

Atmos. Chem. Phys. Discuss., referee comment RC1  
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## Comment on acp-2022-119

Anonymous Referee #1

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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-RC1>, 2022

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The authors report and discuss peroxy radical measurements performed during flights with the aircraft HALO across Europe. Because there are only few flight measurements of radicals over Europe, these measurements are valuable. However, it is not very clear, what the improvement in the understanding of tropospheric fast photochemistry really is from the manuscript. The author mainly compare measurements with different approaches of steady state calculations. Results are mainly descriptive, but there is little discussion about the meaning for the understanding of photochemistry. The presentation quality needs to be improved. It is partly unclear, how equations for steady state calculations are derived and what the meaning is. This manuscript needs major improvements to be suitable for publication in ACP.

Abstract: The definition of RO<sub>2</sub>\* is unclear. In the first sentence it sounds as if this is the sum of RO<sub>2</sub>+HO<sub>2</sub>, but later it looks as if also OH is included. Please clarify and be precise and accurate with definitions.

Abstract L22: How can a production rate agree with a concentration?

Abstract L23: RO<sub>2</sub> is not directly produced from the photolysis of ozone and HONO, but OH is that then further reacts to produce RO<sub>2</sub>\* species. Please be accurate how you phrase this.

Abstract L25: For an abstract the statement about the PSS is vague and not well-defined. Please expand here, which processes are considered in the PSS and what quantity is calculated.

Abstract L30: Really  $RO+NO_x$  ? If  $RO_2^*$  is the sum of  $RO_2+HO_2+OH$ , it is not clear to me, why this statement is about radical interconversion, because radical interconversion reactions cancel out. Please rephrase and clarify.

L90: Reaction R25 should be mentioned as well.

L91: The first half of the sentence is not clear. What do you mean with insolation? Do you mean PSS? This would not be required to ensure rapid photochemical processes. Please rephrase and clarify.

L102: Specifically since the manuscript is about airborne measurements, the temperature and if necessary also the pressure should be given, if values for reaction rate constants are mentioned.

L103: The typical reader may not know, what exactly is meant with "weighted average rate coefficient" and why this is required. Please clarify and rephrase.

L126: It is not obvious, why the measurements of trace gases in Reactions R1 to R26 other than required in Equation 1 minimizes the number of assumptions for calculating  $RO_2^*$ . My expectation would have been that this would allow to perform also full model-calculations of  $RO_2^*$  concentrations, which could be compare PSS calculations. Please explain in more detail.

L135: Please avoid to define and use abbreviations like IOP and MPC and others that are not common. The typical reader will forget them, while reading the manuscript. It only makes it difficult to follow the line of arguments.

L143: What do you mean with "stable flight layers"?

L168: Please add also the pressure, for which you calculated the concentrations.

L172: Why do you only refer to  $CH_3O_2$  as  $RO_2$ ? Earlier you mention "weighted average rate coefficient" implying that you not only have  $CH_3O_2$ .

L180: I would recommend to give a number how large the humidity effect was for measurements in this work.

L183 ff: The short description of miniDOAS data / data evaluation is hard to understand for the non-expert. Please rephrase. It is also not clear at this point, why this instrument is explain in more detail, whereas other instruments more obvious useful to determine the PSS are not explained.

L186: Please explain RT modelling.

L187: Please explain the abbreviation HAIDI.

L191: Please explain what you mean with "common and related species".

L202: I would avoid a conclusion about the reason for high RO<sub>2</sub> in specific regions before doing the analysis. Your arguments are plausible but there are also other plausible explanations giving the contrary conclusion.

L210: I do not understand the argument "comparable". What is exactly compared here? Calculating RO<sub>2</sub>\* from PSS can always been done as long as the time required to reach PSS is short enough that concentrations of species do not significantly change. Please explain and rephrase.

Figure 3: Wouldn't make more sense to show percentiles instead of standard deviations to be independent from outliers?

