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Comment on acp-2022-119

Anonymous Referee #2

Referee comment on "On the understanding of tropospheric fast photochemistry: airborne observations of peroxy radicals during the EMeRGe-Europe campaign" by Midhun George et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-119-RC2>, 2022

This manuscript presents some rare airborne RO₂ measurements over much of Europe. These are useful measurements that should be shared, especially the vertical dependence of concentrations, but the analysis is not focused enough and requires significant revisions.

Major comments:

line 101 (in the intro) shows the photostationary state (PSS) equation for [HO₂ + RO₂], and describes previous studies that compared this value to measured HO₂ + RO₂. The introduction ends with "Consequently, this data set provides an excellent opportunity to gain a deeper insight into the source and sink reactions of RO₂* and the applicability of the PSS assumption for the different pollution regimes and related weather conditions in the free troposphere".

I was looking forward to seeing what insights the authors had to provide regarding the applicability of the PSS assumption... but it does not show up at all later in the main text! The authors make use of the equation $P(\text{RO}_2^*) = L(\text{RO}_2^*)$ quite a bit, but not the above NO-NO₂-O₃-RO₂ photostationary state assumption.

Line 119: in the abstract RO₂* is defined as RO₂ + HO₂. On line 119, it's defined as RO₂ + HO₂ + OH. Quantitatively there's little difference since [OH] is much smaller than the other two terms, but conceptually this is very important. Line 24 states "RO₂* is primarily produced following the photolysis of ozone (O₃), formaldehyde (HCHO), glyoxal (CHOCHO), and nitrous acid (HONO) in the airmasses investigated", which is true for

(RO₂+HO₂+OH) but not for (RO₂ + HO₂). Please be consistent in terminology.

later in abstract: "The dominant removal processes of RO₂* in the airmasses measured up to 2000 m are the loss of OH and RO through the reaction with NO_x during the radical interconversion". This is very confusing – if a reaction is a radical interconversion reaction, then no radicals are lost. Moreover, reactions of RO with NO_x are rare and not discussed at all later in the manuscript.

It appears that one of the main challenges the authors are facing when interpreting their dataset is that their instrument is much less sensitive to CH₃O₂ than HO₂, and so in the limit that all RO₂ are CH₃O₂, then RO₂* = HO₂ + 0.65 × RO₂. This relates to the high NO mixing ratios used in their instrument, as commented on by both reviewers for George et al. 2020. This limits how much can be gleaned from the comparison of calculated RO₂* with measured RO₂*, since a priori the CH₃O₂/RO₂* ratio is not known.

line 231: there is a major error in Equation 2. The penultimate term – the sum of OH + VOC reactions – should not be part of this equation as it reflects radical cycling rather than a primary radical source.

Figures 8-12 and accompanying text: These show variations of the same plot (RO₂ measured vs RO₂ calculated). I would recommend keeping just 2 of these and moving the rest to the SI as not much is revealed by the 3rd – 5th set of plots. This would help shorten the paper and improve the readability.

Additional comments:

Line 40 – remove comma

Line 90 – should say "R23 and R25 are two of the most..."

Section 3: the description of perceas is confusing. Nowhere does it even mention that the sampled air is mixed with NO and CO in amplification mode – the basics of PERCA operation. I do recognize that the instrument has been described in the referenced papers, but just a few more details would be helpful.

line 174: the relative sensitivity to CH₃O₂ vs. HO₂ (α) – was this just based on their

previous study, or was it experimentally determined again in between flights? Similarly, please provide more information on calibrations – how many were done? Were the eCL values stable (and their dependence on humidity) or were different values used for each flight?

That's great that glyoxal and methyl glyoxal, in addition to the other OVOCs, were measured.

Line 202 "Typically, the highest RO₂* mixing ratios were observed below 3000 m over Southern Europe. This is attributed to the higher insolation and temperatures favouring the rapid production of RO₂* from the photochemical oxidations of CO and VOCs"

I question the inclusion of temperature in that sentence. If the authors are simply presenting a *correlation* between highest RO₂ mixing ratios and temperature that is fine, but to *attribute* the high mixing ratios to elevated temperature requires some discussion. Are they inferring that the reaction rate constants are faster at higher temperatures? This is certainly not true for all of the reactions. Or are they referring to the increased emissions of biogenic VOC emissions at higher temperatures, leading to higher bVOC concentrations? This by itself won't necessarily lead to higher RO₂* mixing ratios.

For HONO photolysis, do the calculated numbers reflect the gross OH formation from HONO photolysis or the net amount (subtracting out the reverse reaction OH + NO)?

line 244 and 304: "calculated", not "estimated"

Figure 4: I would have found it more useful to see a plot of altitude vs. P(RO₂*) rather than [RO₂*] colored by P(RO₂*).

line 266- needs some re-wording. "...the high amount of H₂O in the air masses probed results in the O₃ photolysis and subsequent reaction of O(1D) with H₂O (R1-R2a) and is the highest RO₂* radical production rate". The H₂O itself does not cause O₃ photolysis... rather the high H₂O leads to the reaction O(1D) + H₂O being the most important RO₂* source.

line 305: The sentence "The [RO₂*] < 0.5..." is awkward, change to something like "Measurements in which [RO₂*] were less than xyz..."

Figure 7 and text: it's good that someone has done this analysis! I think the correlations

observed in figure 8 are about as good as could be expected, though it's interesting that the impact of NO_x is not so clear.

line 338: "The second solution gives..." I don't see any solutions.... please clarify.

line 340 - "the measured RO₂* (RO₂*_m) mixing ratio" is confusing - what is RO₂*_m(RO₂*_m)? Is this a product of RO₂* and RO₂*_m? Or should it just be RO₂*_m?

line 341: "RO₂*_m and RO₂*_c are the measured and calculated RO₂* respectively for d = 1, i.e. RO₂* = HO₂ and d = 0.5, i.e. HO₂ = RO₂." Confusing. RO₂*_m is measured RO₂, and RO₂*_c is calculated, but for which case - d = 1 or 0.5? This section should be prefaced with some text along the lines of "because not all peroxy radicals are detected equally by the instrument, the comparison of measured and calculated RO₂* values is complicated. To investigate this, we ..."

eq 11: the first term on the right hand side of the equation refers to the RO₂* loss reactions HO₂ + HO₂, RO₂ + RO₂, and HO₂ + RO₂. The 2nd term should represent the RO₂* loss reactions RO₂ + NO₂ and HO₂ + NO₂ and OH + NO₂, but not RO₂ + NO or HO₂ + NO as those are radical interconversion reactions. I recommend simply writing out the full equation as it is confusing to always deal with "HO₂ + RO₂" and "NO_x" in these rate equations.

line 524: dependence, not dependency