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Comment on acp-2021-1021

Anonymous Referee #1

Referee comment on "OH and HO_2 radical chemistry at a suburban site during the EXPLORE-YRD campaign in 2018" by Xuefei Ma et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-1021-RC1, 2022

Review of OH and HO2 radicals chemistry at a suburban site during the EXPLORE-YRD campaign in 2018

The paper presents OH and HO2 observations made in the Yangtze River Delta and compares to model predictions using a box model constrained with the RACM2-LIM1 mechanism. The model-measurement comparison highlighted that OH concentrations were under-predicted by the model under low NO conditions, whilst modelled HO2 agreed reasonable well with the HO2 observed. The impact of monoterpenes on radical concentrations and ozone production was investigated as was heterogeneous HO2 loss. Generally, the results were well presented and the manuscript was reasonably easy to follow although the English used could be improved on. The manuscript would be improved considerably if the results presented were discussed in the context of a wider breadth of previous literature and I have tried to highlight a number of papers that are of relevance to this work in my comments below. I recommend publication once the following comments have been addressed.

Major comments

Pg 3, lines 73 – 78: There was also a field campaign in Beijing in the summer of 2017 (Whalley et al., ACP, 21, 2125 – 2147, 2021) where OH, HO2, total RO2 and kOH observations were made and compared to box model predictions. This work should be discussed and referenced in the context of previous radical measurement studies conducted in the summer in China, particularly in light of the elevated OH concentrations observed. The Beijing results should also be added to Table 3.

Pg 5, lines 127 – 133: The authors state the conversion efficiency of HO2 to OH at 5 ppm NO to be 20%, but should also state the conversion efficiency at 2.5 ppm NO. From laboratory tests, what is the conversion efficiency of an alkene RO2 to OH at 5 ppm and 2.5 ppm NO? The authors should discuss these details in relation to what is seen in other FAGE instruments, e.g. Fuchs et al., AMT, 4, 1209-1225, 2011 and Whalley et al., AMT, 6, 3425 – 3440, 2013.

Pg 6, lines 140 – 147: Some key details on the chemical removal technique should be added to this paper. The concentration of propane added, the % removal of ambient OH, discussion of any losses of ambient OH to the chemical modulation device and % removal of OH internally. Again, the authors should discuss these details in relation to what is seen in other FAGE instruments, e.g. Woodward-Massey et al., AMT, 13, 3119 – 3146, 2020 and Cho et al., AMT, 14, 1851 – 1877, 2021.

Section 2.4: How were photolysis frequencies treated in the model? Was the model constrained with all measured photolysis rates?

How detailed is the a-pinene oxidation scheme in RACM2? It would be useful to reference the a-pinene oxidation mechanism that was used.

The authors state that a first-order loss term equal to 8 hrs gave an observed to modelled ratio of 1.09 for PAN. Other box modelling studies, however, have had to impose a boundary layer height dependent loss rate to reproduce the diurnal trends observed for model-generated intermediates (e.g. Whalley et al., ACP, 21, 2125 – 2147, 2021). How well did the model predict the diurnal variation of PAN/ other model-generated species such as formaldehyde and glyoxal? How sensitive was the model-predicted OH and HO2 concentrations to the imposed loss rate?

Section 3.3: The modelled breakdown of OH reactivity and a comparison to the observed total reactivity was presented in Whalley et al., ACP, 21, 2125 – 2147, 2021 for the Beijing campaign and it would be useful to compare the modelled reactivity from EXPLORE-YRD to this. In Beijing a significant missing reactivity was determined and so the impact missing reactivity may have on the modelled radical concentrations during EXPLORE-YRD should be evaluated.

Pg 10, line 252: How sensitive is the model-generated contribution to OH reactivity to the physical loss rate imposed?

Section 4.2.1, lines 318 – 319: The good agreement between modelled and observed median HO2 should be discussed in light of possible missing OH reactivity (which, if caused by missing VOCs, could act as a source of modelled RO2 and HO2). This could also be discussed in section 4.2.3 which shows that the model to measured agreement for HO2

is reduced when loss to aerosols is considered.

Pg 13, line 335: Can the authors provide the % of OH that is recycled from isoprene via the H-shift mechanism?

Pg 14, lines 368 – 370: I disagree with this statement. Firstly, OH is underestimated by the model. Secondly, there are no OH reactivity observations or RO2 observations to test the model against. A much fuller discussion on the a-pinene oxidation mechanism used in this work is needed (see my later comment).

Pg 18, lines 455 – 457: The lower P(Ox) determined from modelled peroxy radicals relative to the observed demonstrates that the model under-predicts the observed HO2 concentration at NO concentrations greater than 1 ppb. This finding has been observed in a number of previous urban radical measurement campaigns and some discussion of this finding should be presented in this manuscript (perhaps in section 4.2).

Pg 18, lines 459 – 472: Whalley et al., ACP, 21, 2125 – 2147, 2021 highlighted that large RO2 species, such as those deriving from a-pinene, form RO species upon reaction with NO and these RO species can isomerise to form another RO2 species rather than forming HO2 directly. Are these types of RO isomerisations considered in the RACM2 mechanism? A discussion of the a-pinene oxidation mechanism used and the impact this may have on the calculated ozone production rate is warranted here.

Minor comments

Title: 'radicals' to 'radical'

Pg 4, line 84: 'has come up to be responsible for..' to 'has been considered as a possible reason for..' note that, even in isoprene-rich environments, the inclusion of the LIM1 recycling is still not sufficient to reproduce the observed OH concentrations (e.g. Stone et al, ACP, 11, 6749-6771, 2011)

Pg 4, line 91: please also reference Woodward-Massey et al., AMT, 13, 3119 – 3146, 2020

Pg 4, line 96: remove 'been'

Pg 6, line 139: Please state the limit of detection for OH and HO2

Pg 11, 265 – 267: Please provide the references for the campaign referred to here.

Pg 12, line 299: Define ‘OLND’ and ‘OLNN’

Pg 15, line 391: I’m not aware of a laboratory study where an uptake coefficient of 1 has been measured.

Pg 17, lines 429 – 430: Is this Ox loss determined from the model?

Pg 17, equation 5: Define Ï□

Pg 18, line 478: ‘filed’ to ‘field’