Comment on acp-2022-119

Anonymous Referee #2

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(RO2) = L(RO2*) quite a bit, but not the above NO-NO2-O3-RO2 photostationary state assumption.*

The NO-NO_2-O_3-HO_2+RO_2 PSS radical calculation in Eq.1 assumes that NO_2 is in a steady state and has been shown in the past to be very sensitive to the accuracy of the NO_2 to NO ratio. This ratio calculated from the NO (in-situ) and NO_2 (miniDOAS remote) measurements during the EMeRGe campaign is considered to have a sufficiently large error for not to be a valuable approach to calculate the [HO_2+RO_2]

In the present paper, we assume that the peroxy radicals are in PSS, i.e., the production and losses of radicals are considered to a good approximation to be equal. During the campaign, a large amount of the trace species involved in the radical formation and loss mechanisms were measured. In this work an analytical expression for the PSS calculation of the total sum of peroxy radicals which takes into consideration only measured species is used. The efficiency of this analytical expression as predicting tool is investigated by comparing the calculated RO_2^* PSS with the RO_2^* measurements on-board.

A sentence has been included on Line 111 to emphasise this aspect.

"The PSS radical calculation made on the assumption of the NO_2 steady state is very sensitive to the accuracy of the NO_2 to NO ratio and the O_3 measurements."

- *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.*

Answer:

The definition of RO_2^* has been checked for consistency. RO_2^* is mentioned now in the abstract as:

> "RO_2^* is to a good approximation the sum of peroxy radicals reacting with NO to produce NO_2

And in the main text on Line 119 (Line 127 in the revised manuscript) is defined more precisely as:

> "The available on-board measurements of RO_2^* are defined as the total sum of OH, RO and peroxy radicals (i.e., $RO_2^* = OH + \sum RO + HO_2 + \sum RO_2$, where RO_2 are the organic peroxy radicals producing NO_2 in their reaction with NO). As the amount of OH and RO is much smaller, RO_2^* to a good approximation is the sum of HO_2 and those RO_2 radicals that react with NO to produce NO_2)"

- *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 NOx 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 NOx are rare and not discussed at all later in the manuscript.*

Answer:

This has not been indeed explained adequately. The abstract and the rest of the manuscript have been checked to remove sentences leading to confusion.

In the revised manuscript the sentence mentioned by the referee has been re-written as:

"The dominant terminating processes for RO_2^* in the pollution plumes measured up to 2000 m are the formation of nitrites and nitrates from radical reactions with NO_x."

- *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.*

Answer:

The ratio CH_3O_2/HO_2 is definitely a challenge for the interpretation of PeRCEAS data in complex environments. The PeRCEAS instrument is calibrated in the laboratory for a 1:1 HO_2 to CH_3O_2 mixture at the NO mixing ratios used for the measurement on the field. The results are interpreted by assuming a ratio of 1:1 and investigating the impact of systematic deviations from this ratio in the composition of the air masses observed. Thus, in line 483 in original manuscript (see below) the impact of having ratios of HO_2/RO_2 different than 1:1 in the disagreement between RO_2^* measured and calculated has been estimated for measurements during the E-EU-03 flight. A 3:1 and a 1:3 ratio of HO_2:RO_2, would lead to either a 10% decrease or a 10% increase in the $RO_2^*{}_m$ retrieved and this uncertainty is well below the in-flight uncertainty of the PeRCEAS instrument.

Line 507 in the revised manuscript:

"Taking CH_3O_2 as a surrogate for all RO_2 might lead to uncertainties in the RO_2^* calculations in the presence of OVOCs with larger organic chains. On the experimental side, changes in the HO_2 to RO_2 ratio affect the accuracy of the PeRCEAS retrieval of the total sum of radicals. As noted in section 3, in this study $RO_2^* = HO_2 + 0.65 \times RO_2$, and the eCL is determined for a 1:1 mixture of HO_2:CH_3O_2, i.e. $\delta = 0.5$ is used for the RO_2^* retrieval. However, the HO_2 to CH_3O_2 ratio is not expected to remain constant in all the air masses probed. For a 3:1 ratio of HO_2:RO_2, the $RO_2^*{}_m$ would decrease by 10 %. Similarly, a HO_2:RO_2 ratio of 1:3 would lead to an increase of 10 % in the reported $RO_2^*{}_m$. This uncertainty is well below the in-flight uncertainty of the PeRCEAS instrument indicated by the error bars in Fig. 14 (George et al., 2020), and cannot account for the overall 20 % underestimations. However, it might reduce the differences observed between $RO_2^*{}_m$ and $RO_2^*{}_c$ in particular cases. A complete explanation of the variability of RO_2^* in the pollution plumes measured within the IOP in Europe is beyond the scope of this analysis and requires an investigation by high-resolution chemical models."

