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Comment on acp-2022-207

Anonymous Referee #2

Referee comment on "Radical chemistry at a UK coastal receptor site - Part 1: observations of OH, HO_2, RO_2, and OH reactivity and comparison to MCM model predictions" by Robert Woodward-Massey et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-207-RC2, 2022

We thank the referee for their careful reading of the manuscript and for their helpful suggestions. Our responses are given in italics below each comment, together with any changes to the text. The main change is that the two papers have been merged into one paper, and a lot of material has been moved into the SI.

This paper presents measurements of OH, HO2, RO2, and total OH reactivity at a coastal site during the 2015 ICOZA (Integrated Chemistry of OZone in the Atmosphere) campaign. The authors compare the measurements to predictions by both a photostationary state model as well as a zero-dimensional model based on the Master Chemical Mechanism (MCM 3.3.1). The authors find that in general the MCM model was able to reproduce the measured OH concentrations during the campaign, but overpredicted the measured concentrations of HO2 under lower NOx conditions when air arrived to the site from the northwest-southeast sectors, while underpredicting the measurements when more polluted air arrived to the site from the southwest sector. The authors also found that the model underpredicted the measured RO2 concentrations for both lower and higher NOx air that arrived from all sectors. The authors also find that the measured total OH reactivity was consistently greater than that calculated by the model.

The measurements described add to a growing dataset that suggest that our understanding of radical chemistry under a range of conditions may be incomplete, and as a result are of interest to the atmospheric chemistry community. The results are consistent with several previous measurements, and the authors suggest several possible reasons for the model discrepancies based on these previous results, including missing halogen chemistry and autooxidation of RO2 radicals reducing the rate of conversion to HO2 radicals. Unfortunately, the impact of these proposals on their model results are not included in this paper, as they are discussed in the companion paper. While the companion paper focuses on the impact of their proposed mechanisms on the radical budgets, this paper would benefit from some additional discussion of the impact of the proposed mechanisms on the modeled radical concentrations.

We have now merged the Part 1 and Part 2 companion papers into a single merged paper, with quite a bit of material moved to the SI. In this way the impact of the proposed

mechanisms on both the modelled radical concentrations and also the radical budgets can be combined. There is certainly overlap on the impact on the modelled concentrations and the radical budgets.

Specifically, the authors should consider including their model results when they reduced the rate of the RO2 +NO propagation rate as discussed in sections 4.4 and 4.5 as it appears that a reduction in this rate, perhaps due to the competition of RO2 autooxidation with radical propagation, improves the agreement with the measured HO2 and RO2 concentrations. While including an expanded discussion of the model results would add to an already lengthy manuscript, the authors should also consider condensing and or moving some of the discussion of previous measurements into a supplement.

By combining the two papers into a single merged paper, we have been able to condense the material considerably, and have moved a significant amount of material to the SI. The reduced rate means that RO2 will have a longer lifetime and therefore the RO2 concentration will increase in the model, and slower HO2 production via RO2+NO means that the HO2 concentration will decrease – with autoxidation not expected to be a factor under the conditions at Weybourne.

Additional comments:

1) The authors conducted interference measurements during two different periods, finding that unknown interferences contributed less than 20% to the measured OH signal. It appears that these measurements occurred during both NW-SE and SW periods. Did the authors see a significant difference in the interference measurements from the different wind sectors?

No, we did not see a significant difference from the different wind sectors.

2) The authors should consider highlighting the NW-SE and SW periods on Figure 5 to help illustrate the impact of the different air masses on the radical measurements.

The top panel of Figure 2 shows the wind direction, from which the NW-SE and SW periods can be ascertained (either points high on the plot, or low on the plot). Fig. 5 is quite complex already, and we do not want to complicate it further, as there are quite a few changes in wind direction from NW-SE during the campaign. In the caption to Figure 5 we will point to Figure 2 for information about the time-series of wind direction.

Given that the main focus of the paper is on the measurement/model discrepancy of the radical concentrations, there are several sections and figures in the paper that could be moved to a supplement to improve readability. In particular, sections 3.3 and 3.4 along with figures 9 and 10 could be moved to a supplement.

We have merged the two companion papers, and moved significant sections into the SI. Included in the material moved to the SI are the sections mentioned above and the accompanying figures.

3) The authors could also condense much of the discussion of previous measurements by including a table summarizing the previous measurements/model agreement under the different NO conditions and referencing the table in the discussion.

We have constructed a new table which summarises the previous measurements, whilst retaining key information in the text.

4) As mentioned above, the authors should consider adding the reduced RO2+NO model results to Figures 5-7 to illustrate how this model improves the agreement with the measurements. This illustration of the impact of the reduced rate is not included in the companion paper.

A model with reduced RO2+NO was not run. Rather in the second paper the impact of reducing the RO2+NO on the budgets of RO2, HO2 and OH was considered. As the two papers have now been merged, we will merge together the material on reducing the RO2+NO rate, discussing the impact on the budget, and likely impact on their concentrations.