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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

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?

L135-137: "In line with Tan et al. (2019), we did not explicitly consider equilibrium reactions of the type HO2 + NO2 â□□ HO2NO2 and RO2 + NO2 â□□ 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?

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?

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.

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?

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.