

## Comment on acp-2022-119

Anonymous Referee #3

*The manuscript presents airborne RO<sub>2</sub>\* observations from the EMeRGe-Europe campaign which was designed to study the chemistry in the outflows from major population centres. The concentration and variability of RO<sub>2</sub>\* with altitude, latitude and inside and outside of the urban plumes is of interest to the community. The authors compare the observations to a couple of steady state calculations for RO<sub>2</sub>\*. Some details on the % breakdown of the primary sources of RO<sub>2</sub>\* are provided, but there is little discussion on the main sinks for RO<sub>2</sub>\*, which I think should be added to the manuscript. There are some major problems with the manuscript currently: The steady state calculations used are flawed; see my major comments below. Many of the figures are extremely 'busy', and I believe some of the axes have been labelled incorrectly, and so it becomes very difficult to follow the discussion related to these plots.*

*It is difficult for a reader to draw any solid conclusions on the observations and comparison to calculated RO<sub>2</sub>\* because, not only are there unknowns relating to VOCs present, which impact the calculated RO<sub>2</sub>\*. The VOCs present also affect the ambient HO<sub>2</sub>:RO<sub>2</sub> ratio, so the absolute sensitivity of the instrument becomes uncertain. I do think that the results from this study should be published, but major revisions to the analyses performed are needed before publication.*

*Major comments*

- Equation 2: The sum of OH+VOC reactions do not constitute a primary source of radicals and should be removed from this equation*

**Answer:**

The Eq. 2 has been corrected and the rest of the text has been modified to draw a clear line between the radical primary production and initiating and terminating processes.

- Equation 3 & 5: The authors need to be clear that the photolysis rates for HCHO and CHOCHO account only for the radical forming channels.*

**Answer:**

The text introducing the Eq. 3 and Eq.5 has been modified to prevent misunderstanding.

- Figure 4, 5 and 6: I don't see the value in binning p(RO<sub>2</sub>\*) as a function of production rate. I think total production rate as a function of altitude and observed [RO<sub>2</sub>\*] would be easier to visualise and take information from. I suggest p(RO<sub>2</sub>\*) is broken down into %precursor contribution in figure 4 (so figure 5 wouldn't be needed). I also find figure 6 extremely difficult to read. From this figure it is impossible to see the HONO concentration profile for example. I suggest showing the altitude profiles of the key RO<sub>2</sub>\* precursor species as shown in figure 2 (there is no need to break these profiles down into p(RO<sub>2</sub>\*)production rate. In figure 6, I would focus on HONO, OVOC and O<sub>3</sub> altitude profiles as H<sub>2</sub>O (v) and j(O<sub>1</sub>D) profiles are provided in figure 2.*

**Answer:**

By binning as a function of production rates it is possible to distinguish between different regimes of the production rates. This enables in a further step a separate analysis of the extreme and most common conditions during the EMeRGe campaign in Europe. The Fig. 6 has been modified for improving readability of the HONO profiles.

- Section 4.3: This section is difficult to follow and take away any clear conclusions. I don't think anything is gained from gradually increasing the analytical expression. I suggest just beginning with the most comprehensive expression and discussing the components of the expression that have the biggest impact on [RO<sub>2</sub>\*c]. Although additional terms have been added to equation 8*

and 9, a number of these terms represent propagation of one radical species to another and so should not be considered. The  $P(\text{ROx})$  and  $D(\text{ROx})$  expressions given in Tan et al., (2019) and Whalley et al., (2021) with the additional photolytic sources from acetaldehyde, acetone and glyoxal available from EMERGE would seem to me like the most robust expression to use.

**Answer:**

In the revised version of the manuscript the changes in the analytical expression used for the analysis have been minimised. The analytical expression Eq. 5 is extended only once to Eq. 6. This enables to analyse first qualitatively the relationship between the  $\text{RO}_2^*$  measured and the square of the  $P_{\text{RO}_2^*}$  in the two latitude windows of the campaign. In Eq. 6  $\text{RO}_2^*$  the radical yields from VOC oxidations and formation of nitrates and nitrites are included (by introducing  $1-\rho$ ), and the  $\text{HO}_2$  to  $\text{RO}_2^*$  ratio ( $\delta$ ).

