub>x</sub> emissions (174 Tg/yr compared to 171 Tg/yr in CMIP6) and CO emissions (1027 Tg/yr compared to 970 Tg/yr). The global distribution of the inventories is also similar (Fig. 1), with slightly larger CO emissions in the SH tropics in PD SIMFIRE-BLAZE, but smaller in the NH tropical region. NO<sub>x</sub> and VOC emissions are similar in both inventories across all latitude bands (Fig. 1b, d). The seasonality of emissions is also consistent across both inventories in terms of NO<sub>x</sub> and VOC emissions, however for CO the peak in emissions is slightly later for the SIMFIRE-BLAZE inventory (Fig. 3). The slightly higher emissions in PD SIMFIRE-BLAZE result in a simulated tropospheric O<sub>3</sub> burden of 360 Tg/yr, an increase of 1% relative to the PD CMIP6 TOMCAT-GLOMAP simulation (Table 2)."

#### **Other Comments:**

**Line 158:** "within the quantifiable uncertainty of fire emissions (Lee et al., 2013)". What do the authors mean here? For present-day or preindustrial? And is Lee et al. the correct reference? That paper does not mention LMFire at all.

**Authors' response:** Thank you for this comment as this point was not clear. The reference in question does not explicitly concern the LMfire inventory but finds substantial uncertainty in magnitude of emissions between inventories to be a common occurrence and estimates that uncertainty range for wildfire emissions is a factor of 4 larger/smaller. This is further supported by a recent study which found the total emission from 6 biomass burning datasets differed by a factor of 3.8 (Pan et al., 2020). This point is discussed with explicit reference to the relevant inventories in Hamilton et al. (2018), which should also have been included as a reference. This has now been corrected and the point reformulated more clearly in the text.

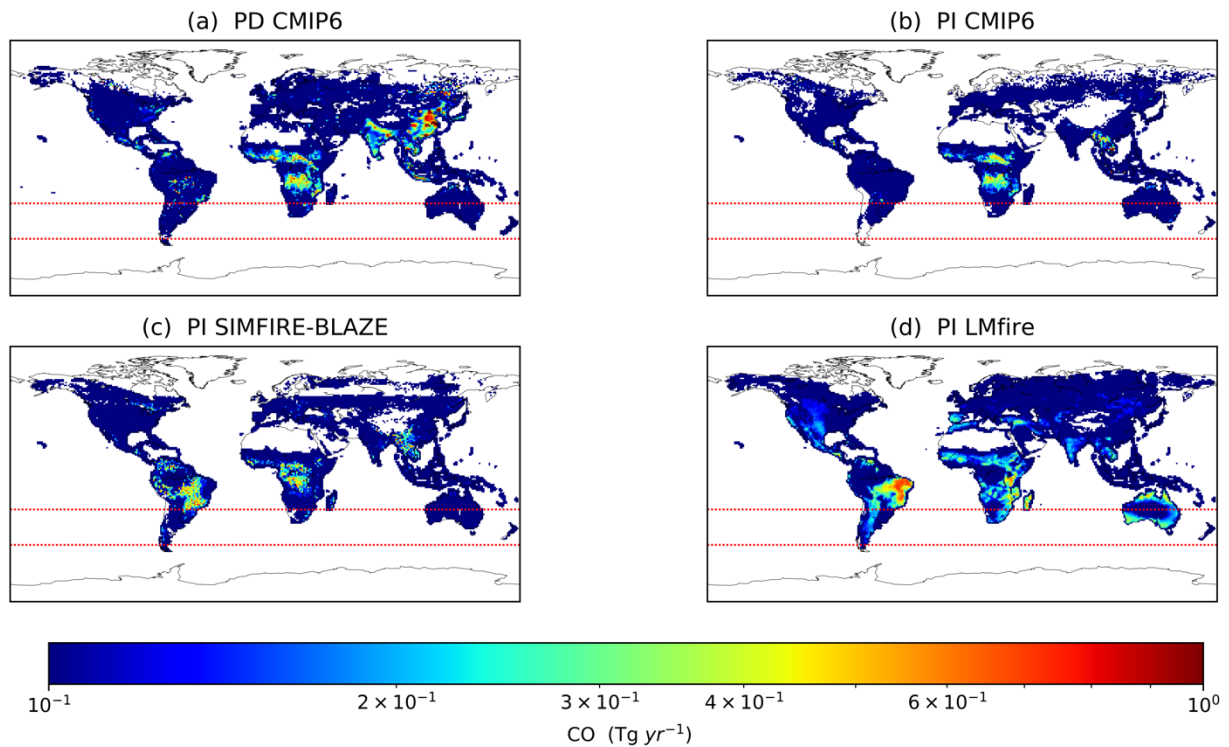
#### **Changes in manuscript:**

##### **L183-185**

"Although the PI LMfire and PI SIMFIRE-BLAZE emissions are substantially larger than the PI CMIP6 emissions, both inventories fall within the current uncertainty range for fire emissions, deemed to differ by up to a factor of ~4 (Lee et al., 2013; Hamilton et al., 2018; Pan et al., 2020)."

**Figure 1a:** LMfire has large CO emissions between 25 and 50S. What is burning there? Australia? Argentina?

**Authors' response:** As the reviewer correctly suggests, the increased CO emission between 25S and 50S is primarily due to increased burning in Australia in the LM fire emissions. Smaller increases in Argentina and South Africa also contribute to the relatively large change in emissions in LMfire, as shown in Figure 1.



**Figure 1. Global annual CO emissions in the (a) PD CMIP6 inventory, (b) PI CMIP6, (c) PI SIMFIRE-BLAZE and (d) PI LMfire. Red parallels indicate 20°S-50°S.**

**Changes in manuscript:**

**L228-229**

“The largest increase occurs due to increased SH burning in the LMfire inventory, substantially increasing CO emissions from Australia and South America (particularly Eastern Amazonia and Argentina).”

**Figures 2a, b, c:** What are those black lines in South America and Africa? In the difference maps, they seem to correspond to a brutal change in emissions, with differences between datasets switching sign suddenly.

**Authors’ response:** We agree this was introducing some confusion - thank you for the comment. The black lines in question were actually topographical features (the Amazon and Congo Rivers), which are too prominent at that projection and resolution. The Figure 2 has now been updated so this is clear.

## **Responses to reviewer #2:**

**General points:** This is an interesting study – and makes an important point: pre-industrial emissions from fires and biogenic sources are a major source of uncertainty for ozone radiative forcing. As explained below, it could benefit from some clarifications. In particular, why are these new estimates of PI emissions better than those used by CMIP6? Some details of the modelling need to be clarified – I was baffled by the discussion of CH<sub>4</sub> emissions for simulations where I thought CH<sub>4</sub> concentrations were prescribed. If the points below can be cleared up, then I am happy to recommend this paper should be accepted for publication in ACP.

**Authors' response:** We would like to thank the reviewer for their general comments on the manuscript and positive remarks on the study. We have endeavoured to address all specific comments and our responses and corrections are detailed below.

Specific comments:

L25 of up to -> by up to

**Authors' response:** Corrected.

L56 “human impact on. . . anthropogenic emissions. . .” Reword. I think we can be fairly sure there is a human impact on anthropogenic emissions. . .

**Authors' response:** This has been reworded to make the point more clearly.

### **Changes in manuscript:**

#### **L53-56**

“While human activities such as deforestation, land-use change and fire management are known to affect natural emission sources of O<sub>3</sub> precursor gases, their impact on emissions net change remains very uncertain (Mickley et al., 2001; Arneth et al., 2010).”

L99 State thickness (metres or hPa) of the lowest model level.

**Authors' response:** We have now added this information within the text.

### **Changes in manuscript:**

#### **L102**

“Biomass burning and biogenic emissions are emitted into the lowest model level, which extends from the surface to 951 hPa. “

L119 Do the prescribed surface CH<sub>4</sub> concentrations have spatial variation, or just a constant value everywhere? Given later comments about CH<sub>4</sub> emissions, please clarify further how CH<sub>4</sub> is handled by the model.

**Authors' response:** We agree this should have been stated much more clearly. The global mean CH<sub>4</sub> concentration is scaled to observations for a particular year, but the spatial variation is maintained. Therefore, an emissions inventory is still required and spatial differences in CH<sub>4</sub> emissions between inventories are still relevant. We have now altered the text in the manuscript to make this clear.

### **Changes in manuscript:**

#### **L99-101**

“The annual global mean surface CH<sub>4</sub> mixing ratio is scaled in TOMCAT-GLOMAP based on observed global surface mean concentration for the year being simulated; however, the spatial variation in CH<sub>4</sub> concentrations is maintained in the model.”

L146 “Total PI fire emissions. . . SIMFIRE-BLAZE. . . are 28% larger than. . . PI CMIP6”. It would be instructive to know PD fire emissions predicted by the SIMFIRE-BLAZE model. Can the model reproduce the present-day GFED distribution, or something similar? It may be that the higher PI values indicate a bias in this model towards higher values. It is hard to know how to verify or evaluate the PI fire emissions without some measure of the model's abilities – and presumably evaluation for present-day is the best evaluation possible. If this is not the case, then at least some discussion of how much faith we should have in these PI values is required.

L155 Similarly for the LPJ-LMfire model.

**Authors' response:** This point is closely related to a comment from Reviewer 1. We have now conducted a comparison between PD emissions from CMIP6 and the SIMFIRE-BLAZE model, finding comparable emission magnitudes and distributions and resulting in very similar simulated tropospheric ozone concentrations (now included in Table 2 of the manuscript). We have also now quantified the effect of using the PD SIMFIRE-BLAZE emissions as the PD anchor for the RF calculations, finding similar RF as with the PD CMIP6 simulation (see table below).

Comparison of O<sub>3</sub> RF from each PI emissions inventory relative to the two PD inventories, CMIP6 and SIMFIRE-BLAZE.

