

Atmos. Chem. Phys. Discuss., referee comment RC2  
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## Comment on acp-2021-689

Anonymous Referee #2

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Referee comment on "Tropospheric ozone changes and ozone sensitivity from the present day to the future under shared socio-economic pathways" by Zhenze Liu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-689-RC2>, 2021

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Liu et al. examine the changes in tropospheric ozone between present day conditions and several future scenarios in model runs from UKESM1 as contributed to the AerChemMIP model intercomparison project. They show that the future tropospheric ozone burden and surface ozone mixing ratio are sensitive to the changes in the emissions of short-lived ozone precursors (NO<sub>x</sub> and NMVOC) and to changes in the assumed surface mixing ratio of methane. In the high-emissions SSP3-7.0 scenario the tropospheric ozone burden and the surface mixing ratio of ozone increases, while these decrease in variants of this scenario in which the emissions of ozone precursors or the methane mixing ratio decrease.

Some high-emission regions show different trends to the trend in global surface ozone mixing ratio, which the authors relate to the modelled NO<sub>x</sub>-sensitivity of the ozone production regime in those areas, for example declining NO<sub>x</sub> emissions are associated with ozone surface mixing ratio increases in winter in all future scenarios in Europe and North America, but decreases in summer, consistent with NO<sub>x</sub>-saturated (or VOC-limited) conditions in these regions in present-day winter and NO<sub>x</sub>-limited conditions in present-day summer.

So far, these results are not particularly novel. Where Liu et al. attempt to bring some novelty to the analysis is with a determination of the modelled local ozone production regime in individual model grid cells based on the modelled ratio of NO<sub>x</sub> and VOC mixing ratios (the authors call this "concentration", but they have clearly used molar mixing ratios in their calculations). Such an analysis is potentially interesting, as it would enable determination of the ozone production regime from a single model run rather than from a comparison of two runs. The authors do indeed do exactly this, and their results do make sense (eg. areas with high NO<sub>x</sub> emissions are generally NO<sub>x</sub>-saturated, and these can change to NO<sub>x</sub>-limited as the NO<sub>x</sub> emissions are reduced). Unfortunately, the authors do not give enough information about their method to enable a proper understanding of it. This is itself unfortunate, since the novelty of the paper depends strongly on this analysis.

Firstly, for such an important piece of analysis, the authors give no mention of any previous work that has performed it. This reviewer is not aware of any previous published attempt to quantify the ozone production regime in global model grid cells. If the authors are also similarly unaware of such work, they should say so! Alternatively, they should discuss their approach in the context of any previous work. And while there may not be a lot of literature on the simulated chemical regime in global model grid cells, there is certainly a mature literature on the general topic of ozone production regimes.

The authors define the ozone production regime based on the relative abundance of NO<sub>x</sub> and VOC, citing Sillman (1995) as a source for this. But Sillman (1995) discusses this regime based on the ratio of nitric acid and peroxides, based on the products of the NO<sub>x</sub>-dependant dominant loss pathway for radical species; when NO<sub>x</sub> is high, the dominant loss pathway is NO<sub>2</sub> + OH → HNO<sub>3</sub>, while when NO<sub>x</sub> is low, the dominant loss pathway is HO<sub>2</sub> + HO<sub>2</sub> → H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>. The relative abundance of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> from radical termination reactions has in fact been used already in regional modelling studies as an indicator of the ozone production regime for the purpose of ozone source attribution (Dunker et al. 2002, Kwok et al. 2015). Did the authors consider a similar approach?

Kleinman (1994) showed that these regimes of radical loss are equivalent to the ozone production regimes and can also be characterised by the ratio of the NO<sub>x</sub> source to the radical source. The addition of VOC to a NO<sub>x</sub>-saturated system results in the production of carbonyl compounds (especially HCHO) which act as a source of radicals by their photolysis, hence the equivalence between "NO<sub>x</sub>-saturated" and "VOC-limited" chemical conditions.