- *Section 4.3: This section begins with a series of correlation plots of  $\text{RO}_2^*$  measured vs the square root of the primary production of  $\text{RO}_2^*$ . I wondered if these figures could be put into context, by drawing on previous research by Ehhalt and Rohrer (JGR-Atmos., 105,3565–3571, 2000) and Vaughan et al. (ACP, 2149-2172, 2012)? These papers demonstrate the linear dependence of OH on  $p(\text{OH})$  (or  $j\text{O}1\text{D}$ ) and square root dependence of  $\text{HO}_2$  on  $p(\text{OH})$  (or  $j\text{O}1\text{D}$ ) using the following expression:  $[\text{OH}]$  or  $[\text{HO}_2]$  or  $[\text{RO}_2^*] = (a \times j\text{O}1\text{D} + c)$ . Where 'a' represents the influence of all chemical sources and sinks, 'b' accounts for the effect of combining all photolytic processes that produce OH,  $\text{HO}_2$  or  $\text{RO}_2^*$  into a single power function of  $j(\text{O}1\text{D})$  and 'c' is the contribution from all light independent processes. This sort of analyses may be revealing in highlighting differences between different regions that could, for example, be related to differences in VOCs. It may highlight times when, light-independent processes, such as ozonolysis reactions are of significance.*

**Answer:**

The parametrisation of  $[\text{HO}_2] = a \times j\text{O}(1\text{D})^b + c$  has mostly been applied to conditions with low NO (< 20 pptv), in which the  $\text{HO}_2 + \text{NO}$  reaction can be taken as negligible in the calculation of the  $\text{HO}_2$  rate except in Kanaya et al., 2001. The low NO condition is not applicable to EMERGE measurements in Europe since  $\text{NO} > 50$  pptv in 75 % of the air masses probed. In addition, the power relation between  $\text{HO}_2$  and  $j\text{O}(1\text{D})$  requires constant CO and  $\tau_{\text{OH}}$ , for a constant NO value or range (Vaughan et al. 2012). The EMERGE data set does not satisfy this condition as the air masses sampled have different composition and origin. Furthermore, as mentioned in Kanaya et al (2001) the steady state equation cannot be simplified for  $\text{RO}_2^*$  to a form such as the Eq. 7 in Vaughan et al. 2012 as the chemistry is more complex when  $\text{HO}_2$  and  $\text{RO}_2^*$  are taken into consideration together.

References:

Penkett, S. A., P.S. Monks, L. J. Carpenter, K. C. Clemitshaw, G. P. Ayers, R. W. Gillett, I. E. Galbally, and C. P. Meyer, Relationship between ozone photolysis rates and peroxy radical concentrations in clean marine air over the Southern Ocean, J. Geophys. Res., 102, 12,805-12,817, 1997.

Carpenter L. J, P. S. Monks, B. J. Bandy S. A. Penkett, I. E. Galbally, and C. P. Meyer, A study of peroxy radicals and ozone photochemistry coastal sites in the Northern and Southern Hemisphere J. Geophys. Res., 102, 25,417-25,427, 1997.

Kanaya, Y., Sadanaga, Y, Nakamura, K. and Akimoto, H., Behaviour of OH and  $\text{HO}_2$  radicals during the observations at a remote island of Okinawa (ORION99) field campaign. 1. Observation using a laser induced fluorescence instrument, JGR, Vol 106, NoD20, pp 24,197-24,208, 2001.

- *Section 4.3: It would be useful to show the breakdown of the termination pathways of  $\text{RO}_2^*$  as a function of altitude in this section; similar to the primary production pathways presented earlier.*

**Answer:**

The plot has been introduced as proposed by the RC3 as Fig.9 in Line 392 of the revised manuscript:

“Figure 9 shows the fractional contribution of the destruction rate ( $D_{RO_2^*}$ ) calculated for a 1:1 mixture of  $HO_2$  and  $CH_3O_2$  using the reactions included in Eq. 6 as a function of altitude. The data are classified into three groups according to the rate of destruction of  $RO_2^*$  mixing ratio  $D_{RO_2^*} < 0.01 \text{ pptv s}^{-1}$  (a),  $0.01 < D_{RO_2^*} < 0.9 \text{ pptv s}^{-1}$  (b), and  $D_{RO_2^*} > 0.9 \text{ pptv s}^{-1}$  (c) to show the lowest, most common, and highest ranges, respectively, encountered during the EMerGe campaign. For 90 % of the measurements,  $0.01 < D_{RO_2^*} < 0.9 \text{ pptv s}^{-1}$  applies, while the rest of the data are equally distributed in the other two  $D_{RO_2^*}$  ranges. The data in each group are always binned over 500 m when available.

As can be seen in Fig. 9, the  $\pm 1\sigma$  standard deviation of the obtained bins is very high. In spite of this, the  $HO_2 - CH_3O_2$  and  $HO_2 - HO_2$  reactions seem to dominate the radical destruction processes in the air masses probed. Their combined contribution is  $> 70 \%$  in all the cases except in the 1000 m bin of  $D_{RO_2^*} > 0.9 \text{ pptv s}^{-1}$ . Other significant radical losses occur through the HONO and  $HNO_3$  formation. The contribution of the  $CH_3O_2 + CH_3O_2$  reaction to the total  $RO_2^*$  destruction rate is  $< 5 \%$ .”