	Tropospheric O <sub>3</sub> RF (Wm <sup>-2</sup> )
PD CMIP6 – PI CMIP6	0.38
PD CMIP6 – PI SIMFIRE-BLAZE	0.35
PD CMIP6 – PI LMfire	0.27
PD SIMFIRE-BLAZE – PI CMIP6	0.38
PD SIMFIRE-BLAZE – PI SIMFIRE-BLAZE	0.36
PD SIMFIRE-BLAZE – PI LMfire	0.26

More detail on this has now been included in the manuscript.

**Changes in manuscript:**

**L129-137:**

“The PD simulations used anthropogenic emissions from the MACCity emissions dataset (from EU projects MACC/CityZEN; Lamarque et al., 2010) and CCMI biogenic emissions (Sindelarova et al., 2014). Two PD simulations were performed, namely the main PD simulation (PD CMIP6) driven by the Global Fire Emissions Database version 4s (GFEDv4s) inventory as employed in CMIP6 (Randerson et al., 2017; van Marle et al., 2017), and PD SIMFIRE-BLAZE which has been optimised against 3 global burned area datasets (Knorr et al., 2014). A PD simulation is not available for LMfire, a PI fire model not designed to undertake a PD simulation. To isolate the effect of revised natural PI emissions on PI-to-PD tropospheric ozone RF, we compare the 6 PI simulations against the main PD CMIP6 simulation. The other PD simulation, i.e. PD SIMFIRE-BLAZE, is also included in our analysis in order to explore the additional uncertainty in RF introduced by PD emission inventories uncertainties. However, as PD tropospheric ozone RE was shown to be well constrained by satellite observation (Rap et al., 2015), this additional uncertainty is known to be small.”

### **L163-170**

“The fire emissions in the PD SIMFIRE-BLAZE model are very similar to the PD CMIP6 inventory, with only slightly increased global NO<sub>x</sub> emissions (174 Tg yr<sup>-1</sup> compared to 171 Tg yr<sup>-1</sup> in CMIP6) and CO emissions (1027 Tg yr<sup>-1</sup> compared to 970 Tg yr<sup>-1</sup>). The global distribution of the inventories is also similar (Fig. 1), with slightly larger CO emissions in the SH tropics in PD SIMFIRE-BLAZE, but smaller in the NH tropical region. NO<sub>x</sub> and VOC emissions are similar in both inventories across all latitude bands (Fig. 1b, d). The seasonality of emissions is also consistent across both inventories in terms of NO<sub>x</sub> and VOC emissions, however for CO there is a later and larger peak in emissions in the SIMFIRE-BLAZE inventory (Fig. 3). The small emission increases in PD SIMFIRE-BLAZE result in a simulated tropospheric O<sub>3</sub> burden of 359.9 Tg, an increase of 1% relative to the PD CMIP6 TOMCAT-GLOMAP simulation (Table 2).”

Perhaps the key question here is whether the fire models used here are better than the fire models used in the CMIP6 base case. Are they clearly better, or are they just different? My non-expert reading of this is that they are just different. Please do try to convince me they are better.

**Authors' response:** We agree it is important to explain this better. The main purpose of our study is to quantify the impact of the existing large uncertainty in preindustrial natural emissions on tropospheric ozone radiative forcing. While there is not enough evidence to claim that one particular inventory outperforms all others in all regions, there is however evidence to suggest they are all plausible. Hamilton et al. (2018) made the case that the revised fire modelling inventories employed here arguably represent PI to PD changes in the paleoenvironmental archives of fire activity of the historical period with more accuracy than the CMIP6 inventory. Here, we add to the Hamilton et al. (2018) analysis by also comparing simulated CO from each inventory with ice-core records from the Wang et al. (2010) dataset. This comparison further supports the argument that the PI biomass burning emissions in CMIP6 are too small. We have now reformulated the text to better communicate this point, emphasising the improved performance in comparison to proxy records as clear indication that the revised inventories offer important insight to the uncertainties in tropospheric O<sub>3</sub> in the preindustrial atmosphere.

### **Changes in manuscript:**

#### **L182-190**

“Although the PI LMfire and PI SIMFIRE-BLAZE emissions are substantially larger than the PI CMIP6 emissions, both inventories fall with the current uncertainty range for fire emissions, deemed to differ by up to a factor of ~4 (Lee et al., 2013; Hamilton et al., 2018; Pan et al., 2020). In Hamilton et al. (2018), both the SIMFIRE-BLAZE and LMfire PI inventories were shown to compare more favourably than CMIP6 to changes in PI to PD ice core BC measurements in the Swiss Alps. Furthermore, the LMfire emissions result in simulated aerosol concentrations that were closer to Northern Hemisphere (NH) ice core records in Greenland and Wyoming than both the CMIP6 and SIMFIRE-BLAZE emissions (Hamilton et al., 2018). In addition to the extensive examination of paleoenvironmental archives with PI fire emissions datasets by Hamilton et al. (2018), here we compared simulated annual mean surface PI CO concentrations in Antarctica for each fire emissions inventory using the Southern Hemisphere (SH) ice core CO record from Wang et al. (2010).”

#### **L199-203**

“The combined evaluation of these inventories in Hamilton et al. (2018) and here indicates that although the revised PI fire inventories differ considerably from each other and are substantially larger than CMIP6 in some regions, they result in simulated PI atmospheric concentrations that more closely represent the changes observed in paleoenvironmental archives of changes in Industrial Era fire activity than CMIP6 estimates do. Therefore, their respective impacts on PI tropospheric O<sub>3</sub> concentrations and RF estimates need to be carefully considered.”

Figure 1, and all the figures, are of a poor resolution. I can just about make out the necessary details, but these need to be improved for the final version.

**Authors' response:** The figures have been replaced with higher resolution images so the details should be clearer now.

In Figure 1c, the PD CMIP6 CH<sub>4</sub> emissions from fire total 566.6 Tg. This sounds suspiciously high – isn't that more like the value for the total PD CH<sub>4</sub> emission flux?

**Authors' response:** We thank the reviewer for identifying this error. The plot and value in question is indeed the PD emission of CH<sub>4</sub> from all PD sources, not just biomass burning. Emissions from all sources are used in the plot to demonstrate the shift in magnitude of emissions from PI to PD. This mistake has now been rectified:

#### **Changes in manuscript:**

##### **Figure 1 caption:**

“Annual latitudinal mean preindustrial emissions (in Tg/yr) of (a) CO, (b) NO<sub>x</sub>, (c) CH<sub>4</sub> and (d) VOCs), in PD CMIP6 (solid black line), PD SIMFIRE-BLAZE (dashed black), PI CMIP6 (dashed green), PI SIMFIRE-BLAZE (dotted orange), PI LMfire (dashed purple) inventories,. In (e), annual latitudinal mean BVOC emissions in (Tg/yr) in PD CCMI (solid black line), PD LPJ-GUESS (dashed dark green), PI LPJ-GUESS (dotted light green).”

##### **L220-222**

“Figure 1a-d shows annual latitudinal emissions of CO, NO<sub>x</sub>, CH<sub>4</sub> and VOCs from all sources for the different fire inventories considered, while Figure 1e compares BVOC emissions (i.e. isoprene and monoterpenes) from the biogenic emissions inventories.”

L192 delete PI.

**Authors' response:** Corrected.

L193 “The main driver of this increase [in fire emissions] is industrial emissions. . .” This must be wrong?

**Authors' response:** As clarified above this does refer to the PI to PD change in emissions from all sources, where the most important driver is in fact anthropogenic emissions from industry. This is now made clear with the updated plot caption and in the text.

L210 I don't understand why CH<sub>4</sub> emissions are presented and discussed; surely if CH<sub>4</sub> concentrations are prescribed, the CH<sub>4</sub> emissions are irrelevant and redundant? Am I missing something?

**Authors' response:** We agree this should be clarified to avoid confusions. As mentioned in the response to an earlier comment, while the global mean CH<sub>4</sub> concentration is scaled, the spatial variation is maintained. Therefore, simulated CH<sub>4</sub> will vary spatially between simulations with different CH<sub>4</sub> emissions. However, we acknowledge that due to the scaling the impact of changes to CH<sub>4</sub> emissions on ozone formation is likely to be small. We have made this clear now in the text.

#### **Changes in manuscript:**

##### **L99-101**

“The global mean surface CH<sub>4</sub> mixing ratio is scaled in TOMCAT-GLOMAP to a best estimate based on observed global surface mean concentration for the year being simulated, meaning that spatial variation in CH<sub>4</sub> concentrations is maintained.”



## L244-245

“Due to the scaling of global mean surface CH<sub>4</sub> concentrations in TOMCAT-GLOMAP, the effect of changes in amount of CH<sub>4</sub> emitted is likely small, however the change in distribution may impact the formation and loss rates of tropospheric O<sub>3</sub>.”

L214 their size -> the magnitude

**Authors' response:** Corrected.

L218 So presumably the emission factors for different VOCs vary between the models? Please clarify.

**Authors' response:** As the reviewer suggests, VOC emission factors do vary between models, although differences in burned area and vegetation type also contribute to the differences in VOC emission. This is now clarified in the text.

## Changes in manuscript:

### L248-254

“In terms of fire-emitted VOC species, their magnitude and distribution of emissions are fairly consistent between PD and PI inventories. PI CMIP6 are 87% of PD CMIP6 values, with PI SIMFIRE-BLAZE at 97% (303 Tg/yr). Total global VOC emissions are largest in LMfire at 349 Tg/yr, 29% larger than PI CMIP6 (271 Tg/yr) and 13% larger than PD CMIP6 (310 Tg/yr). The distribution of total global VOC emissions is relatively uniform across all inventories; however individual species do have larger variability between inventories. Formaldehyde and acetylene for example have substantially increased SH emissions in SIMFIRE-BLAZE and LMfire, due to differences in emission factors, vegetation type and burned area between the fire models.”

Figure 2: are the maps emissions per 2.8 degree x 2.8 degree grid box?

