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Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
https://doi.org/10.5194/acp-2022-213-RC2, 2022

Comment on acp-2022-213

Anonymous Referee #2

Referee comment on "Radical chemistry at a UK coastal receptor site - Part 2: experimental radical budgets and ozone production" by Robert Woodward-Massey et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-213-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 manuscript reports an investigation of the ROx radical budget for the ICOZA 2015 field campaign. This is the follow-up of a first publication where the authors reported the measurements of OH, HO2 and RO2 and a comparison to zero-dimensional box modeling. In this companion paper, the authors provide a detailed description of the ROx radical budget (OH, HO2 and RO2 taken all together as a group of species), providing insights into initiation and termination processes of this group of radicals. An original aspect of this publication is that the authors also investigated individual budget closures for OH, HO2 and RO2, providing additional insights into propagation routes within these radicals. Another originality of this work is the use of ancillary measurements of radical sources and sinks to perform an experimental assessment of these radicals budgets.

It is shown that while a reasonable closure of the ROx budget is observed (only a small imbalance between production and destruction rates for air masses from SW origin), individual radical budgets highlight that our knowledge on radical propagation pathways is still incomplete, especially propagation routes between HO2 and RO2.

This reviewer thinks that this work is of interest for the scientific community and deserves publication. Individual HO2 and RO2 budgets are usually not investigated with this level of details and this publication highlights the benefits of assessing these radicals' budgets in addition to the budgets of ROX and OH. I therefore recommend publication in ACP after the authors address the following minor comments:

L89-91 : " Given the short lifetimes of OH, HO2, and RO2 radicals (on the order of seconds to minutes), we can assume that their concentrations are in steady-state and hence expect their production and destruction rates to be equal at a location such as the WAO where incoming air is homogeneous. " - It is not clear to this reviewer whether a lifetime of tens of seconds/minutes is not too long to assume steady-state. This aspect was discussed for ROx modeling in the nocturnal boundary lawer by Geyer et al. (J. Geophys. Res. 109, doi:10.1029/2003JD004425, 2004). Could the authors comment on this?

The assumption of steady-state is a central assumption in order to calculate the concentrations of radicals using a box-model. For OH, with a lifetime of < 1 sec, this is always satisfied, and at a clean site where there are no local sources, for example of NOx, which may perturb the NO2/NO ratio from its expected value, we expect this to be the case also for longer-lived radicals such as HO2 or RO2. Actually for these species, minutes is probably not entirely correct, with the levels of NOx encountered at Weybourne, the lifetime is likely to be < 1 minute. We have modified the text to 1 minute. We have also referenced the work of Geyer et al.

L135-137: "In line with Tan et al. (2019), we did not explicitly consider equilibrium reactions of the type HO2 + NO2 aDD HO2NO2 and RO2 + NO2 aDD RO2NO2 (e.g, peroxyacetyl nitrate (PAN) formation and decomposition) in the budget analyses, and assume these processes result in no net gain or loss of the radical species" - Both of these equilibrium reactions can act as a source or a sink of peroxy radicals, depending on ambient and environmental conditions. What is the range of lifetimes for HO2NO2 and RO2NO2? Could neglecting these reactions lead to significant biases in production and destruction rates of HO2 and RO2?

The HO2NO2 and CH3O2NO2 destruction and production balance in the model – so represent no net loss or production of peroxy radicals. Only at extremes in temperature would the equilibrium be skewed. For example at Hudson Bay in the Arctic, the formation of HO2NO2 was identified as an important radical reservoir, reducing HOx concentrations during the day and enhancing them at night (Edwards et al, 2011). However, these conditions are not relevant for Weybourne in summer. The acyl peroxy radicals is the only way to form PAN in the MCM, and we state that the acyl peroxy constitutes 7-8% of the RO2 pool. For typical temperatures of the campaign HO2NO2 and PAN (and other PANs) will be in equilibrium. We have made this clearer in the text and added this reference.

Edwards, P., et al. (2011), Hydrogen oxide photochemistry in the northern Canadian spring time boundary layer, J. Geophys. Res., 116, D22306, doi:10.1029/2011JD016390.

Section 2.1.3: The reaction of OH with some VOCs can lead to the prompt formation of HO2 (e.g. isoprene, aromatics). The authors may want to comment on the potential bias introduced in P(HO2) calculations when assuming that VOC+OH reactions only lead to RO2 formation. Same question for P(RO2) in section 2.1.4 - What is the potential bias introduced in P(RO2) calculations?

The yield of HO2 from OH oxidation of these species is explicitly contained in the MCM mechanism and so HO2 formation is included. For the Beijing field campaign the formation of HO2 from VOC + OH → HO2 versus the formation of RO2 from VOC+OH → RO2 was investigated during the AIRPRO campaign (Whalley et al., 2021) – and HO2 production was not insignificant, owing to the presence of VOCs like isoprene and aromatics in the Beijing in summer. We will modify the wording to make clear that prompt formation of HO2 is included.

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., Lewis, A. C., Mehra, A., Worrall, S. D., Bacak, A., Bannan, T. J., Coe, H., Percival, C. J., Ouyang, B., Jones, R. L., Crilley, L. R., Kramer, L. J., Bloss, W. J., Vu, T., Kotthaus, S., Grimmond, S., Sun, Y., Xu, W., Yue, S., Ren, L., Acton, W. J. F., Hewitt, C. N., Wang, X., Fu, P., and Heard, D. E.: Evaluating the sensitivity of radical *chemistry and ozone formation to ambient VOCs and NO_x in Beijing, Atmos. Chem. Phys., 21, 2125–2147, https://doi.org/10.5194/acp-21-2125-2021, 2021.*

L453-455: "In contrast, model-calculated P(Ox) starts to fall off a little above 1 ppbv NO in NW-SE air, but generally increases with NO in SW air." - For SW air, it seems that the increasing trend stated by the authors is very dependent on one data point at approximately 2 ppb NO. This reviewer thinks that this is a bit overstated.

We agree. We have modified the text to: "In contrast, model-calculated P(O_x) starts to fall off a little above 1 ppbv NO in NW–SE air, but generally increases with NO in SW air, but the latter is largely due to a single point at 2 ppb NO".

L466-73: The authors discuss the impact of the various recycling hypotheses (HO2+Y, RO2+X, RO2+Z) on the HO2 and RO2 budgets. The discussion focuses on the comparison of median diel profiles of production and destruction rates. Could the authors comment whether the NO-dependence of observed imbalances changes when the proposed recycling processes are accounted for?

That is a good question, but we feel it is beyond the scope of the paper to further analyse the impact of X, Y and Z on the HO2 and RO2 budgets as a function of NO, given that the identity of X, Y, and Z is not known (we have adopted an approach used by other workers where the concentrations of X, Y and Z are chosen to represent an equivalent NOx concentration). On reflection, and also considering a comment by Referee 1 for this paper, we have decided to omit the section on X, Y, and Z from the paper.

L566-567: "It is therefore recommended that more studies are conducted to measure RO2 + NO rate constants, in particular for more complex, functionalised RO2." - On the basis of the arguments discussed L536-541 to explain a lower-than-expected RO2-to-HO2 propagation rate, the authors may want to recommend to study the fate of RO radicals.

A good suggestion, especially for complex RO which may be involved in autoxidation processes. We have added this recommendation.