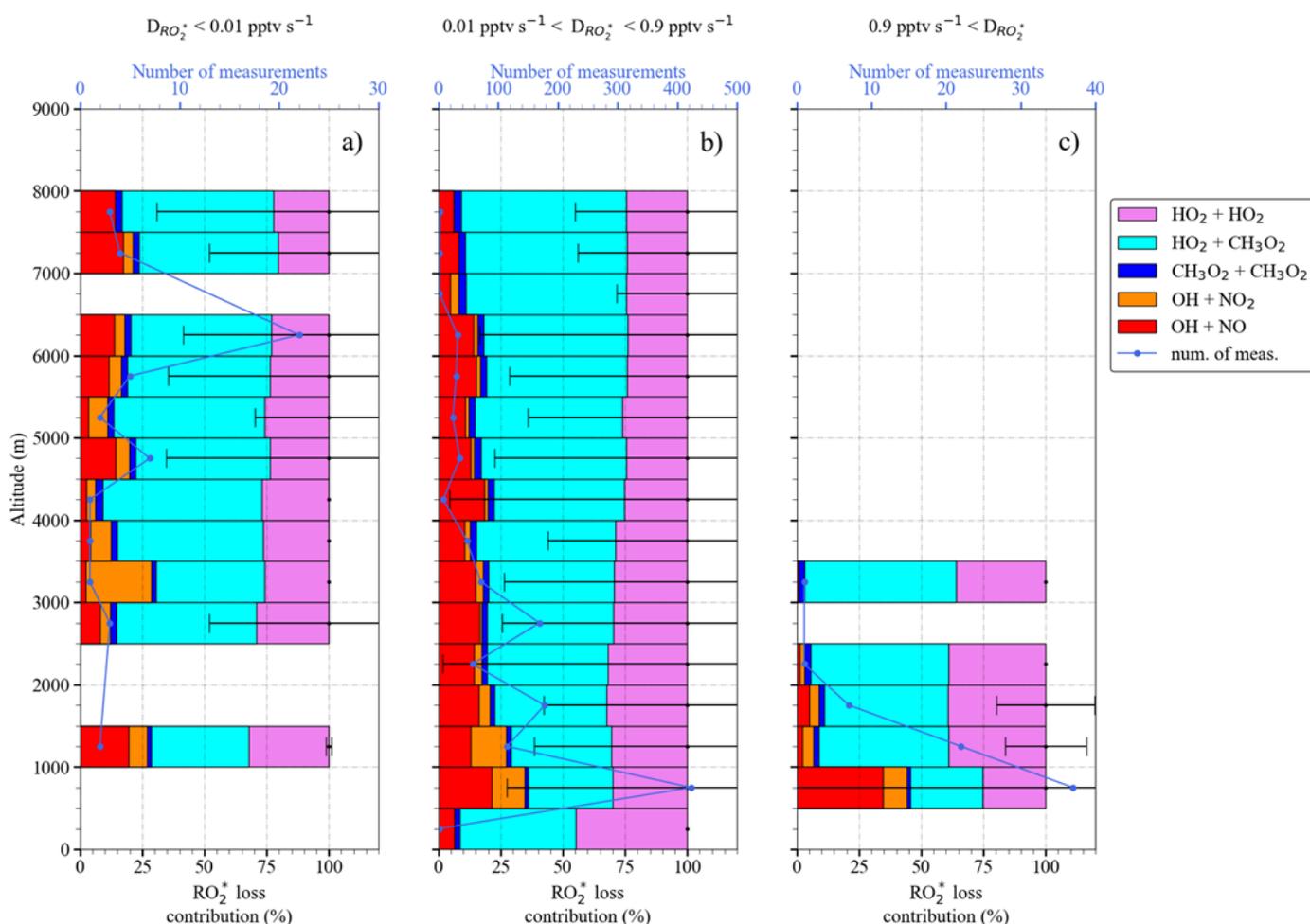


Figure 9:  $RO_2^*$  destruction rate  $D_{RO_2^*}$  and fractional contributions from loss reactions in Eq.6 as a function of altitude, for: a)  $D_{RO_2^*} < 0.01 \text{ pptv s}^{-1}$ , b)  $0.01 \text{ pptv s}^{-1} < D_{RO_2^*} < 0.9 \text{ pptv s}^{-1}$ , and c)  $D_{RO_2^*} > 0.9 \text{ pptv s}^{-1}$ . Note the different scales in the number of measurements.”

- *Figures 10, 11, & 12: The colour coding for the different parameters considered, other than for the sum of VOCs (fig. 12c), don't show a clear trend and I suggest the majority of these figures are moved to the SI, so as not to detract focus from the main discussion.*

**Answer:**

New figures have been introduced in the revised manuscript in order to answer different issues raised by the referees, and the Figures 11 and 14 in the original manuscript have been moved to the supplementary information.

