

Comment on acp-2022-213

Anonymous Referee #1

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-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.

This paper presents the experimental budget analysis of OH, HO₂, RO₂, and the sum of all three radicals (RO_x) at a site on the east coast of UK in summer 2015 as a part of the ICOZA campaign. The data was split into two subsets, i.e. SW and NW-SE, according to the wind sectors. The RO_x budget was closed within experimental uncertainty, indicating no significant missing primary sources or termination processes. The OH destruction rate was slightly larger than its production rate, indicating a missing OH production process. The most severe imbalance occurred in the HO₂ and RO₂ budget analysis. The HO₂ production rate exceeded the destruction rate by the similar rate as the RO₂ destruction rate exceeding the production rate. Such imbalance elevated with NO mixing ratios.

To reconcile the imbalance in HO₂ and RO₂ budget, the authors performed several sensitivity tests. The most efficient case was reducing the RO₂+NO reaction rate constant by a factor of 5. However, the change in the reaction rate constant contradict with literature reports.

The gross in situ ozone production rate was also calculated from observed and modelled radical concentrations. Large discrepancy was found in the ozone production rate derived from measured and modelled radical concentrations.

The results are of interest to the atmospheric chemistry community, to show key processes of RO_x radical chemistry and unveil missing chemical processes. The paper is well structured and nicely written. I am in favor of publication after some of the issue being addressed. Also, the author may consider to concise the writing so that the main message(s) can be more prominent.

We have merged the two companion papers, and moved a considerable amount of material into the SI, and this has led to a more concise delivery of the main messages.

General comments:

1. The uncertainty analysis is missing. The authors stated the experimental uncertainty of radical destruction rates. But what about the production rates? Was it possible that the ROx budget in the SW air was also balanced if uncertainty of P(ROx) was considered. It would be useful to add one vertical bar at the time when the discrepancy was largest. The paper discussed the possible mechanism behind the experimental budget imbalance, which was fine. But the imbalance in the HO2 and RO2 budget could also be explained by measurement interference, for example, the RO2 measurement interference. An evaluation of possible interference and its contribution to close/enlarge the imbalance of radical budget should be added in the revised version to complete the discussion.

A discussion of possible interferences was part of the companion paper. The two papers are now combined, and so interferences will be more prominent. The uncertainty of the measurements and the interferences are not sufficient to explain the imbalance of the radical budgets. We have added the uncertainty in the discussion.

I would suggest to add the time series of radical budget in supplement at least. So the readers could see the variability of the experimentally determined budget.

Many thanks for the suggestion. We will add such a time series for the budgets in the Supplementary Information.

The selection of the amounts of X, Y, Z looks quite arbitrary. It would be good to reconstruct the context to give the reason why such amounts of X, Y, Z were used. The amount of X was chosen to be 100 ppt as suggested in another paper, which conducted at a very different environment. The simplification of X mechanism was not really correct as the X species will have impact on OH, HO2, and RO2 radical budgets. The RO2^{OH} conversion is possible, such as RO2 unimolecular isomerization, which should be nominated to a different term other than 'X'. Although I don't expect a big change to the HO2 and RO2 budget, it's more comparable to previous papers.

The amounts are arbitrary, and were chosen as there was some precedent from another paper as the referee points out. It is just a hypothesis as a possible reason to explain the discrepancy, and we realise that there are many assumptions and approximations, such as the one suggested by the referee. We could work out a production rate of OH from RO2 isomerisation ($k_{isom}[RO_2]$) that closes the OH budget – this would use the total RO2 concentration – and so the assumption would have to be made that all RO2 radicals make OH. We do not feel there is previous literature supporting that RO2 to OH would account for all the missing OH, as OH generation tends to lead to a slowing down on the rate of autoxidation. Also, the modelled to measured OH is in reasonable agreement, even if there are both missing sources and sinks of OH which may in some cases cancel, although OH is underpredicted at low NO. On reflection, and also considering the comment of the other referee on this paper, we have decided to take out the section in the paper regarding the use of X, Y and Z species being postulated to help to explain the differences between the model and measurements.