- *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.*

Answer:

The radical propagating reactions in Eq. 2 have been removed.

- *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.*

Answer:

The text has been shortened and the figures 11 and 14 in the original manuscript have been moved to the supplementary information.

Additional comments:

- *Line 40 – remove comma*

Answer:

done

- *Line 90 – should say "R23 and R25 are two of the most…"*

Answer:

done

- *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.*

Answer:

The description of PeRCEAS has been extended in Line 161 to account for the criticisms of the referee:

"Each channel has a separate chemical reactor and detector, which operate alternatively in both background and amplification modes to account for the rapid background variations during airborne measurements. In both modes NO is continuously added to the air sampled at the reactor, while CO is only added in the amplification mode to initiate the chain conversion of RO_2^* into NO_2. In the amplification mode, the sum of the NO_2 produced from ambient RO_2^* through the chain reaction, the ambient NO_2, the NO_2 produced from the ambient O_3 – NO reagent gas reaction and the NO_2 produced in the inlet from any other sources (e.g. thermal decomposition of PAN) is measured."

- *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.*

Answer:

The relative sensitivity to CH_3O_2 vs. HO_2 has been determined for the conditions applied during the measurements with a series of laboratory measurements in a previous study. The eCL calibrations are not possible once the instrument is installed in the aircraft and are therefore made before and after the campaigns. There was no significant difference (within errors) in sensitivity or dependence on humidity) observed in those experiments.

This information has been included in the revised text:

"The HO_2 and RO_2 detection sensitivity depends on the reagent gas NO concentration due to the rate coefficient of reaction R22 being larger than that for R19. The average eCL for a 1:1 HO_2 to CH_3O_2 mixture under the DUALER conditions during the campaign in Europe was determined to be 50 ± 8 from laboratory calibrations, where the error is the standard deviation estimated from the reproducibility of the experimental determinations. Likewise, the ratio $\alpha = \mathrm{eCL}_{CH_3O_2}/\mathrm{eCL}_{HO_2}$ was determined to be 65% for the measurement conditions (George et al., 2020). The values obtained from calibrations before and after the campaign agreed within the experimental uncertainties.”

- *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.*

Answer:

We agree with the referee in the speculative character of this sentence which referred to a potential combination of higher insolation and temperatures favouring not only higher emissions of bVOC but also stagnant conditions with high photochemical processing which could affect the RO_2* levels. Following also the comment of reviewer 1, the sentence has been removed.

- *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)?*

Answer:

The calculations in this work are made using the Eq. 6 which considers the net amount of radical formation from HONO photolysis through R3 and R19. In the revised version of the manuscript a text has been included to explain in detail the terms of the Eq. 6 in the revised manuscript:

Line 359:

$$“(2j_1[O_3]\beta + j_3[HONO])(1-\rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] = \delta[RO_2^*](k_{23}[NO] + k_{24}[O_3])\rho + 2k_{15}\delta(1-\delta)[RO_2^*]^2 + 2k_{16a}\left((1-\delta)[RO_2^*]\right)^2 + 2k_{14}(\delta[RO_2^*])^2 \qquad \text{(Eq. 6)}$$

where β is the effective yield of OH in the reaction of $O(^1D)$ with H_2O given by:

$$\beta = \left(\frac{k_{2a}[H_2O]}{k_{2a}[H_2O] + k_{2b}[O_2] + k_{2c}[N_2]}\right),$$

On the left hand side of Eq. 6, 1-ρ accounts for the effective yield of HO_2+RO_2 through the radical initiation reactions R2a and R3 and reactions R5 to R7 and R12. As the calculation is constrained with on-board measurements, only the reactions of measured VOCs were considered in R12. Similarly, ρ accounts for the effective yield of HONO, HNO_3 and H_2O formation through reactions R19 to R21 and the HO_2 + NO and HO_2 + O_3 reactions (R23 and R24 respectively) on the right hand side of Eq. 6.

Consequently, ρ is given by:

$$\rho = \frac{(k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO])}{(k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO])}$$

“

- *Line 244 and 304: “calculated”, not “estimated”*

Answer:

done

- *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*).*

Answer:

The vertical profile and the altitude latitude distribution of P(RO_2^*) are now included as proposed by the referee, as Fig. S2 and S3 in the supplementary information.