**Authors' response:** The figure shows the emissions on a 1°×1° resolution. The emissions are regridded to the TOMCAT resolution of 2.8 x 2.8 within the model. This is now made clear in the figure caption.

## Changes in manuscript:

### Figure 2 caption

“Annual BVOC (isoprene + monoterpenes) emissions at 1°×1° in the two present-day biogenic emissions inventories (CCMI and LPJ-GUESS) and the preindustrial LPJ-GUESS inventory. Top panels (a-c) show total emissions per year, while lower panels (d-f) show differences between the three inventories. Total annual emissions and difference in annual emissions are also shown.”

Figure 3: Why show CH<sub>4</sub> emissions?

**Authors' response:** This point is addressed in an earlier response.

L259 . . .When there parameters at. . . -> when these parameters are

**Authors' response:** Corrected.

L261 resulting -> results

**Authors' response:** Corrected.

Figure 4: Are the CO, NO<sub>x</sub> and VOC emissions really combined fire + biogenic + anthropogenic? Wouldn't it be clearer to just show how the fire emissions change, separately from other categories?

**Authors' response:** Yes, the emissions magnitudes in the figure are the combined totals. We agree there are different ways one could present our results in this figure and we have

considered a few options. In the end we decided on this version as it illustrates how each sector contributes to tropospheric O<sub>3</sub> formation, as well as displaying the differences between simulations and results. We feel this figure contributes to the study by adding a lot of information in a manner that is easy to interpret, for various levels of expertise.

L285-290 The discussion of OH trends and NH/SH ratios is interesting, but seems a bit tangential? I suggest better integrate or remove.

**Authors' response:** We agree this discussion was indeed a bit tangential and did not add substantially to the manuscript other than to confirm the relatively large SH emission increase in the LMfires inventory. We followed the reviewer's suggestion and have now removed it from the revised manuscript. The rest of the discussion of OH changes has also been shortened and rewritten to make the relevance of the discussion clearer.

### **Changes in manuscript:**

#### **L320-328**

"The hydroxyl radical (OH), which plays a key role in regulating tropospheric O<sub>3</sub> concentrations, had lower PI concentrations than in PD due to the higher concentrations of OH precursors NO<sub>x</sub> and O<sub>3</sub> in PD outcompeting the effect of increased CH<sub>4</sub> and CO concentrations which deplete OH (Naik et al., 2013). This is consistent in the TOMCAT PI simulations, with airmass-weighted global mean concentrations of tropospheric OH, at 1.06, 1.06 and 1.11 ×10<sup>6</sup> molecules cm<sup>-3</sup> in CMIP6, SIMFIRE-BLAZE and LMfire, respectively, compared to 1.12 ×10<sup>6</sup> molecules cm<sup>-3</sup>) in PD CMIP6. Each of these values fall within one standard deviation of the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) multi-model mean of 1.13 ± 0.17 (Naik et al., 2013)."

L327 "The decrease in OH is the most likely reason for the simulated increase in CO and O<sub>3</sub>."

This is a bit over-simplistic. BVOCs have increased. This will generate more CO and consume OH, as those extra VOCs are oxidised. Depending on the collocation of the VOCs, CO and NO<sub>x</sub>, this could either increase or decrease O<sub>3</sub> – in this case it increases O<sub>3</sub>, indicating that the VOC and CO increases must be in areas with sufficient NO<sub>x</sub> to produce O<sub>3</sub> (BVOC emissions in very low NO<sub>x</sub> regions can, at least locally, decrease O<sub>3</sub>).

**Authors' response:** Thank you for pointing this out - we agree this needs to be better explained. We have now expanded to include additional detail.

### **Changes in manuscript:**

#### **369-372**

"The decrease in OH is the likely responsible for the simulated increase in CO, as OH is consumed by VOC oxidation. The increase in global tropospheric O<sub>3</sub> indicates that the simulated increases in VOC and CO concentrations are co-located with high NO<sub>x</sub> concentrations, as in low NO<sub>x</sub> BVOCs may decrease local O<sub>3</sub> concentrations."

L340 "ice core observations" – I think these are oxygen isotope measurements from ice cores.

**Authors' response:** Corrected.

L344-345 0.4 +/- 0.2: the range here is a 5-95% confidence interval; 0.41 +/- 0.12: the range here is +/-1 standard deviation (i.e. encompassing 68% of the data). So these two are essentially the same, just using different range definitions. Please clarify this.

**Authors' response:** Thank you for pointing out this error. We have now simplified this sentence in the manuscript.

**Changes in manuscript:**

**L387-388**

“ The estimated tropospheric O<sub>3</sub> RF, based on the CMIP6 PI and PD control simulations, is 0.38 Wm<sup>-2</sup> (Fig. 4 and Table 2), comparing well with the IPCC AR5 5-95% confidence interval of 0.4 ± 0.2 Wm<sup>-2</sup> (Myhre et al., 2013; Stevenson et al., 2013). “

## References

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## **Tropospheric ozone radiative forcing uncertainty due to pre-industrial fire and biogenic emissions**

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**Abstract** Tropospheric ozone concentrations are sensitive to natural emissions of precursor compounds. In contrast to existing assumptions, recent evidence indicates that terrestrial vegetation emissions in the pre-industrial were larger than in the present-day. We use a chemical transport model and a radiative transfer model to show that revised inventories of pre-industrial fire and biogenic emissions lead to an increase in simulated pre-industrial ozone concentrations, decreasing the estimated pre-industrial to present-day tropospheric ozone radiative forcing ~~by up to 34%~~ (0.38 Wm<sup>-2</sup> to 0.25 Wm<sup>-2</sup>). We find that this change is sensitive to employing biomass burning and biogenic emissions inventories based on matching vegetation patterns, as collocation of emission sources enhances the effect on ozone formation. Our forcing estimates are at the lower end of existing uncertainty range estimates (0.2 – 0.6 Wm<sup>-2</sup>), without accounting for other sources of uncertainty. Thus, future work should focus on reassessing the uncertainty range of tropospheric ozone radiative forcing.

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## 30 1 Introduction

Tropospheric ozone (O<sub>3</sub>) is a short-lived greenhouse gas formed in the atmosphere through photochemical oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO<sub>x</sub>). These precursor gases have both natural and anthropogenic sources, and increased anthropogenic emissions are thought to have caused an increase in global tropospheric O<sub>3</sub> of 25-50% since 1900 (Gauss et al., 2006; Lamarque et al., 2010; Young et al., 2013). The Intergovernmental Panel on  
35 Climate Change (IPCC) current best estimate for tropospheric O<sub>3</sub> radiative forcing (RF) over the industrial era is  $0.4 \pm 0.2$  Wm<sup>-2</sup> with a 5%-95% confidence interval, making tropospheric O<sub>3</sub> the third most important anthropogenic greenhouse gas after CO<sub>2</sub> and CH<sub>4</sub> (Myhre et al., 2013). The present-day (PD) radiative effect (RE) of tropospheric O<sub>3</sub> is relatively well constrained (Rap et al., 2015). The large uncertainty range ( $0.2$ - $0.6$  Wm<sup>-2</sup>) is caused by a number of factors such as the radiative transfer scheme employed, the model used to simulate tropospheric O<sub>3</sub> and tropopause definition, however it is primarily  
40 associated with a poor understanding of pre-industrial (PI) O<sub>3</sub> concentrations (Myhre et al., 2013; Stevenson et al., 2013). Although measurements of tropospheric O<sub>3</sub> exist as far back as the late 19<sup>th</sup> century, there are limited reliable quantitative measurements of tropospheric O<sub>3</sub> prior to the 1970s (Volz and Kley, 1988; Cooper et al., 2014). Recently Checa-Garcia et al. (2018) found that differences in PI estimates between Coupled Model Intercomparison Project phase 5 (CMIP5) and CMIP6 cause an 8-12% variation in O<sub>3</sub> RF estimates, but did not explicitly assess uncertainty in natural PI emissions. Recent analysis  
45 of oxygen isotopes in polar ice cores indicates that tropospheric O<sub>3</sub> in the northern hemisphere increased by less than 40% between 1850 and 2005, suggesting that O<sub>3</sub> RF may be lower than the  $0.4$  Wm<sup>-2</sup> estimate (Yeung et al., 2019).

As well as anthropogenic sources, O<sub>3</sub> precursor gases such as methane (CH<sub>4</sub>), carbon monoxide (CO) and NO<sub>x</sub> have natural emission sources, e.g., wildfires, wetlands, lightning and biogenic emissions. Wildfires, for example, emit large quantities of  
50 CO, NO<sub>x</sub>, CH<sub>4</sub> and non-methane volatile organic compounds (NMVOCs) (van der Werf et al., 2010; Voulgarakis and Field, 2015), which influence the chemical production of O<sub>3</sub> (Wild, 2007). Changes in the natural environment therefore influence the concentration and distribution of tropospheric O<sub>3</sub> (Monks et al., 2015; Hollaway et al., 2017). While human activities such as deforestation, land-use change and fire management are known to affect natural emission sources of O<sub>3</sub> precursor gases, their impact on emissions net change remains very uncertain (Mickley et al., 2001; Arneth et al., 2010). An accurate  
55 representation of PI natural emissions is therefore very important for quantifying the PI to PD tropospheric O<sub>3</sub> RF calculations.

Recent studies suggest that the relationship between humans and fire (Bowman et al., 2009) is more complex than previously assumed (Doerr and Santín, 2016). The expansion of agriculture and land-cover fragmentation since PI has decreased the abundance and continuity of fuel, inhibiting fire spread (Marlon et al., 2008; Swetnam et al., 2016) and hence total emissions.  
60 Furthermore, at the global scale, increased population density results in declining fire frequency (Knorr et al., 2014; Andela et al., 2017). Increased agricultural land coupled with active fire suppression and management policies mean that human activity has likely caused total fire emissions to decline since the PI (Daniau et al., 2012; Marlon et al., 2016; Hamilton et al., 2018).

