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## Comment on acp-2022-207

Anonymous Referee #1

Referee comment on "Radical chemistry at a UK coastal receptor site - Part 1: observations of OH, HO<sub>2</sub>, RO<sub>2</sub>, 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-RC1>, 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.*

The authors report measurements of radicals at a coastal site in the UK. In general, campaigns with a full set of radical measurements are sparse, so that further exploration of radical concentrations in different chemical conditions are valuable. The paper has a companion paper investigating the chemical budgets of radicals. In this manuscript the authors focus on the description of measurements and model-measurement comparisons. A large part of the manuscript is very descriptive, also in the discussion part, which puts the results into the context of results from other campaigns reported literature. Little new results are shown in the sense of improving the understanding radical chemistry in the atmosphere. Therefore, this manuscript rather fits a measurement report instead of a research article. It should be considered to change the manuscript category.

*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. We feel that combining the results of the two papers does provide new understanding of the chemistry of the atmosphere over a range of NO<sub>x</sub>, and combines a unusually broad range of measurements of radicals (OH, HO<sub>2</sub>, RO<sub>2</sub>), OH reactivity with full supporting measurements to constrain the model and to quantify the radical budgets.*

The authors need to improve the manuscript by a concise writing. It is not clear, if separate papers for the measurements / model results and chemical budget would have been required, if the authors had carefully planned to focus the writing of new findings and had cut on lengthy descriptions of figures that can be easily grasped by seeing the figures. In addition, there are some sections, in which it is not clear, if there is a deeper meaning of the analysis that is shown or if the analysis has only be done, because a similar analysis has been done in other papers and therefore, these sections could have been omitted. The manuscript as it is written

now clearly suffers from having the interpretation of model results and of the chemical budgets separated in 2 papers due to the close connection between both. Specifically the PSS calculations for OH shown in this paper is essentially the same as doing a chemical budget presented in the other paper. Merging the 2 papers would clearly be the best to present the insights into radical chemistry and likely also possible, because parts of the papers are similar, since the same data set is analysed and results from each paper is described in the other paper, and descriptive and unnecessary parts can be omitted.

*On reflection we feel that separate papers are not warranted for the radical measurements/model comparisons and the radical budget, for the reasons outlined by the referee. Hence we have merged the two papers, and with conciseness in mind, have reduced the material considerably looking for overlaps between the two papers, and have moved a lot of material into the SI to support the results in the main paper.*

The presentation quality of figures also needs considerable improvements. Font sizes in most of the figures contain are too small to be readable and scaling of axis are not appropriate. Light colours of text as used in the current figures are not suitable for reading (e.g. yellow).

*Where possible we have resized some of the figures to mitigate against this, and where possible altered the figures, and moved quite a few figures to the SI where the figures are presented at a considerably larger size.*

Additional specific comments:

L50: For this type of paper, just showing H-abstraction to form RO<sub>2</sub> may oversimplifying the chemistry. Overall, some of the text-book like introduction may not be required.

*We have removed a considerable amount of the text-book like material, in that way it should then not be considered selective via omission of e.g. addition processes.*

L84: I assume that you mean "their photolysis can also be important radical sources"

*Yes that is what is meant. We have used the suggested rewording.*

L94: The conclusion in Novelli et al. is not that Criegee intermediates are the reason for interferences observed in the field, because reactant concentrations in their work were much higher than atmospheric concentration.

*We have removed this reason for the observed interferences.*

L144: Are you sure that the purity of NO was 99.95%? Typically the best purity that is available is only 99.5%.

*Checking the BOC specifications, the purity is now quoted as N2.8, which is 99.8%. This has been changed in the materials section.*

Fig. 2 It may be a good idea to improve visibility by splitting the figure into 2 panels by time.

*We feel that the data being shown all together provides an overview of the campaign in one panel. We have now positioned the figure so it is landscape on a single page so easier to see.*

L330: The statement about HONO is rather short and does not really reflect the high variability that is observed. On some days, values during the day were even higher than during the night.

*We agree that HONO is quite variable – and have added a statement to that effect.*

L384: Looking at the entire time series, the second peak that appears in the median diel profile looks more like an artefact of the median calculation than a real feature of the diel profile as it sounds in this statement.

*We agree, it is just a single point on the median diel profile. We have removed the sentence regarding the second peak.*

L411: I would avoid giving information in the text that is repeating what can be seen in the legend of the figure

*We have removed the repetition, and tried to do this where this may occur elsewhere.*

Fig 7: Here, it may make sense to have the same scale of the y-axis for sRO<sub>2</sub> and cRO<sub>2</sub>.

*There is quite a difference between sRO<sub>2</sub> and cRO<sub>2</sub> (factor of 3) and we feel that some detail will be lost if the y-axes are the same.*

Fig. 8: Labels of the pie chart are not easy to read. Names may need further explanation in the figure caption. Numbers of fraction could be useful as well as the total median RO<sub>2</sub> concentration.

*We have made these bigger and defined them in the caption (using the definitions in Section 3.2 of Paper 1). We have also given the total median RO<sub>2</sub> in the caption for the 2 wind directions. We feel the fractions can be estimated by eye using the figure, and the numerical values are given in the text.*

L430 ff: Is the relative abundance of specific RO<sub>2</sub> radicals consistent with measured OH reactants? This should be discussed.

*That is a good idea but it is very difficult for some RO<sub>2</sub> because they can have multiple sources. Even for the simplest CH<sub>3</sub>O<sub>2</sub>, this may derive from several VOCs, not just CH<sub>4</sub> but*

following further degradation of larger RO<sub>2</sub>. We do indicate the major VOCs which the RO<sub>2</sub> derive from, but in this section.