Line 301: "(for the vertical profile and the latitudinal distribution of $P_{RO_2^*}$ see Fig. S2 and S3 in the supplementary information).

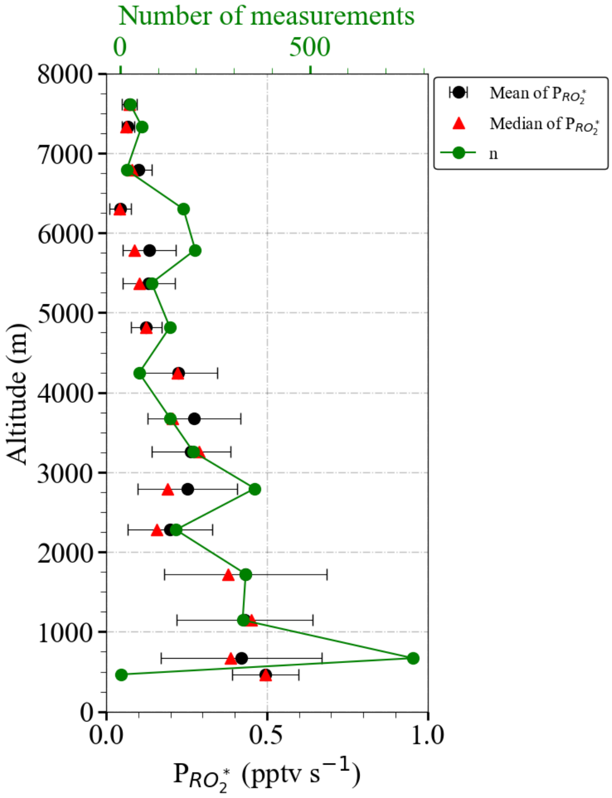

Figure S2: Composite average vertical profiles of $P_{RO_2^*}$. The measurements are binned over 500 m altitude. The error bars are the ± 1σ standard deviation of each bin. Median values (red triangles) and the number of individual measurements, n, for each bin (in green) are additionally plotted.

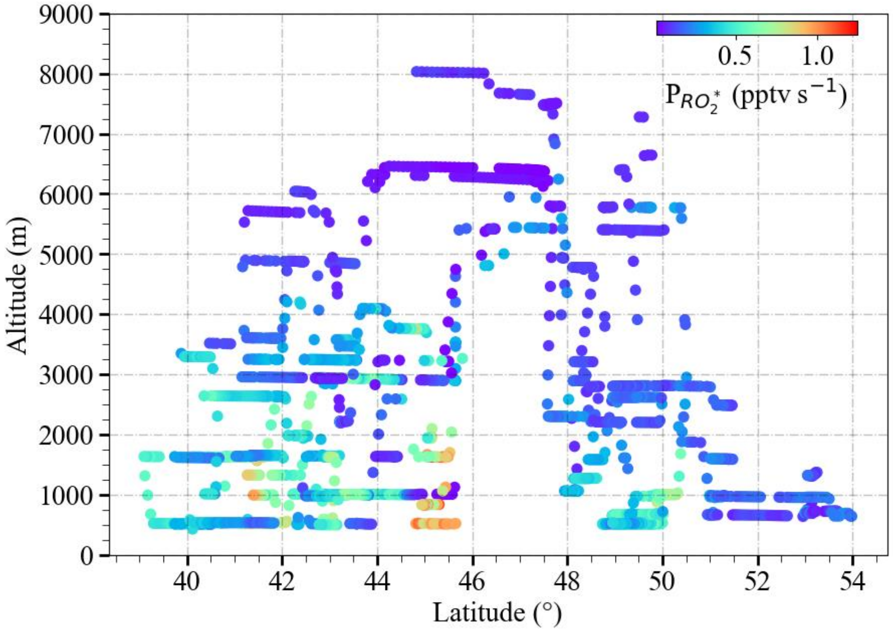

Figure S3: $P_{RO_2^*}$ as a function of latitude and altitude for the EMeRGe measurements in Europe.

The composition and photochemical activity of the air masses sampled during the investigated 7 flights change significantly during the tracks and the production of radicals is expected to present a complex pattern with the altitude. The idea of the figure 4 is to identify relations between the $P(RO_2^*)$ calculated and the RO_2^* measured, under the assumption that the terms included in the $P(RO_2^*)$ are sufficient. In addition, Figure 4 helps to identify more and less frequent $P(RO_2^*)$ regimes, as a basis for the analysis in Figures 5 and 6.

