Impact of HO_2 aerosol uptake on radical levels and O_3 production during summertime in Beijing

Dyson et al.

Reply to Anonymous referee #2

We thank the referee for their comments, addressed individually below. The referee's comments are given in normal type with our response in italics. Changes to the manuscript are then given in red type.

1. Since the measured and modeled OH, HO2, and RO2 concentrations have been discussed in detail in Whalley et al., 2021, the authors should focus this paper on the impact of HO2 uptake on the modeled concentrations. In that light, I would recommend removing Section 2.2 and referencing the Whalley et al., 2021 ACP paper (and updating the reference to the discussion paper).

   We have revised the manuscript to move Section 2.2 to the SI.

2. I would also suggest moving the description of the LN/Q and absolute O3 sensitivity calculation (lines 570-603) to section 2 after the model description, and instead focusing on the results in Section 3.

   We have revised the manuscript, moving the description of LN/Q and O3 sensitivity to section 2.

3. The authors provide a brief description regarding potential reasons for the discrepancy between the modeled radical concentrations with the measurements, which are discussed in detail in Whalley et al. (2021). However, at first read the description here does not appear to be consistent with the description in Whalley et al. For example, line 462 states that the overprediction of HO2 by the model may be due to "an under-prediction in the rate of reaction of RO2 with NO to produce a different RO2 species…" while the conclusion in Whalley et al. 2021 is that the "propagation rate of RO2 to HO2 may be substantially slower than assumed." While I believe the reasoning is consistent between the two papers, the wording here could be clarified to remove any potential confusion.

   We agree with the referee and for clarity have revised line 460 onwards in the manuscript to read:

   "the over-prediction of HO_2 could be due, in part, to the propagation rate of RO_2 to HO_2 being significantly slower than currently included in the model. This could be due to a lack of understanding of the rate of reaction of RO_2 with NO to produce different RO_2 species, i.e. $RO_2 + NO \rightarrow RO_2$', which would lead to propagation of RO_2 to different, more oxidised RO_2 species, competing with the recycling of RO_2 via RO_2 to give HO_2. It is also possible, that the overestimation in the propagation rate of RO_2 to HO_2 could be due to a lack of RO_2 autoxidation pathways included within the model which could lead to the formation of highly oxygenated molecules as opposed to HO_2. The higher, measured RO_2 concentrations could, therefore, suggest that the lifetime of total RO2 is longer than currently considered within the model."

4. Similar to that described in Sakamoto et al. (2019), the authors include uptake of RO2 radicals into account when analyzing the impact of aerosol uptake on ozone production sensitivity. Given the authors suggestion that the overprediction of HO2 and underprediction of RO2 is due to isomerization of complex RO2 or RO radicals that effectively increases the lifetime of RO2 radicals and slows the propagation of RO2 to HO2, can the authors comment on whether uptake of RO2 radicals in this scenario could impact the concentration of RO2 radicals and the rate of ozone production? What effective lifetime of RO2 radicals would heterogeneous uptake be competitive and impact RO2 concentrations? Perhaps include a plot similar to Figure 8 for RO2 loss to address this?

   We would expect that if the uptake of RO_2 to aerosol is significant, then the concentration of RO_2 radicals within the model would decrease, in turn decreasing the HO_2 concentration due to an increase in RO_2 radical sinks. This would slow the propagation of RO_2 to HO_2, and therefore decrease the HO_2 radical overprediction within the model if this process is included. Looking at Table 4 in this work, at maximum 7.3 % of total loss of HO2 in MCM_gamma is via uptake. Li et al., (2020) measured ambient uptake of isoprene-RO2 and gave the mean loss of HO2 onto aerosols as 0.0014 s^{-1}, just under double the loss rate of RO2 onto aerosols, at 0.0008 s^{-1}. Looking at Figure 3 in Whalley et al., (2021), a full comparison of median production and destruction rates for OH, HO2, total RO2 and ROx for the Beijing Summer campaign is given, showing the gas phase loss of RO2 to be much higher than HO2. This, coupled with the lower loss rate of RO2 measured by Li et al., (2020), suggests the RO2 uptake would not be significant to impact RO2 concentrations for this campaign.

Li, J., Kohno, N., Sakamoto, Y., Pham, H.G., Murano, K., Sato, K., Nakayama, T. and Kajii, Y., 2022. Potential factors contributing to ozone production in AQUAS–Kyoto campaign in summer 2020: Natural source-related missing OH reactivity and heterogeneous HO2/RO2 loss. Environmental Science & Technology, 56(18), pp.12926-12936.

Whalley, L.K., Slater, E.J., Woodward-Massey, R., Ye, C., Lee, J.D., Squires, F., Hopkins, J.R., Dunmore, R.E., Shaw, M., Hamilton, J.F. and Lewis, A.C., 2021. Evaluating the sensitivity of radical chemistry and ozone formation to ambient VOCs and NO x in Beijing. Atmospheric Chemistry and Physics, 21(3), pp.2125-2147.