L224: I cannot follow the argument that differences between mean and median values indicate more or less variability. Median and mean values could be exactly the same, if the distribution of values is symmetric independent on how big the range of values is. It is also not obvious, if you want to say that there is a change how similar median and mean values are. I do not see that the similarity depends on the height.

Line 235: "becomes" instead of "become"

L235: Please clarify what you mean with "low NO<sub>x</sub> conditions" and why this impacts the significance of H<sub>2</sub>O<sub>2</sub> photolysis.

L238: Please define OVOC before using it in Eq 2

L237. This statements needs explanation. Why can you assume that photolysis of OVOCs is more important compared to reaction with OH? This is not obvious. Which were the most important OVOCs and VOCs and can you quantitatively show that your assumption is valid? Can you also show this for ozonolysis reactions? If you want to calculate the RO<sub>2</sub>\* production rate you may not need to consider OH reaction, because this is a radical conversion reaction and not a primary production, which you may want to calculate. This should be clarified, if you talk about production. Please explain and extend your description.

L238: How large were the concentrations of these OVOCs? What do you mean concretely, if you take this as "surrogate"? Equation 3 only considers 4 OVOC species, which rather indicates that you neglect others.

L244: I assume that measurements allowed a calculation of the air concentration density rather than an estimate.

L245ff: Avoid explaining details of a figure that is explained in the legend and / or caption of the figure.

L291: The section header referring to PSS. From what is written earlier, one would expect calculations using Equation 1, but then you start with calculations using Eq 5. Also later in this Section Eq 5 is stated as PSS calculation instead of Equation 1 and not used at all in the end. This is confusing. Please be consistent. It is not clear, why Equation 1 is introduced earlier at all.

L297: It is a bit contradictory to state "interconversion reactions occur without losses", because interconversion implies that the radical nature is not lost.

L298 ff: Please justify that you can calculate the loss of RO<sub>2</sub>\* -RO<sub>2</sub>\* reaction by an weighted average rate coefficient? What do you use as weights? Without knowing the distribution between HO<sub>2</sub> and RO<sub>2</sub> it is hard to imagine how this loss rate can be accurately calculated. It is not obvious how this is mathematically done, if you expand the right side of Eq. 5 using [HO<sub>2</sub>] and [RO<sub>2</sub>] concentrations. If you assumed e.g. [HO<sub>2</sub>] = [RO<sub>2</sub>] = 0.5 [RO<sub>2</sub>\*], this should be clearly said and written down what this means for the equation. The assumption of [HO<sub>2</sub>] = [RO<sub>2</sub>] would be expected if the loss of [HO<sub>2</sub>] and [RO<sub>2</sub>] is dominated by reaction with NO. Please expand, if this is the case for measurements in your work. In this case, it would be also essential to show and discuss NO measurements and peroxy radical loss rates with NO. What about the loss of RO<sub>2</sub>\* due to the reaction of NO<sub>2</sub>+OH? Could this have been significantly contributed to the RO<sub>2</sub>\* loss? Your analysis between differences, if you divide data sets between North and

South may hint that this loss process was relevant.

L318: I do not understand the statement about the validity of results. Please explain and rephrase.

L330: It would be good, if names of e.g. photolysis frequencies in Equation 5 and 6 were consistent. It should be emphasized that the point of assuming that RO<sub>2</sub> consist only of CH<sub>3</sub>O<sub>2</sub> is only, in order to have one RO<sub>2</sub> species and therefore not considering differences in RO<sub>2</sub>+RO<sub>2</sub> and RO<sub>2</sub>+HO<sub>2</sub> reaction rate constants. In general, I would recommend to start with Equation 6 and then you easily derive Equation 5. By doing this, you also will be able to explain what you mean with average weighted reaction rate constant in Equation 5.

L338: It is rather confusing that the negative solution is mentioned at this point, but not when you discuss Eq. 5, where the form of the quadratic equation is identical.