- *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 O1D 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.*

Answer:

The text has been accordingly reworded:

"Typically, the high amount of H_2O in the air masses probed leads to the reaction of O^1D with H_2O (R1-R2a) being the highest RO_2^* radical production rate (≥ 50 %) below 4000 m"

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

Answer:

The sentence has been accordingly re-worded as:

"Measurements in which $[RO_2^*]$ were less than 0.5×10^{12} molecules cm^{-3} , $\sqrt[2]{P_{RO_2^*}}$ less than 1000 and with $j_{O(^1D)}$ $> 5 \times 10^{-5}$ were made above 6000 m, where the amount of RO_2^* precursors is low."

- *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 NOx is not so clear.*

Answer:

Thanks. The correlations have indeed a significant spread and the impact of NOx is difficult to be identified. However, a closer analysis reveals that for similar NOx concentrations and J_{O1D} in North and South of 47°N, the concentrations of the radicals measured are much higher in the South, indicating the differences in VOC sources and that the radical yields coming from the oxidation of VOC are probably responsible for the increase in the amount of the radicals measured.

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

Answer:

This sentence refers to the solutions of Eq. 6 which can be solved as a quadratic equation respect to [RO_2^*]. One solution is negative and is therefore assumed not to have any physical meaning. The [RO_2^*] calculated are taken from the second solution of the quadratic equation:

$$[RO_2^*] = \frac{-(-L_{RO_2^*}) - \sqrt[2]{L^2_{RO_2^*} - 4(-2k_{RO_2^*})P_{RO_2^*}}}{2(-2k_{RO_2^*})}$$

In Line 406, the text has been modified for clarification:

"Since Eq. 6 is quadratic in [RO_2^*] it can be solved for $[RO_2^*]_c$ where c stands for calculated, as:

$$[RO_2^*]_c = \frac{-(-L_{RO_2^*}) - \sqrt[2]{L^2_{RO_2^*} - 4(-2k_{RO_2^*})P_{RO_2^*}}}{2(-2k_{RO_2^*})} \qquad \text{(Eq. 7)"}$$

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

Answer:

$RO_2^*{}_m$ stands for RO_2^* measured and $RO_2^*{}_c$ for RO_2^* calculated. $RO_2^*{}_c$ is defined in Line 406 and $RO_2^*{}_m$ in Line 416 of the revised text. From this line, only the abbreviations $RO_2^*{}_m$ and $RO_2^*{}_c$ are used in the text.

- *line 341: "RO2*m and RO2*c are the measured and calculated RO2* respectively for δ =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 – δ = 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 …"*

Answer:

The introductory sentence in Line 324 (now Line 352 in the revised text) has been extended for clarifying this aspect:

"As stated in section 3, HO_2 and RO_2 are not speciated but retrieved as RO_2^* by the PeRCEAS instrument. Because not all peroxy radicals are detected equally by the instrument, the comparison of measured and calculated RO_2* values is complicated. To investigate this, changes in the HO_2 to the total RO_2^* ratios, have been taken into consideration by δ, i.e., [HO_2] = δ[RO_2^*] and [CH_3O_2] = (1- δ) [RO_2^*] in the analysis. As a first approach, RO_2 is assumed to consist only of CH_3O_2 to reduce the complexity of the calculations by considering only CH_3O_2 reaction rate constants. Moreover, in a previous study the ratio $\alpha = eCL_{CH_3O_2}/eCL_{HO_2}$ was determined to be 65% for the measurement conditions (George et al., 2020)."

- *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 "NOx" in these rate equations.*

Answer:

Eq. 11 (now Eq 9 in the revised manuscript) refers to the analysis made by Cantrell et al. (2003b) and the terms of their analysis are just transcribed. The first term on the right hand refers to radical-radical reactions and the second term to RO_2^*-NOx reactions where RO_2^* is considered to be the sum of HO_2+ RO_2 and K_{RR} and K_{RN} are effective rate coefficients, whose value is retrieved from the fitting of the curves obtained from real data. Except for the production rates there is no calculation made. As explained in the text, the production rates calculated by Eq.2 in the manuscript and the EMeRGe measurements in Europe are used to obtain the Figure 16. The text of the Sect. 4.4.1 has been partly reworded for clarification.

- *line 524: dependence, not dependency*

Answer:

corrected