**Deleted:** (Mickley et al., 2001; Arneth et al., 2010). An accurate representation of PI is PI to PD tropospheric O<sub>3</sub> RF calculations.



65 Paleoenvironmental archives of fire activity also reflect a decline of fire over the industrial era in many regions (Marlon et al., 2016; Rubino et al., 2016; Swetnam et al., 2016). This change in understanding of PI fire emissions has been shown to have a strong influence on aerosol RF: Hamilton et al. (2018) estimated a 35-91% decrease in global mean cloud albedo forcing over the industrial era when using revised PI fire emission inventories.

70 Emissions of biogenic VOCs (BVOCs), such as isoprene and monoterpenes, from vegetation also affect tropospheric O<sub>3</sub> formation. Isoprene contributes to the formation of peroxyacetylnitrate (PAN), which has a lifetime of several months in the upper troposphere (Singh, 1987), allowing long-range transport of reactive nitrogen and enhancing O<sub>3</sub> formation in remote regions. PAN formation is also highly dependent on NO<sub>x</sub> concentrations, meaning that changes in distribution of emissions as well as the magnitude will impact O<sub>3</sub> formation. Previous studies of PI tropospheric O<sub>3</sub> have often assumed that PI BVOC  
75 emissions were equivalent or lower than those in PD (Stevenson et al., 2013). In Stevenson et al. (2013), only one model of the ensemble included PI isoprene emissions that were larger than in the PD simulation. However, BVOC emissions are sensitive to climate, CO<sub>2</sub> concentrations, vegetation type, and foliage density; each of which has changed since the PI (Laothawornkitkul et al., 2009; Hantson et al., 2017) and needs to be accounted for when calculating O<sub>3</sub> RF.

80 **The aim of this study** is to examine the effect of revised PI fire and BVOC emission inventories on PI to PD tropospheric O<sub>3</sub> RF estimates. We use a global chemical transport model (CTM) and a radiative transfer model to investigate the impact of these revised natural PI emission inventories on tropospheric O<sub>3</sub> PI concentrations and its PI-PD RF. The IPCC 5<sup>th</sup> assessment report moved to the concept of effective radiative forcing (ERF) (Myhre et al., 2013) to more completely capture the expected global energy budget change from a given driver. However, here we employ the more traditional stratospherically adjusted RF  
85 as it can be estimated with more certainty than ERF and previous studies suggest that ERF and RF are likely to be similar for O<sub>3</sub> change (Myhre et al., 2013; Shindell et al., 2013). We note that a number of factors not considered here also introduce uncertainty when simulating PI tropospheric O<sub>3</sub> concentrations, e.g. changes to lightning and soil NO<sub>x</sub> emissions, O<sub>3</sub> deposition and atmospheric transport. However, the purpose of this study is to address and focus on the uncertainty associated with natural emissions in the pre-industrial, utilising the revised inventories of fire and biogenic emissions.

## 90 **2 Methods**

### **2.1 TOMCAT-GLOMAP**

We used the TOMCAT global three-dimensional offline chemical transport model (CTM) (Chipperfield, 2006) coupled to the GLOMAP modal aerosol microphysics scheme (Mann et al., 2010) to simulate tropospheric composition and its response to emissions changes. The model used a 2.8°×2.8° horizontal resolution with 31 vertical levels from the surface to 10 hPa All  
95 simulations were run with 6-hourly 2008 meteorology from European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-Interim reanalyses with a 1-year spin-up (Dee et al., 2011). The model includes a detailed representation of hydrocarbon

chemistry and isoprene oxidation, and has previously been shown to accurately reproduce observed concentrations and distributions of key tropospheric species such as O<sub>3</sub>, CO, NO<sub>x</sub> and VOCs (Monks et al., 2017; Rowlinson et al., 2019). The annual global mean surface CH<sub>4</sub> mixing ratio is scaled in TOMCAT-GLOMAP based on observed global mean surface concentrations for the year being simulated; however, the spatial variation in CH<sub>4</sub> concentrations is maintained in the model. Biomass burning and biogenic emissions are emitted into the lowest model level, which extends from the surface to 951 hPa.

## 2.2 Radiative transfer model

Tropospheric O<sub>3</sub> RFs were calculated using the SOCRATES radiative transfer model (Edwards and Slingo, 1996) with six bands in the shortwave (SW) and nine in the longwave (LW). This version has been used extensively in conjunction with TOMCAT-GLOMAP for calculating O<sub>3</sub> radiative effects (Bekki et al., 2013; Rap et al., 2015; Kapadia et al., 2016; Scott et al., 2018). We used the fixed dynamical heating approximation (Fels et al., 1980) to account for stratospheric temperature adjustments, i.e. changes in stratospheric heating rate calculated in the model due to the O<sub>3</sub> perturbation are applied to the temperature field, with the model run iteratively until stratospheric temperatures reach equilibrium (Forster and Shine, 1997; Rap et al., 2015).

<i>Simulation</i>	<i>Fire emissions</i>	<i>Biogenic emissions</i>
<i>PD CMIP6</i>	GFEDv4	CCMI
<u><i>PD SIMFIRE-BLAZE</i></u>	<u>SIMFIRE-BLAZE</u>	<u>CCMI</u>
<i>PI CMIP6</i>	CMIP6	CCMI
<i>PI SIMFIRE-BLAZE</i>	SIMFIRE-BLAZE	CCMI
<i>PI LMfire</i>	LMfire	CCMI
<i>PI CMIP6-BIO</i>	CMIP6	LPJ-GUESS
<i>PI SIMFIRE-BLAZE-BIO</i>	SIMFIRE-BLAZE	LPJ-GUESS
<i>PI LMfire-BIO</i>	LMfire	LPJ-GUESS

**Table 1.** Details of the TOMCAT-GLOMAP simulations performed in this study.

## 2.3 Simulations

We investigate the effect of natural PI emissions on PI to PD changes in tropospheric O<sub>3</sub> concentrations, by contrasting PI against PD model simulations (Table 1). All simulations are run with PD meteorology and global mean surface CH<sub>4</sub> concentrations scaled to be 722 ppb in the PI and 1789 ppb in PD (Etheridge et al., 1998; Dlugokencky et al., 2005; Hartmann et al., 2013; McNorton et al., 2016).

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120 All PI simulations considered anthropogenic emissions set to zero, except for biofuel emissions taken from AeroCom for the  
year 1750 (Dentener et al., 2006). The first set of three PI simulations (i.e. PI CMIP6, PI SIMFIRE-BLAZE and PI LMfire)  
investigate the impact of fire emissions only by keeping BVOC emissions (i.e. isoprene and monoterpenes) at their PD values  
based on the Chemistry-Climate Model Initiative (CCMI) biogenic emissions (Sindelarova et al., 2014). The second set of  
three PI simulations (i.e. PI CMIP6-BIO, PI SIMFIRE-BLAZE-BIO and PI LMfire-BIO) investigate the additional impact of  
125 PI biogenic emissions, by combining each PI fire emission inventory with an estimate of PI BVOC emissions from the LPJ-  
GUESS model (Arneth et al., 2007; Schurgers et al., 2009; Smith et al., 2014).

The PD simulations used anthropogenic emissions from the MACCity emissions dataset (from EU projects MACC/CityZEN;  
Lamarque et al., 2010) and CCMI biogenic emissions (Sindelarova et al., 2014). Two PD simulations were performed, namely  
130 the primary PD simulation (PD CMIP) driven by the Global Fire Emissions Database version 4 with small fires (GFED v4s)  
inventory as employed in CMIP6 (Randerson et al., 2017; van Marle et al., 2017), and PD SIMFIRE-BLAZE (Knorr et al.,  
2014). A PD simulation is not available for LMfire, a PI fire model not designed to undertake a PD simulation. To isolate the  
effect of revised natural PI emissions on PI-to-PD tropospheric ozone RF, we compare the 6 PI simulations against the main  
PD CMIP6 simulation. The other PD simulation, i.e. PD SIMFIRE-BLAZE, is also included in our analysis in order to explore  
135 the additional uncertainty in RF introduced by PD emission inventories uncertainties. However, as PD tropospheric ozone RE  
was shown to be well constrained by satellite observation (Rap et al., 2015), this additional uncertainty is known to be small.

## 2.4 Fire emission inventories

Following Hamilton et al. (2018), we used three PI inventories to investigate the sensitivity of tropospheric O<sub>3</sub> RF to PI fire  
140 uncertainty. The CMIP6 PI inventory is treated as a control, as this has been widely used in previous studies and was developed  
from a set of global fire models, with SIMFIRE-BLAZE and LMfire providing PI perturbation scenarios from this baseline.

### 2.4.1 Pre-industrial and present day CMIP6

CMIP6 provides monthly mean emissions of CO, NO<sub>x</sub>, CH<sub>4</sub> and VOCs from fires. In the PD, CMIP6 emissions are derived  
from satellite estimates of global burden area and active fire detections (Randerson et al., 2012; Giglio et al., 2013). In the  
145 absence of satellite data, PI CMIP6 fire emissions are generated by merging PD satellite observations with fire proxy records,  
visibility records and analysis from six fire models (van Marle et al., 2017). The mean of 1750-1770 emissions is used in this  
study to represent PI emissions. Biomass burning emissions from deforestation and peat fires are assumed to be reduced in the  
PI, while agricultural fires are kept fairly constant with PD due to a lack of information on the PI environment.

#### 2.4.2 Pre-industrial and present day SIMFIRE-BLAZE

150 The SIMFIRE-BLAZE PI fire emission inventory was developed using the LPJ-GUESS-SIMFIRE-BLAZE model. The PI  
emissions employed here are the mean for the period 1750-1770 (Hamilton et al., 2018). The LPJ-GUESS dynamic vegetation  
model predicts ecosystem properties for given climate variables (Smith et al., 2014), which, combined with the HYDE 3.1  
dataset of human land-use change, allows simulation of global PI land cover (Klein Goldewijk et al., 2011). The SIMple fire  
model (SIMFIRE) calculates total burned area (Knorr et al., 2014) with total fire carbon-flux calculated from BLAZE (BLAZE  
155 induced biosphere-atmosphere flux Estimator) (Rabin et al., 2017). Akagi et al. (2011) emissions factors were used with  
separate treatment of herbaceous and non-herbaceous, tropical and extratropical vegetation to produce emission inventories.  
Agricultural fire emissions are not included. Total PI fire emissions of gas species in the SIMFIRE-BLAZE inventory are 28%  
larger than in the PI CMIP6 inventory.