Section 3.2: RO<sub>2</sub>: It looks like an offset between measured and modelled simple RO<sub>2</sub>. Can you exclude that there is an unaccounted instrumental offset?

*We can never completely exclude the possibility of an unaccounted instrumental offset, but our laboratory measurements for a range of VOCs (as described in Whalley et al., 2013) did not reveal any offset. We have assumed that all RO<sub>2</sub> are converted to HO<sub>2</sub> in the ROxLIF reactor and then to OH in FAGE fluorescence cell (following NO addition) with the same efficiency as CH<sub>3</sub>O<sub>2</sub>. If other RO<sub>2</sub> species convert less efficiently, this would mean we are underpredicting the total RO. The only way that the measurement can overestimate RO<sub>2</sub> is if something is decomposing to form RO<sub>2</sub> in the instrument. – Fuchs et al. (2008) estimated HO<sub>2</sub>NO<sub>2</sub> to contribute 1.7% of the measured HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub> contributes 6% to RO<sub>2</sub> (assuming an ambient NO<sub>2</sub> concentration of 10 ppbv). For PAN, Fuchs et al. (2008) expect 0.1 pptv RO<sub>2</sub> per ppbv PAN.*

*H. Fuchs, F. Holland and A. Hofzumahaus, Measurement of tropospheric RO<sub>2</sub> and HO<sub>2</sub> radicals by a laser-induced fluorescence instrument, Review of Scientific Instruments, 79, 084104 (2008).*

*Whalley, L. K., Blitz, M. A., Desservettaz, M., Seakins, P. W., and Heard, D. E.: Reporting the sensitivity of laser-induced fluorescence instruments used for HO<sub>2</sub> detection to an interference from RO<sub>2</sub> radicals and introducing a novel approach that enables HO<sub>2</sub> and certain RO<sub>2</sub> types to be selectively measured, Atmos. Meas. Tech., 6, 3425–3440, <https://doi.org/10.5194/amt-6-3425-2013>, 2013.*

Section 3.3: This analysis does not give much insights as it is done here. More discussion and comparison with previous findings with interpretation of different and similar results would be needed.

*There is a comparison with previous findings later in Section 4.1. We have signposted this from section 3.3. Also, combining the two papers will help – as the budget analysis for the radicals highlights processes that may be missing – which links to the model-measurement comparison.*

Section 3.4: Again, there is little interpretation or discussion of the correlation and it is not clear what is learned from this analysis. What is the meaning of the different slopes? What is expected for what reason?

*It is quite unusual to see plots of RO<sub>2</sub> versus HO<sub>2</sub> owing to the scarcity of simultaneously measured data so these correlation plots, and the corresponding ones for modelled values are quite novel. However, we agree there could be more discussion, for example regarding the modelled correlation plot at night, which is very different. Also, combining the two papers into one allows the budget analysis for HO<sub>2</sub> and RO<sub>2</sub>, as RO<sub>2</sub> degradation provides a source of HO<sub>2</sub>.*

L465: The offset does not necessarily indicate that some RO<sub>2</sub> sources (= type of RO<sub>2</sub> radicals) do not form HO<sub>2</sub> as it sounds in the statement. It can also be that the lifetimes of HO<sub>2</sub> and RO<sub>2</sub> were much different or RO<sub>2</sub> loss channels did not lead to HO<sub>2</sub> formation, but the RO<sub>2</sub> from all sources may still generally form HO<sub>2</sub>. If there were mainly RO<sub>2</sub> sources in the night but little HO<sub>2</sub> present, why would you expect that there is a correlation between RO<sub>2</sub> and HO<sub>2</sub>, when the reaction of RO<sub>2</sub>+NO as most important pathway to HO<sub>2</sub> is not relevant in the night?

*We agree and have incorporated the above into the discussion. There is a correlation but the gradient is much greater (RO<sub>2</sub>:HO<sub>2</sub>) at night suggesting nighttime RO<sub>2</sub> converts to HO<sub>2</sub> much less efficiently at night when NO is low, compared with the daytime. However, small amounts of RO<sub>2</sub> will be converted to HO<sub>2</sub>, so a correlation still exists (either because there is a small amount of NO present or the RO<sub>2</sub>+RO<sub>2</sub> self-reaction can form HO<sub>2</sub>).*

Section 3.6 / Figure 15: Would you expect that an exponential behaviour of BVOC emissions is visible for the range of temperature that is experienced in the campaign? Can you make an estimate, how much RO<sub>2</sub> concentrations will change, if you assume additional VOCs in the model to account for the gap between measured and modelled OH reactivity?

*Over the range of T in the plot (13-24 degrees) we would not expect to see an exponential behaviour, but there clearly is a dependence. In the companion budget analysis paper, we discuss the additional RO<sub>2</sub> that is made from missing OH reactivity, which is given by missing kOH/DRO<sub>2</sub>, where DRO<sub>2</sub> is the destruction rate of RO<sub>2</sub>. As we have now merged the two papers, discussion of how RO<sub>2</sub> concentrations will change is covered.*

Section 4.4: It would be good to have some numbers of reactive halogen species that would be required to explain observations.

*We state that for Mace Head during NAMBLEX where it was found that up to 40% of HO<sub>2</sub> could be lost to IO under low-NO<sub>x</sub> conditions, for measured IO levels of 0.8–4.0 pptv 675 (Commane et al., 2011). There have been no measurements of IO, HOI or I<sub>2</sub>, nor BrO, at Weybourne, and there are no exposed sea-weed beds like at Mace Head, and so it is not expected that halogen levels are so high. However, the levels that were seen at Mace Head are the sort of concentrations that would be needed to explain the observations.*