L342: The effect that RO<sub>2</sub>\* measurements can be affected by differences in the detection sensitivity of RO<sub>2</sub> and HO<sub>2</sub> should have been discussed for the results with  $\delta=0.5$  (Equation 5).

L344: Please make rather quantitative than qualitative statements about the level of agreement. What effect do you expect from differences in reaction rate constants among RO<sub>2</sub>, if you do not assume that all RO<sub>2</sub> is CH<sub>3</sub>O<sub>2</sub>?

L356: It is not clear, which processes you are referring to, if you mention VOC oxidation processes. OH + VOCs would be a radical interconversion process and ozonolysis reactions and Cl chemistry may be not of importance for conditions of the campaign.

L358: Again it is confusing, if you talk about radical conversion reactions, but in fact you mean radical termination reactions. Please rephrase and be clear with the definition throughout the manuscript.

Equation 8 / 9: Similar it is confusing that you name reaction rate constants referring to radical conversion reactions and move the loss into a loss factor. What is the value of the loss factor? It would be easier, if you added more explanation, which loss reactions (products) you include. I read the first loss term as non-radical products from HO<sub>2</sub> + NO and HO<sub>2</sub> + O<sub>3</sub>, it is not clear to me, what for example the product of HO<sub>2</sub>+O<sub>3</sub> would be. The factor rho associated with this term is explained as OH loss during the OH-RO<sub>2</sub>\* interconversion, which does not fit, what I read from the equation. There is more explanation needed, what is meant with this term. It is also not clear to me, if the second

loss term (organic nitrate formation  $k_{25}$  and  $k_{22}$ ) is correct and why this is connected to  $RO_2+RO_2$  reactions ( $k_{16b}$ ). This needs to be explained in more detail. It would be much easier to understand, if you introduced yields of products produced from radical termination reactions.

L367 ff: It sounds as if you state that the reaction of  $OH+HCHO$  and  $OH+CH_3CHO$  are the dominant radical precursor reactions, though so far you only discuss photolysis of them.  $OH$  reactions would also not be primary sources, but radical conversion reactions. In this context and for the same reason, it is also not clear, what you mean with  $RO_2^*$  production from  $CHOCHO$  and  $CH_3OH$  oxidation. Please clarify and rephrase.

L373: The context of the statement about the importance of  $HO_2+NO$  and  $HO_2+O_3$  is not clear and seems displaced at this point.

L421: How can you exclude that there is no over-estimation of loss processes instead of an under-estimation of production processes? What is the impact in the uncertainty of the  $HO_2/RO_2$  ratio in the case, when VOCs concentrations were high?

L422: Why would  $OH$  recycling processes increase the calculated  $RO_2^*$ , if radical regeneration terms cancel out in the calculations for the sum measurement of  $RO_2^*$ ?

L436: It would be interesting to see a more quantitative analysis of the impact of the uncertainty in  $HCHO$  measurements on the results.

L490 ff: The calculation of  $OH$  concentrations does not really fit this manuscript and would require a much deeper description than currently done. The statement that the  $OH$  calculated from Eq 5 is higher than reported  $OH$  concentration means that  $OH$  reactivity is underestimated cannot easily be justified. I would recommend to cancel this entire paragraph. It does not add anything to the content of the manuscript and may even be rather misleading as it is now.

Section 4.4.1. / Equation 11: Again the definitions of the effective rate coefficients is not clear. Also the use of  $NO_x$  makes it hard to see, what exactly is calculated. This makes it very difficult to follow any of the subsequent quantitative statements. The connection to previous Equations is also not clear. What is the difference to Equation 9, which should consider radical loss in  $NO_x$  reactions? What is used for the production rate for example? The authors should make much clearer what is calculated and what the meaning of the calculation is. As it is written now, it is not clear, what the authors want to discuss in this section.