160 The fire emissions in the PD SIMFIRE-BLAZE model are very similar to the PD CMIP6 inventory, with only slightly increased  
global NO<sub>x</sub> emissions (174 Tg/yr compared to 171 Tg/yr in CMIP6) and CO emissions (1027 Tg/yr compared to 970 Tg/yr).  
The global distribution of the inventories is also similar (Fig. 1), with slightly larger CO emissions in the SH tropics in PD  
SIMFIRE-BLAZE, but smaller in the NH tropical region. NO<sub>x</sub> and VOC emissions are similar in both inventories across all  
latitude bands (Fig. 1b, d). The seasonality of emissions is also consistent across both inventories in terms of NO<sub>x</sub> and VOC  
165 emissions, however for CO the peak in emissions is slightly later for the SIMFIRE-BLAZE inventory (Fig. 3). The slightly  
higher emissions in PD SIMFIRE-BLAZE result in a simulated tropospheric O<sub>3</sub> burden of 359.9 Tg, an increase of 1% relative  
to the PD CMIP6 TOMCAT-GLOMAP simulation (Table 2).

#### 2.4.3 Pre-industrial LPJ-LMfire

The LPJ-LMfire model calculates dry matter consumed by fire and simulates natural wildfire ignition from lightning (Pfeiffer  
170 et al., 2013; Murray et al., 2014). Land use is prescribed for the year 1770 using the KK10 scenario from Kaplan et al. (2011);  
climate forcing comes from an 1020-year detrended, interannually variable equilibrium dataset representing late 19<sup>th</sup> century  
conditions (see Pfeiffer et al. (2013), sec. 3.4 for details). Akagi et al. (2011) emissions factors were again used to calculate  
the gas-phase fire emissions from dry biomass burned in each grid cell. Burned area is calculated based on fuel availability.  
LMfire includes emissions from managed agricultural burning, with 50% of the litter on 20% of used croplands burden  
175 annually. Also included are emissions from post-harvest agricultural burning, with 10% of harvested agricultural crop material  
is assumed to be burned each year. Total PI fire emissions in LMfire are approximately double the SIMFIRE-BLAZE inventory,  
and thus four times larger than CMIP6 emissions.

## 2.5 Assessment of PI fire emissions

180 [Although the PI LMfire and PI SIMFIRE-BLAZE emissions are substantially larger than the PI CMIP6 emissions, both inventories fall with the current uncertainty range for fire emissions, deemed to differ by up to a factor of ~4 \(Lee et al., 2013; Hamilton et al., 2018; Pan et al., 2020\). In Hamilton et al. \(2018\), both the SIMFIRE-BLAZE and LMfire PI inventories were shown to compare more favourably than CMIP6 to changes in PI to PD ice core BC measurements in the Swiss Alps. Furthermore, the LMfire emissions result in simulated aerosol concentrations that were closer to Northern Hemisphere \(NH\) ice core records in Greenland and Wyoming than both the CMIP6 and SIMFIRE-BLAZE emissions \(Hamilton et al., 2018\).](#)

185 In addition to the [extensive](#) examination of paleoenvironmental archives with PI fire emissions datasets by Hamilton et al. (2018), [here we](#) compared simulated annual mean surface PI CO concentrations in Antarctica for each fire emissions inventory using the Southern Hemisphere (SH) ice core CO record from Wang et al. (2010). Simulated Antarctic CO concentrations using PI CMIP6 emissions are 37 ppb, substantially lower than the Wang et al. (2010) 1750 value of  $45 \pm 5$  ppb. This CMIP6 value is closer to the 650-year minimum that occurred in the mid-17<sup>th</sup> century (38 ppb). When using SIMFIRE-BLAZE and

190 LMfire emissions, Antarctic CO concentrations for 1750 are estimated at 48 ppb and 61 ppb, respectively. The overestimation when using LMfire suggest that SH CO emissions may be high for 1750; however, they are comparable to the peak CO concentration measured in the late 1800s ( $55 \pm 5$  ppb) when fire emissions also peaked (van der Werf et al., 2013). As 1850 is also sometimes used as the PI baseline year when calculating RF, we suggest LMfire provides a realistic upper bound to possible PI fire emissions.

195 [The combined evaluation of these inventories in Hamilton et al. \(2018\) and here indicates that although the revised PI fire inventories differ considerably from each other and are substantially larger than CMIP6 in some regions, they result in simulated PI atmospheric concentrations that more closely represent the changes observed in paleoenvironmental archives of changes in Industrial Era fire activity than CMIP6 estimates do. Therefore, their respective impacts on PI tropospheric O<sub>3</sub> concentrations and RF estimates need to be carefully considered.](#)

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## 2.6 Biogenic emission inventories

### 2.6.1 Present-day CCMI

The PD control biogenic emissions were provided from the CCMI inventory. CCMI mean annual BVOC emissions, comprising isoprene and monoterpenes, are derived using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) model (Guenther et al., 2012) under the MACC project (Sindelarova et al., 2014). The CCMI inventory estimates global BVOC emissions at 623 Tg/yr, in reasonable agreement with surface flux measurements and other modelling studies (Arnth et al., 2008; Sindelarova et al., 2014; Rap et al., 2018).

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## 2.6.2 Pre-industrial and present day LPJ-GUESS

Alternative biogenic emissions were produced using the LPJ-GUESS dynamic vegetation model simulating isoprene and monoterpenes (Arnth et al., 2007; Schurgers et al., 2009). Total PD emissions and distribution in the LPJ-GUESS inventory (i.e. 607 Tg/yr) are similar to the PD CCMI inventory (Fig. 2). For the PI emissions, the LPJ-GUESS biogenic emissions inventory is based on the mean for the period 1750-1770, estimated to be 836 Tg/yr. There are large spatial differences between the PI LPJ-GUESS and PD CCMI inventories, with significantly higher emissions in South America and Central Africa, and lower emissions in South-East Asia in the PI LPJ-GUESS inventory (Fig. 2).

## 215 3 Results and discussion

### 3.1 Pre-industrial emission inventories

Figure 1a-d shows annual latitudinal fire emissions of CO, NO<sub>x</sub>, CH<sub>4</sub> and VOCs from all sources for the different fire inventories considered, while Figure 1e compares BVOC emissions (i.e. isoprene and all monoterpenes) from the biogenic inventories. There is large variation in simulated CO emissions between the three PI fire inventories: 644 Tg/yr in SIMFIRE-BLAZE (69% larger than CMIP6) and 1152 Tg/yr in LMfire (200% larger). Estimates of CO emissions using LMfire results in total global emissions which are larger than the PD estimate, which also includes anthropogenic sources. The larger PI biomass burning emissions in LMfire are a result of a number of factors not present in the other PI inventories such as the inclusion of high-latitude fire occurrence, agricultural fire emissions and differing emission factors (Hamilton et al., 2018). The largest increase occurs due to increased SH burning in the LMfire inventory, substantially increasing CO emissions from Australia and South America (particularly Eastern Amazonia and Argentina). In the CMIP6 simulations, global CO emissions are increased by a factor of 2.5 between PI and PD from 382 Tg/yr to 970 Tg/yr. The main driver of this increase is industrial emissions, particularly in the NH mid-latitudes.

Global NO<sub>x</sub> emissions also vary considerably between PI inventories, with values in the SIMFIRE-BLAZE inventory increasing 13% compared to the CMIP6 inventory (36 Tg/yr compared to 32 Tg/yr). This difference is largely due to increased emission in NH mid-latitudes within SIMFIRE-BLAZE. NO<sub>x</sub> emissions in LMfire are 112% larger than the CMIP6 total (68 Tg/yr), with the most significant increases in the extra-tropics.

As CH<sub>4</sub> emissions from fires are significantly smaller than CO emissions (Voulgarakis and Field, 2015), increased PI fire estimates do not substantially alter total CH<sub>4</sub> emission. CH<sub>4</sub> emissions in SIMFIRE-BLAZE and LMfire are similar in amount and distribution, 15% and 9% lower than CMIP6, respectively. There is an increase in SH CH<sub>4</sub> emissions in both SIMFIRE-BLAZE and LMfire compared to CMIP6 but a decrease in the NH and SH mid-latitudes. Total PI CH<sub>4</sub> emissions are greatest in CMIP6 at 241 Tg/yr, approximately 43% of PD emissions. PD SIMFIRE-BLAZE emissions of CH<sub>4</sub> from biomass burning

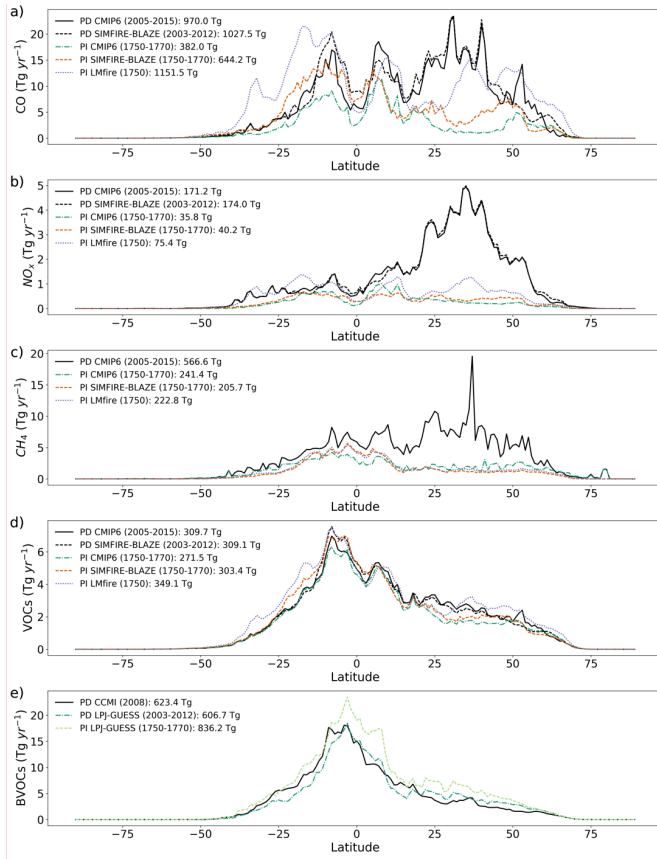
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240 were not available therefore PD CMIP6 CH<sub>4</sub> was applied in the PD SIMFIRE-BLAZE simulation. Due to the scaling of global mean surface CH<sub>4</sub> concentrations in TOMCAT-GLOMAP, the effect of changes in amount of CH<sub>4</sub> emitted is likely small, however the change in distribution may impact the formation and loss rates of tropospheric O<sub>3</sub>.

