

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2022-706

Anonymous Referee #1

Referee comment on "Large simulated future changes in the nitrate radical under the CMIP6 SSP scenarios: implications for oxidation chemistry" by Scott Archer-Nicholls et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-706-RC1>, 2022

General Comments

Archer-Nicholls *et al.* report model results on historical trends and future projections in nitrate radical (NO_3) abundance in the lower atmosphere at global scale. There is a focus on regional hot spots, especially South Asia, where both the historical trends and future projections show large differences. There is also a focus on the relevance of these changes for oxidation of biogenic volatile organic compounds (BVOC), which in turn are relevant to the efficiency with which these species produce secondary organic aerosol (SOA). The future projections are based on a set of emissions scenarios from the recent literature. Figure 2 shows the core result of the analysis of global maps of O_3 , NO_2 and NO_3 differences between the present day, preindustrial, and a series of future projections. Presuming that the O_3 and NO_2 differences are correct, the NO_3 differences can be largely, although not fully, understood in terms of the changes in NO_x emissions and their effects on O_3 distributions.

The paper is of interest to ACP and publishable with minor revisions, as outlined below. The most important comment, listed first below, is that the scope of the paper is somewhat limited compared to what it could be. The paper stops at mixing ratios and oxidation rates, without really predicting more about the associated changes in fates of BVOC oxidation products.

Major Comments

While the paper is of value in assessing trends in NO_3 mixing ratio and BVOC oxidation rates, it stops short of assessing other important quantities such as organic nitrogen and SOA mass. For example, mass yields tend to be oxidant specific, and that effect is not captured here. Previous papers that have examined the mass yield dependences for SOA or organic nitrogen should be cited and compared to this model where possible. Relevant

references are listed below.

- von Kuhlmann et al., *Sensitivities in global scale modeling of isoprene*. Atmos. Chem. Phys., 2004. **4**: p. 1-17.
- Horowitz, L.W., et al., *Observational constraints on the chemistry of isoprene nitrates over the eastern United States*. J. Geophys. Res., 2007. **112**(D12): p. D12S08.
- Hoyle, C.R., et al., *Anthropogenic influence on SOA and the resulting radiative forcing*. Atmos. Chem. Phys., 2009. **9**(8): p. 2715-2728.
- Brown, S.S., et al, *Nocturnal isoprene oxidation over the Northeast United States in summer and its impact on reactive nitrogen partitioning and secondary organic aerosol*. Atmos. Chem. Phys., 2009. **9**: p. 3027-3042.
- Pye, H.O.T., et al., *Global modeling of organic aerosol: the importance of reactive nitrogen (NO_x and NO₃)*. Atmos. Chem. Phys., 2010. **10**(22): p. 11261-11276.
- Hoyle, C.R., et al, *A review of the anthropogenic influence on biogenic secondary organic aerosol*. Atmos. Chem. Phys., 2011. **11**: p. 321-343.

7.Schwantes, R.H., et al. , *Comprehensive isoprene and terpene chemistry improves simulated surface ozone in the southeastern U.S*. Atmos. Chem. Phys. Discuss., 2019. **2019**: p. 1-52.

Specific Comments

Line 9: The nitrate radical is not always, or perhaps even in an integrated or average way, the principal oxidant during the night. This is more typically ozone. Figures within the paper show the importance of ozone compared to nitrate radical. Suggest rephrasing as either "principal oxidant together with ozone", or as "principal oxidant in areas with substantial NO_x pollution."

Line 24: Omit the word "rapidly". Reaction 1 is quite slow.

Line 28: See comment above from the abstract – need to qualify NO₃ as most important nighttime oxidant since it always acts together with O₃ and in locations without NO_x emissions is an unimportant oxidant. A small but important caveat. See for example Edwards *et al.* Nature Geosci, 2017. **10**(7): p. 490-495.

Line 75: Worth noting here also that the rate constant for reaction (1) has among the strongest temperature dependence of any major atmospheric bimolecular reaction, so the source reaction is also sensitive to temperature increases. This effect is certainly more modest than the N₂O₅ equilibrium but worth noting.

Line 100: Agree with the caveats stated here that the simplification of a large, fixed uptake coefficient for N_2O_5 will affect the model predictions of various processes, including BVOC oxidation. It would be useful to see a sensitivity test with a smaller uptake coefficient (e.g., 0.01 rather than 0.1 since the former is likely the more appropriate order of magnitude for the troposphere) for predictions regarding major process chemistry using the specific model in this paper rather than the reference to Jones et al. The authors may wish to comment on the feasibility of inclusion of such a test, or at least qualitatively predict the outcome, if they elect not to do so. See McDuffie *et al.* *Journal of Geophysical Research: Atmospheres*, 2018. **123**(8): p. 4345-4372. for a discussion of the complexity in the N_2O_5 uptake coefficient and its range of variability.

Line 134: Doubling of monoterpenes to account for isoprene is not clear. It was stated above that isoprene is treated separately as its own species?

Line 139, 141: The expressions for kNO_3 appear incomplete or else the units are other than expected for a bimolecular rate constant. The prefactor should be a much smaller number if these units are in $\text{cm}^3 \text{s}^{-1}$.

Line 159-161: There appear to be other features in the comparison of figure 1 for model measurement disagreement. Most obvious is boundary layer height, and presumably vertical mixing throughout the model. The NO_2 gradient near the surface is very strong in the model but not as strong in the observations. This is reflected in the ozone simulation as well. The large NO_3 at higher altitude relative to the model is also certainly a consequence of the NO_2 at higher altitude, again something that could be attributed to vertical mixing that is too small (vertical gradients that are too large) in the model.

Line 167-174 and Table 1: A useful comparison of model to observations for NO_3 . The authors state that these are all from surface observations. Related to the preceding comment, the vertical distribution is likely the most difficult aspect for a coarse resolution model, and even observations with small differences in elevation above surface might differ considerably in how accurately they are simulated. The authors may wish to add this caveat to the discussion.

Figure 3: Useful here would be to also plot absolute temperature across the top axis to provide the reader an easy reference to the temperature changes that are actually inferred by the models. Similarly, rather than a natural logarithm, a base 10 log on the y axis would make the translation of the equilibrium ratios easier to understand at glance rather than having to invert an exponential function.

Line 260-262: The choice of presentation using rates is somewhat misleading since it is an average rate over a diel cycle and a month. An integral (i.e., a total mass within a given time period) would be a more appropriate quantity in figures 4 and 5. The figures themselves would presumably not change, but the mass would place the figures in better context for emissions inventories of BVOC, which are typically in mass units rather than

rates.

Line 297: The caveat about diel boundary layer variability is almost certainly not limited to East Asia, as implied.

Technical corrections

Line 99: Its rather than it's

Line 122: -pinene is missing either an alpha or a beta, likely.

Figure 1c: NO_3 is given in ppbv when pptv is almost certainly what was intended.

Line 295: No comma after the word include