So, the ozone production regime depends on more than just the local ratio of NO<sub>x</sub> and VOC. At any given ratio between NO<sub>x</sub> and VOC, the chemical system could be NO<sub>x</sub>-saturated or NO<sub>x</sub>-limited depending on several other factors: the intensity of solar radiation; the background abundance of ozone itself; and the OH reactivity of the VOC present. For example, the same ratio of NO<sub>x</sub> and VOC could lead to NO<sub>x</sub>-limited conditions in summer and NO<sub>x</sub>-saturated conditions in winter. Similarly, the same ratio of NO<sub>x</sub> and VOC could be NO<sub>x</sub>-limited if the VOC are highly reactive (eg. biogenic isoprene) but NO<sub>x</sub>-saturated if the VOC are relatively unreactive (eg. most anthropogenic VOC). By defining the ozone production regime in terms of the relative abundance of NO<sub>x</sub> and VOC, the authors miss all this complexity.

Another issue that the authors should address is the potential dependence of their ozone sensitivity metric on model resolution. The lifetime of NO<sub>x</sub> is relatively short, and the error of instantaneously diluting concentrated NO<sub>x</sub> emissions (characteristic of NO<sub>x</sub>-saturated regions) into relatively large grid cells has been well studied (eg. Wild et al., 2006).

This reviewer recognises that it may be challenging to diagnose the chemical regime in all grid cells of a global model from the relative strengths of the sources of NO<sub>x</sub> and radicals, and that perhaps the mixing ratios of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> may not have been saved in the model output before this analysis. But the authors should at least discuss their approach and its limitations in the context of the previous literature on the topic. A good place for

this discussion would be around the top of page 14, and an even better place for it would be collected in a new Subsection 2.3.

Along with this discussion, the authors should give more information about exactly what they did. Clearly the method has some use (as shown by the analysis in Sections 5 and 6), but for others to reproduce this work, more information is required. For example, which VOC are included in the quantification of the total VOC? Is it all VOC including intermediate oxidation products? Are there criteria for selecting which VOC to include? Is the OH reactivity of each individual VOC accounted for? Is methane included in the total VOC? If not, why not? What about CO? Which grid cells were used in the determination of the threshold ratio? Just the surface? Just the boundary layer? All the tropospheric grid cells?

I hope that the authors see that a lot more information is needed for the interested reader to understand what was done, how it relates to earlier work, how it could be reproduced, and what the potential limitations might be.

#### General comment

The authors should avoid using the term "concentration" when they mean "mixing ratio" (multiple places throughout the text and figures).

#### Minor comments

Page 2, line 25: "positive radiative forcing on climate forcing" is better as "positive radiative forcing".

Page 2, line 36: There has been a decrease in extreme ozone events, but the overall trend in ozone exposure is less clear, and recent work indicates a modest rise in ozone-related mortality (Sicard et al., 2021).

Page 2, lines 45 and 50: see the major comment above.

Page 4, line 101: Lin et al. (2020) showed that vegetation can also be a smaller sink for ozone in warmer climates due to reduced deposition. Is this effect also included in the study?

Page 9, line 160 and page 16, line 256, and in the abstract: Do increases in BVOC (mostly isoprene) really offset decreases in anthropogenic and biomass burning VOC? Butler et al., (2018) showed that biogenic VOC produce more ozone than anthropogenic VOC over these regions, so wouldn't an equal increase in BVOC at the expense of other VOC lead to an increase in ozone?

Page 14, line 232: Please provide more information about how the "dominant" source region was identified in each part of the NO<sub>x</sub>-VOC space.

Page 16, line 258 and page 18, line 267: How can changes in methane cause large changes in ozone itself, but not in ozone sensitivity to NO<sub>x</sub> and VOC? Methane is after all another VOC. This needs more discussion.

Page 19, line 283, and in the abstract: Further emission controls on VOC and CH<sub>4</sub> are unlikely to lead to reductions in winter ozone in these regions, as local photochemical production is extremely slow during winter. Reduced NO<sub>x</sub> emissions in winter act to reduce the titration of background ozone, so once the titration effect has been removed, what remains is the background ozone.

## References

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