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245 In terms of fire-emitted VOC species, their magnitude and distribution of emissions are fairly consistent between PD and PI inventories. PI CMIP6 are 87% of PD CMIP6 values, with PI SIMFIRE-BLAZE at 97% (303 Tg/yr). Total global VOC emissions are largest in LMfire at 349 Tg/yr, 29% larger than PI CMIP6 (271 Tg/yr) and 13% larger than PD CMIP6 (310 Tg/yr). The distribution of total global VOC emissions is relatively uniform across all inventories; however, individual species do have larger variability between inventories. Formaldehyde and acetylene for example have substantially increased SH emissions in SIMFIRE-BLAZE and LMfire, due to differences in emission factors, vegetation type and burned area between the fire models.

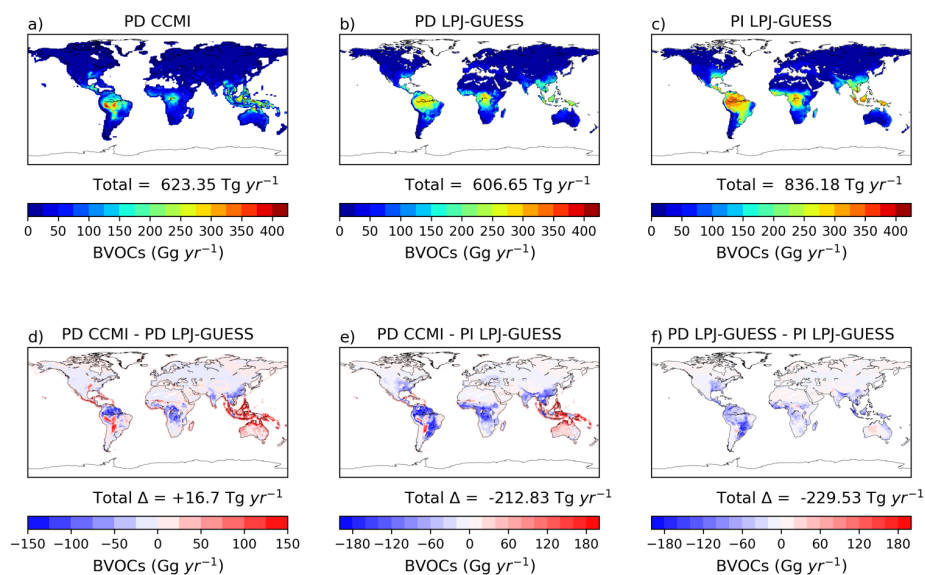
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**Commented [MR1]:** Updated figure includes PD SIMFIRE-BLAZE emissions.

255 **Figure 1: Annual latitudinal mean pre-industrial emissions (in Tg/yr) of (a) CO, (b) NO<sub>x</sub>, (c) CH<sub>4</sub> and (d) VOCs), in PD CMIP6 (solid black line), PD SIMFIRE-BLAZE (dashed black), PI CMIP6 (dashed green), PI SIMFIRE-BLAZE (dotted orange), PI LMfire (dashed purple) inventories. In (e), annual latitudinal mean BVOC emissions (in Tg/yr) in PD CCMI (solid black line), PD LPJ-GUESS (dashed dark green), PI LPJ-GUESS (dotted light green).**

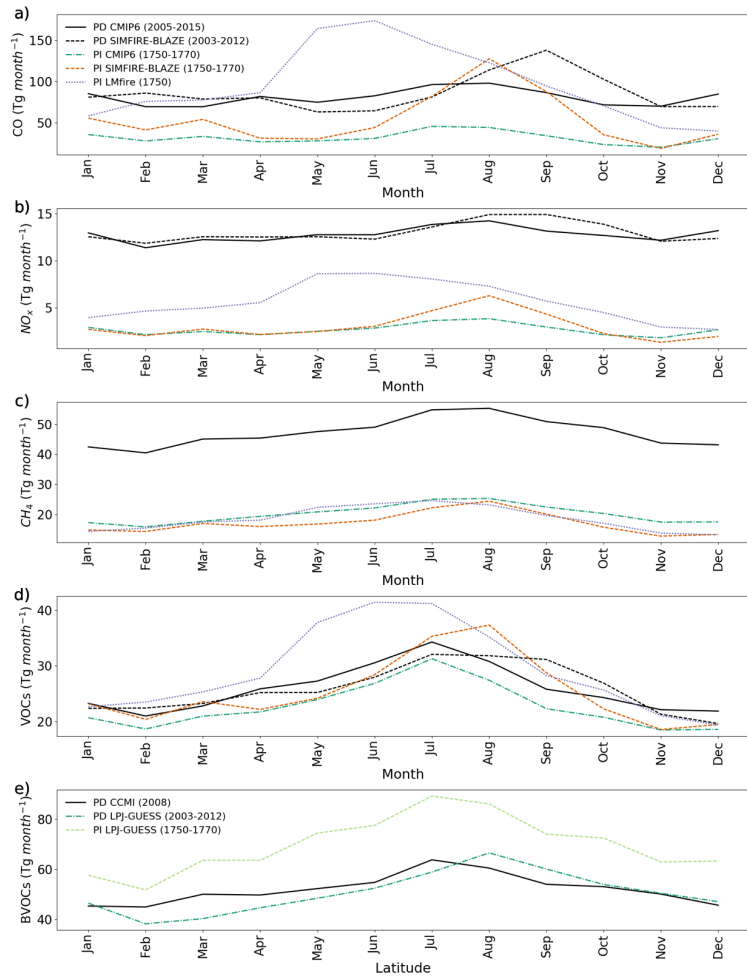




260 **Figure 2: Annual BVOC (isoprene + monoterpenes) emissions at 1°x1° resolution in the two present-day biogenic emissions inventories (CCMI and LPJ-GUESS) and the pre-industrial LPJ-GUESS inventory. Top panels (a-c) show total emissions per year, while lower panels (d-f) show differences between the three inventories. Total annual emissions and difference in annual emissions are also shown.**

265 The BVOC emissions in the two PD inventories (CCMI and LPJ-GUESS) are similar (Fig. 1c), although a small positive NH gradient exists in PD LPJ-GUESS compared to PD CCMI. Total BVOC emissions are 16.7 Tg larger in the PD CCMI inventory than PD LPJ-GUESS (Fig. 2). However, the PI LPJ-GUESS BVOC estimate (836 Tg/yr) is 37% larger than its PD equivalent and 34% larger than PD CCMI, although with a similar spatial distribution (Fig. 2). The largest difference is in South American emissions, where PI LPJ-GUESS emissions are up to 120 Tg larger than PD. The reduction of BVOC emissions between PI and PD is due to a combination of crop expansion, land cover changes and CO<sub>2</sub> inhibition (Hantson et al., 2017). Our results are consistent with previous studies reporting between ~25% (Lathière et al., 2010; Pacifico et al., 2012; Hollaway et al., 2017) and ~35% (Unger, 2014) larger PI values than PD.

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**Commented [MR[2]:** Updated figure includes PD SIMFIRE-BLAZE emissions

275 Figure 3: Total monthly emissions (in Tg/month) of (a) CO, (b) NO<sub>x</sub>, (c) CH<sub>4</sub> and (d) VOCs and total monthly BVOC emissions (e), for PD CMIP6 (solid black line), PD SIMFIRE-BLAZE (dashed black), PI CMIP6 (dashed green), PI SIMFIRE-BLAZE (dotted orange), PI LMfire (dashed purple), PD LPJ-GUESS (dashed dark green) and PI LPJ-GUESS (dotted light green). The legend in panel a) also applies to panels b), c) and d).

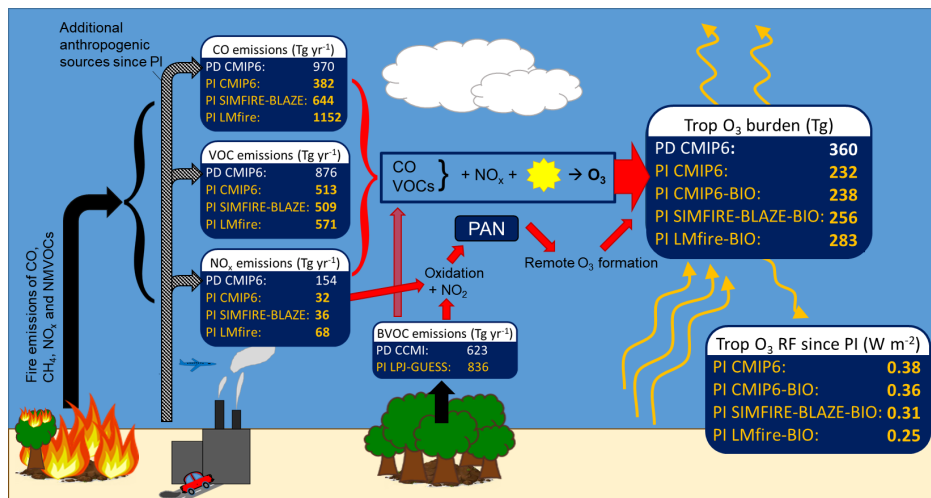
280 The seasonality of the fire emissions in the PD and PI inventories used here is demonstrated in Fig. 3. CMIP6 PI and PD emissions have an extremely similar seasonal cycle for all species, with monthly values offset by larger emissions in PD. This is expected as the PI CMIP6 emissions are based on GFED4s climatology and monthly patterns were assumed not to have changed over time (van Marle et al., 2017). The seasonal cycle of CO emissions (Fig. 3a) varies substantially across the 3 PI inventories, with LMfire estimating peak emissions in May-June as opposed to July-August in CMIP6 and SIMFIRE-BLAZE.