As the authors proposed that reducing the reaction rate of RO₂ to HO₂ propagation was the most likely explanation to reconcile the HO₂ and RO₂ budgets, should the P(Ox) also be calculated with the reduced reaction rate constant?

The impact on P(Ox) would be simply multiplying the value of P(Ox) by the ratio of the rate of RO₂ to HO₂ production with and without the reduction in rate coefficient for RO₂+NO. The impact of this for the HO₂ and RO₂ budgets was shown in Figure 11. However, we feel that there are already a large number of figures, and hence we will make a statement in the text that the value of P(Ox) will be impacted by a change in the rate coefficient, and refer to Figure 11.

2. If HO₂ uptake and Cl chemistry was not important radical processes, I would suggest moving the relevant figures to the supplement and reduce the context further.

Yes, that is a good suggestion. We have done this and just retained a sentence or two that uptake and Cl chemistry was done, and the results are in the SI.

3. The first part of the discussion seems to be a repetition of what have been done and belongs to the conclusion. It should be shortened massively.

We have done this, and further reduction in material enabling a more concise discussion has been achieved by merging the two companion papers.

4. The comparison to previous works looks interesting and informative. Could it be able to summarize into a table with the three studies side by side?

This is a good idea, and we have introduced a Table to summarise the information that is in the text. There is also a Table for the other companion paper which will summarise information for comparison of measured OH, HO₂ and RO₂ with box-models. This will further aid the reduction in material to make more concise.

5. The citations are not properly used. For example, Mehra et al. 2020, Slater et al. 2020, Whalley et al., 2020, the discussion version is cited while the final version is published. I also noticed the same problem occurs in the accompany paper. I do not have time go through the list, but I think mistake in the reference is not acceptable in any kind of scientific journals. Please carefully check all the reference list.

We apologise for this. When the paper was being initially drafted these papers were still at the ACPD stage, but this was not updated to reflect they are now published in ACP, and this will be updated.

Technical comments:

1. Throughout the paper, it should be the rates of production and destruction. Most of the sentences miss the word 'rate(s)'.

Thanks for pointing that out, we have added the word "rate(s)"

2. Line 106. It's not a good argument that H₂O₂, ROOH and etc. were not measured so they are not considered in the radical budget. I think the contribution of these species is not important. Please give a rough estimate of these species and contribution to the radical budget first and say why they are not included.

We agree that the contribution of these species is not important. H₂O₂ and CH₃OOH, and some other peroxides have been measured at coastal locations. For example, mean concentrations of H₂O₂ and CH₃OOH at Mace Head were 0.23-1.58 ppbv and 0.1-0.15 ppbv, respectively (Morgan and Jackson 2002). At coastal locations peroxide photolysis was shown to be a minor source of OH or HO₂ (via CH₃O) (Sommariva et al., 2004; 2006)). Specifically at Cape Grim, the rate of OH production from CH₃OOH was less than 5% of the rate of production from O(1D)+H₂O (Sommariva et al., 2004), and hence peroxides were not included in the radical budget analyses. This will be added to the revised MS together with these references.

Morgan, R. B., and A. V. Jackson, Measurements of gas-phase hydrogen peroxide and methyl hydroperoxide in the coastal environment during the PARFORCE project, J. Geophys. Res., 107(D19), 8109, doi:10.1029/2000JD000257, 2002

Sommariva, R., Haggerstone, A.-L., Carpenter, L. J., Carslaw, N., Creasey, D. J., Heard, D. E., Lee, J. D., Lewis, A. C., Pilling, M. J., and Zádor, J.: OH and HO₂ chemistry in clean marine air during SOAPEX-2, Atmos. Chem. Phys., 4, 839–856, <https://doi.org/10.5194/acp-4-839-2004>, 2004.