285 This may be a result of increased emissions from SH Africa and Central America, where large fire events are common in late spring. The inclusion of high-latitude fire occurrence and agricultural burning in LMfire may also play a role, as these contribute to fire emissions in the boreal spring season (Hamilton et al., 2018). The SIMFIRE-BLAZE CO emissions exhibit a similar but more pronounced seasonal cycle to that in CMIP6, with peak emissions in August. Similarly, NO<sub>x</sub> and VOC emissions peak earlier in the year in the LMfire inventory relative to SIMFIRE-BLAZE and CMIP6, again with a larger peak

290 in August in SIMFIRE-BLAZE. Monthly CH<sub>4</sub> emissions are broadly consistent across all inventories, with peak emissions in July or August and lower emissions over the NH winter. The seasonality of BVOCs emissions is also consistent across all PI inventories and PD CMIP6, with a peak in July-August. Isoprene emissions are heavily dependent on temperature and photosynthetic active radiation (Malik et al., 2018), therefore reach a maximum in NH summer when the se parameters are optimum for vegetation emissions.

295 Figure 3 indicates similar controls over the modelled seasonality of PI fire occurrence in both PI CMIP6 and PI SIMFIRE-BLAZE, with an increase in estimates fire extent in SIMFIRE-BLAZE results in a more pronounced seasonal cycle. LMfire on the other hand estimates a shift in the seasonality of global fire emissions, with larger fire emissions earlier than other inventories, as well as a broader peak period of emissions. The change in seasonality of precursors will undoubtedly affect the

300 formation and transport of tropospheric O<sub>3</sub>, as atmospheric chemistry and circulation also strong have seasonal cycles. However, the broadly similar pattern of maximum emissions in the NH summer and a minimum in winter, coinciding with similar climatic conditions, means that the substantial difference in volume of precursor emissions across the PI inventories is likely to be more significant than seasonal changes.



305 Figure 4: Summary schematic showing tropospheric O<sub>3</sub> precursor emissions from fire, biogenic and anthropogenic sources, the  
 310 processes of photochemical O<sub>3</sub> formation, the tropospheric O<sub>3</sub> burden and the PI to PD RF. The magnitude of CO, NO<sub>x</sub>, VOC and  
 315 BVOC precursor emissions used in this study is shown for the PD (white text) and each PI inventory (yellow text). The resulting  
 320 calculated tropospheric O<sub>3</sub> burden and RF when using each emission inventory are also shown.

### 3.2 Pre-industrial fire emissions effect on O<sub>3</sub>

310 Annual emissions of O<sub>3</sub> precursors and their contribution to the formation of tropospheric O<sub>3</sub> are shown in Fig. 4. The largest  
 315 difference between simulations is estimates of the global tropospheric CO burden which varies by up to 100 Tg depending on  
 the PI fire emission inventory employed: 195 Tg in the PI CMIP6 simulation, 232 Tg in PI SIMFIRE-BLAZE (18% higher  
 than CMIP6) and 295 Tg in PI LMfire (50% higher) (Table 2).

315 The difference in global NO<sub>x</sub> burden between PI simulations is less pronounced, with increases of 4% and 18% in PI SIMFIRE-  
 BLAZE and PI LMfire respectively, relative to PI CMIP6. The annual mean NH/SH ratio of tropospheric NO<sub>x</sub> burden in PI  
 simulations is 1.09, 1.12 and 1.18 for CMIP6, SIMFIRE-BLAZE and LMfire, respectively. The hydroxyl radical (OH), which  
 plays a key role in regulating tropospheric O<sub>3</sub> concentrations, had lower PI concentrations than in PD due to the higher  
 concentrations of OH precursors NO<sub>x</sub> and O<sub>3</sub> in PD outcompeting the effect of increased CH<sub>4</sub> and CO concentrations which  
 deplete OH (Naik et al., 2013). This is consistent in the TOMCAT PI simulations, with air-mass-weighted global mean  
 concentrations of tropospheric OH, at 1.06, 1.06 and 1.11 × 10<sup>6</sup> molecules cm<sup>-3</sup> in CMIP6, SIMFIRE-BLAZE and LMfire,  
 respectively, compared to 1.12 × 10<sup>6</sup> molecules cm<sup>-3</sup> in PD CMIP6. Each of these values fall within one standard deviation of

the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) multi-model mean of  $1.13 \pm 0.17$  (Naik et al., 2013).

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Changes to the atmospheric concentration and distribution of  $O_3$  precursor species lead to changes in the tropospheric  $O_3$  burden. The PI CMIP6 simulation produced the lowest tropospheric  $O_3$  burden at 232 Tg, slightly below the ACCMIP multi-model mean of 239 Tg for 1850 (Young et al., 2013). In PI SIMFIRE-BLAZE the burden is 242 Tg (4% higher than CMIP6) while in LMfire it is 273 Tg (18% higher), slightly outside the range of estimates of 1850 tropospheric  $O_3$  burden in ACCMIP models (192 Tg to 272 Tg) (Young et al., 2013). The burdens simulated here represent a PI to PD tropospheric  $O_3$  burden change of 55%, 49% and 32% for CMIP6, SIMFIRE-BLAZE and LMfire, respectively. We note that the PI LMfire emissions is the only inventory leading to a simulated PI to PD global burden change of less than 40%, a value consistent with that recently indicated by isotope measurements in ice cores (Yeung et al., 2019). The differences between CMIP6 and SIMFIRE-BLAZE are primarily related to increases in tropospheric  $O_3$  within the Amazon region (Fig. 5a). The change in tropospheric  $O_3$  vertical profile in the PI SIMFIRE-BLAZE simulation compared to PI CMIP6 (Fig. 5c) shows increased annual mean concentrations throughout the troposphere, driven by changes at 30°S and 50°N. Changes between LMfire and CMIP6 simulated tropospheric  $O_3$  profiles are larger, with increased  $O_3$  at all latitudes. Compared to PI CMIP6, there is a mean global increase in  $O_3$  column of 3.7 DU when using LMfire and 1.0 DU when using SIMFIRE-BLAZE. The largest changes occur over Central Asia, Australia and South America where tropospheric column  $O_3$  can be as much as 9.0 DU higher in the PI LMfire simulation than the PI CMIP6 simulation (Fig. 5b). This is reflected in the changes to the vertical  $O_3$  profile, with the largest increases in the subtropics. The difference between LMfire and CMIP6 simulations is greatest between 600 and 800 hPa in the [SH and](#) is roughly constant with respect to changes in altitude over the northern subtropics. The only regions where tropospheric  $O_3$  is higher in the CMIP6 simulation are Central Africa and Indonesia, likely due to the PI CMIP6 emissions being anchored to PD fire observations and thus transferring these patterns to the PI (van Marle et al., 2017).

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The effect of different fire emission inventories on  $O_3$  burden is significantly smaller than the impact on CO concentrations (Table 2), as fire emissions are one of several sources of  $O_3$  variability (Lelieveld and Dentener, 2000).  $O_3$  production is reliant on a number of precursors which do not respond uniformly to the different estimates of fire occurrence in the inventories used here. The relatively minor response of  $NO_x$  concentrations across the three PI emissions estimates (Table 2), and the prevailing  $NO_x$ -limited state across rural environments in PD (Duncan et al., 2010), suggests that increases in CO and VOCs have only a small impact on  $O_3$  production because of  $NO_x$  availability limitations. Moreover, Stevenson et al. (2013) attributed the majority of the PI to PD shift in tropospheric  $O_3$  to  $NO_x$  and  $CH_4$  changes, with a relatively small contribution from CO and NMVOCs despite increasing emissions of both. However, the simulated changes still represent significant shifts in the abundance and distribution of tropospheric  $O_3$  in the PI atmosphere.

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	CO burden (Tg)	NO <sub>x</sub> burden (Tg)	Mean tropospheric OH (x10 <sup>6</sup> mol cm <sup>-3</sup> )	O <sub>3</sub> burden (Tg)	Tropospheric column O <sub>3</sub> (DU)	1750-2010 <u>tropospheric O<sub>3</sub> RF</u> (Wm <sup>-2</sup> )
PD CMIP6	342.6	73.2	1.12	359.9	31.0	-
<u>PD SIMFIRE-BLAZE</u>	<u>351.6</u>	<u>75.0</u>	<u>1.13</u>	<u>363.5</u>	<u>31.2</u>	<u>-</u>
PI CMIP6	195.5	44.8	1.06	231.7	19.9	0.38
PI SIMFIRE-BLAZE	231.5	46.7	1.06	241.6	20.9	0.35
PI LMfire	295.0	52.8	1.11	272.7	23.6	0.27
PI CMIP6-BIO	238.7	44.3	1.00	237.8	20.2	0.36
PI SIMFIRE-BLAZE-BIO	283.4	46.7	1.00	256.0	22.1	0.31
PI LMfire-BIO	337.1	53.4	1.08	282.8	24.4	0.25

Table 2: Annual mean global tropospheric burdens of CO, NO<sub>x</sub> and O<sub>3</sub>, mean tropospheric OH concentration, tropospheric column O<sub>3</sub> for all model simulations and 1750-2010 radiative forcing of tropospheric O<sub>3</sub> estimated for each PI simulation against the PD CMIP6 simulation.

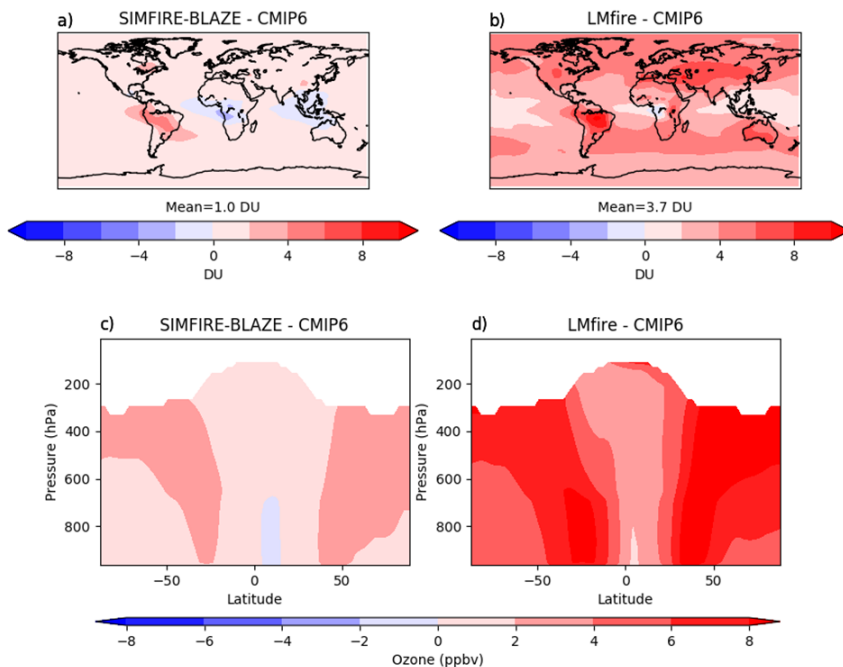


Figure 5: Difference in simulated PI O<sub>3</sub> between revised inventories SIMFIRE-BLAZE and LMfire and the CMIP6 control. Top panels (a, b) compare differences in tropospheric column O<sub>3</sub> in DU, lower panels (c, d) show differences in zonal mean vertical O<sub>3</sub> in ppbv.

### 3.3 Pre-industrial BVOC emissions effect on O<sub>3</sub>

360 We repeated the three PI simulations, replacing the PD biogenic emissions with the PI LPJ-GUESS inventory. In general, the inclusion of PI BVOC emissions increases PI O<sub>3</sub> concentrations, due to an increased VOC source and hence PAN formation (Fig. 4). For CMIP6 fire emissions, the inclusion of PI BVOCs increases the CO burden by 22% and tropospheric O<sub>3</sub> burden by 3%, while mean tropospheric OH concentration decreases by 6%. The decrease in OH is the likely responsible for the simulated increase in CO, as OH is consumed by VOC oxidation. The increase in global tropospheric O<sub>3</sub> indicates that the simulated increases in VOC and CO concentrations are co-located with high NO<sub>x</sub> concentrations, as in low NO<sub>x</sub> BVOCs may decrease local O<sub>3</sub> concentrations.

365 The inclusion of PI BVOCs in the LMfire fire emission simulation causes a 3% decrease in tropospheric OH and increases in tropospheric CO and O<sub>3</sub> of 14% and 4%, respectively.

For SIMFIRE-BLAZE, the inclusion of PI BVOCs decreases OH by 6% and increases CO and O<sub>3</sub> by 22% and 6%, respectively.

370 In all simulations the inclusion of PI BVOCs has only a small effect on the NO<sub>x</sub> burden (~1%). The effect on tropospheric O<sub>3</sub> of including PI BVOCs is notably larger in the simulation using SIMFIRE-BLAZE fire emissions compared to CMIP6 or LMfire. The SIMFIRE-BLAZE simulation combines fire and biogenic emissions produced using the same land-use model, with consistent vegetation distributions. The co-location of isoprene and NO<sub>x</sub> emissions promotes PAN formation, enabling long-range transport of NO<sub>x</sub> and enhancing O<sub>3</sub> production (Hollaway et al., 2017). This synergistic effect has been found to

375 amplify the effect of biogenic emissions on tropospheric O<sub>3</sub> production (Bossioli et al., 2012). Therefore, if PI biogenic

emissions inventories were specifically produced for each fire inventory, the corresponding impact on O<sub>3</sub> would likely be larger than presented here. With the inclusion of PI BVOC emissions, both the SIMFIRE-BLAZE and LMfire simulations result in a PI to PD tropospheric O<sub>3</sub> burden change of 40% or less, in line with estimates from [oxygen isotope measurements from ice cores](#) (Yeung et al., 2019).

### 380 3.4 Effect on ozone radiative forcing

[The estimated tropospheric O<sub>3</sub> RF, based on the CMIP6 PI and PD control simulations, is 0.38 Wm<sup>-2</sup> \(Fig. 4 and Table 2\), comparing well with the IPCC AR5 estimate of 0.4 ± 0.2 Wm<sup>-2</sup> \(Myhre et al., 2013; Stevenson et al., 2013\). We obtain the same 0.38 Wm<sup>-2</sup> RF value when contrasting the PI CMIP6 simulation against the other the other PD simulation \(PD SIMFIRE-BLAZE\). This is consistent with the fact that PD tropospheric O<sub>3</sub> is well constrained by satellite observations \(Rap et al., 2015\).](#)

385 [Given the similarity of the PD simulations, the main PD CMIP6 simulation is used here as the PD for RF calculations in this section.](#) When PI SIMFIRE-BLAZE and PI LMfire emissions are used instead of PI CMIP6 fire emissions, larger PI tropospheric O<sub>3</sub> concentrations lead to 8% (to 0.35 Wm<sup>-2</sup>) and 29% (to 0.27 Wm<sup>-2</sup>) decreases in O<sub>3</sub> RF, respectively. When the PI BVOC emission inventory is used in conjunction with each PI fires emission inventory, O<sub>3</sub> RF is further reduced compared to the control by 5% (to 0.36 Wm<sup>-2</sup>), 18% (to 0.31 Wm<sup>-2</sup>) and 34% (to 0.25 Wm<sup>-2</sup>), for CMIP6, SIMFIRE-BLAZE and LMfire, respectively (Fig. 4). While these reductions in O<sub>3</sub> RF are still within the IPCC uncertainty range, they are caused entirely by uncertainty in PI precursor emissions from wildfires and vegetation. Other key sources of uncertainty (e.g. inter-model spread, use of different radiative transfer schemes) are not accounted for here and would therefore alter estimates further, potentially outside the current 5%-95% confidence range. The most important region for changes to the RF of O<sub>3</sub> is the upper troposphere at subtropical latitudes (Fig. 5d), where there are substantially higher O<sub>3</sub> concentrations in the LMfire simulation. O<sub>3</sub> changes in this region are up to 10 times more efficient at altering the radiative flux than in other regions (Rap et al., 2015). However, the lack of a vertical distribution to fire emissions in TOMCAT affects the simulated changes to the O<sub>3</sub> vertical profile. Previous studies which introduced an injection height scheme found small increases in O<sub>3</sub> production downwind of emission sources (Jian and Fu, 2014), although the change to total O<sub>3</sub> and precursors is relatively small (Bossioli et al., 2012; Zhu et al., 2018).

## 4 Conclusions

400 Revised inventories of PI fire and biogenic emissions substantially decrease estimates of PI to PD tropospheric O<sub>3</sub> RF. When using PI LMfire fire emissions, which represent a plausible upper emissions limit, O<sub>3</sub> RF is reduced to 0.27 Wm<sup>-2</sup>, 29% smaller than the CMIP6 simulation. Large increases in estimated PI fire occurrence drives increases in PI O<sub>3</sub> concentrations (3.7 DU global mean tropospheric column O<sub>3</sub> increase for LMfire inventory) through larger emissions of CO, NO<sub>x</sub> and VOCs. PI CO increases by up to 51% depending on the PI inventory, but the effect on O<sub>3</sub> production is limited by the relatively small increase in NO<sub>x</sub> (-4%). Using PI biogenic emissions, rather than assuming PD values, further increases simulated PI tropospheric O<sub>3</sub>, though the magnitude of this depends on the fire inventory. When accounting for revised emissions from fire and biogenic sources, both the LMfire and SIMFIRE-BLAZE inventories simulated a PI to PD change in tropospheric O<sub>3</sub> burden of approximately 40% or less, in good agreement with estimates from Yeung et al. (2019). Consequently, we find that the estimate of O<sub>3</sub> RF since PI decreases by up to 34% (to 0.25 Wm<sup>-2</sup>) when considering the uncertainty in PI emissions of both fires and  
410 BVOCs.

The impact on tropospheric O<sub>3</sub> from uncertainty in PI natural emissions suggests that previous estimates of O<sub>3</sub> RF over the industrial era are likely too large. Our revised tropospheric O<sub>3</sub> RF estimates are at the lower end of the existing uncertainty range, without yet taking into account other sources of uncertainty. We therefore argue that the impact of uncertainty in PI



415 natural emissions should be further investigated using more models, in order to reassess the current best-estimate and  
uncertainty range of O<sub>3</sub> RF.

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425 <https://doi.pangaea.de/10.1594/PANGAEA.896425>. Other datasets available via Open Science Framework  
\(<https://osf.io/98c2n/>\) or by request from author.](https://doi.pangaea.de/10.1594/PANGAEA.896425)

#### Author contribution

MJR, AR, DSH and RJP conceptualised the study and planned the model experiments. Emission inventories were produced  
by DH, SH, JOK, AA and LN, and processed for use in TOMCAT-GLOMAP by RJP and DSH. All model runs and analysis  
was performed by MJR with guidance from AR, RJP and SRA. The manuscript was written by MJR with comments and  
430 advice from all co-authors.

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