Sommariva, R., Bloss, W. J., Brough, N., Carslaw, N., Flynn, M., Haggerstone, A.-L., Heard, D. E., Hopkins, J. R., Lee, J. D., Lewis, A. C., McFiggans, G., Monks, P. S., Penkett, S. A., Pilling, M. J., Plane, J. M. C., Read, K. A., Saiz-Lopez, A., Rickard, A. R., and Williams, P. I.: OH and HO₂ chemistry during NAMBLEX: roles of oxygenates, halogen oxides and heterogeneous uptake, Atmos. Chem. Phys., 6, 1135–1153, <https://doi.org/10.5194/acp-6-1135-2006>, 2006.

Line 135. 'do not'

Corrected

3. Line 212. Could you give an estimation on how much radical can be produced from NO₃+VOC?

Measurements of NO₃ were not measured during the campaign and a model calculation of the

NO₃ reactivity calculation was not performed. So it is difficult to estimate the fraction of radicals which come from NO₃ chemistry, but any radicals from this source would reduce the budget imbalance at night.

Line 231. The number is different from the figure.

Thanks for spotting this, this has been corrected.

4. Line 247-250. I don't get the picture why to split the data into two sectors. How significant are these two air masses different? I cannot really see from the radical budget analysis.

The two papers have now been combined, and the first paper contained a more detailed rationale of why the data were split into two sectors. Weybourne is a well characterised site, and typically experiences two major types of air mass – a cleaner one from the ocean sector, and another which derives from more polluted regions.

5. Line 258. Be more specific on what is the difference in VOC.

The difference is VOC composition between the two wind sectors was covered in the companion paper (which is referenced), but as the two papers are now combined it will be clearer what the difference in VOC composition was for the two sectors.

6. Line 264-266. Better rephrase this sentence to be clearer.

Again, part of this sentence is summarising what was in the companion paper, and so upon combining the two papers this will no longer be necessary.

7. Line 302-310. The contribution of different species is better scaled to measured kOH rather than calculated kOH. The same applies to Table 2.

The missing reactivity is ~ 50% of the measured values, and so scaling to measured kOH would in effect halve the values stated in the text and in Table 2. Rather than changing the Table and the values in the text, we have restated that the calculated reactivity is approximately half that of the measured value – to make it clearer regarding the contribution of each species.

8. Line 306. 'Small but significant' sounds like a statistic phrasing, which may not fit in the current sentence.

The words “but significant” have been removed

9. Line 350. Is there a reason or reference to support this speculation?

Not to our knowledge, which is why we use the word speculate.

10. Line 358. wrong citation format.

Corrected.

11. Line 403-404. Better to rephrase it to be clearer.

The word “gross” has been removed to make this clearer

12. Line 408. 'HO₂+NO' looks confusing.

This has been reworded to “...for the channel generating HO₂ + NO₂ products”.

13. Line 411 E13. The RONO₂ formation should not be a O₃/NO₂ loss. I guess the authors are referring to PAN formation, i.e. RO₂+NO₂?

If RONO₂ is formed then this removed NO₂, and hence O₃ production via its photolysis.

14. Line 430 and later on. 'FAGE-calculated' looks like a lab jargon. Maybe better to use derived from measurements or others.

Thanks, that is a good suggestion. We have replaced FAGE by “derived from measurements using the FAGE instrument”

15. Line 449-450. Not really needed this sentence.

We have removed this sentence.

16. Line 478-481. Better to rephrase it to be clearer.

This section has been rephrased to: "Reducing the RO₂ + NO rate constant by a factor of 5 is not consistent with accepted laboratory measurements for which uncertainties in the range ~15–35% are reported (Orlando and Tyndall, 2012). It is therefore imperative that more laboratory studies are conducted to measure RO₂ + NO rate constants with a wide variety of RO₂ types."

17. Line 491. What does the 'complete' mean?

We have replaced "the lack of (complete) suppression of HOM signals" with "why HOMs species are not completely removed...."

18. Line 502. How the ozone increase was calculated?

Using equation E14, we have added this to the text.