- Looking at fig. 12c, the calculated  $RO_2^*$  over-predicts the measured  $RO_2^*$  under high VOC loading. This, however, directly contradicts what is written on line 420, where the authors state ' $RO_2^*m$  is systematically underestimated for  $\Sigma VOCs$  greater than 7 ppbv' and, therefore, the subsequent discussion surrounding missing VOCs in the calculation becomes moot. Unless this is a plotting error (axes labelled incorrectly), this mistake means that the conclusions drawn on ln 573, 574 are wrong. Figure 14a, which looks at the ratio of  $RO_2^*m/RO_2^*c$ , does seem to suggest that the axes have been labelled incorrectly in the earlier figures, but the authors need to confirm this is the case and correct these figures.

**Answer:**

The axes of the plots mentioned are labelled correctly. The text was misleading and has been modified for clarification (Line 453):

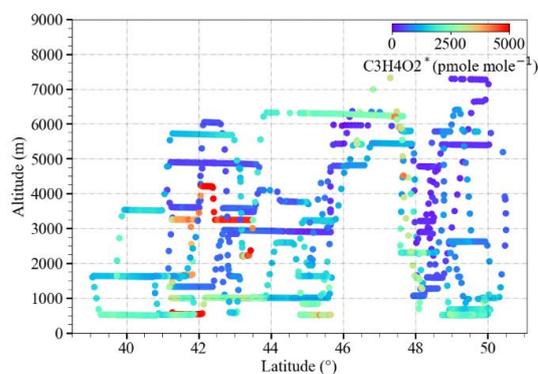
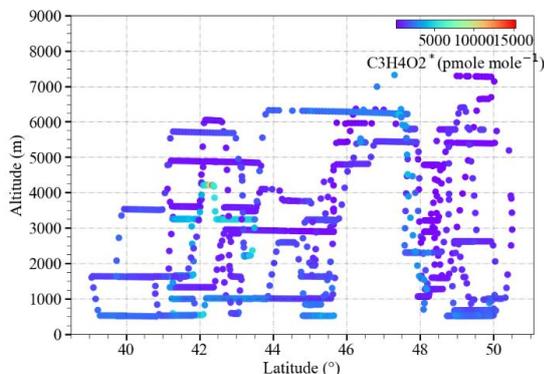
“ $RO_2^*m$  is both underestimated and overestimated for  $\Sigma VOCs$  mixing ratios greater than 7 ppbv. The composition of these air masses is very different, as reflected by the  $\Sigma VOCs/NO$  ratios. This implies that Eq. 7 does not capture the peroxy radical yields adequately from the measured VOCs and OVOC in these cases. The differences between  $RO_2^*m$  and  $RO_2^*c$  may be explained in part by a) changes in OH yields due to additional VOC oxidation processes, which are not in Eq. 7 and/or b)  $RO_2^*$  production from the photolysis of carbonyls, which were not measured and/or c)  $RO_2^*$  production from the ozonolysis of alkenes or unidentified biogenic terpene emissions and/or d) overestimation of the loss processes. For  $VOC < 2ppb$  and  $\Sigma VOCs/NO < 20$ ,  $RO_2^*m$  is systematically overestimated, what might indicate underestimation in the radical losses through nitrite and nitrate formation. “

- Ln 375 – 381: What were the range of concentrations of methylglyoxal during EMERGE? It seems a little surprising to me that, including the production of  $RO_2^*$  from methylglyoxal photolysis, leads to  $RO_2^*c$  systematically overestimating the measured  $RO_2^*m$ . Assuming  $RO_2^*m$  is underestimated by  $RO_2^*c$  in regions of high VOC loading (see comment above on fig 12c), it would be useful to gauge how much additional  $p(RO_2^*)$  is needed in the calculation to bring  $RO_2^*c$  into agreement with the observations.

**Answer:**

The figures below show the measured mixing ratios of methylglyoxal\*, i.e. ,  $CH_3C(O)C(O)H^*$  in the air masses probed during the EMERGE flights. As explained in the text, the  $CH_3C(O)C(O)H^*$  measured is the sum of methylglyoxal, and a fraction of other substituted dicarbonyls (mainly 2,3-butanedione), with similar visible absorption spectra. For the calculation, methylglyoxal was assumed to be half of the measured  $CH_3C(O)C(O)H^*$  as recommended by Zarzana et al. (2017) and Kluge et al. (2020) from other experiments. However, this fraction might change substantially in the different air masses measured, depending on the amount of the dicarbonyls present. Therefore, the calculation of the concentration of methylglyoxal is subject to a high uncertainty and was not considered in the final analysis.

The figures are colour coded in two ranges of mixing ratios in order to visualize the highest and the most common mixing ratios observed.



The highest value of methyl glyoxal\* was around 15 ppbv (plot left), and the highest value of methyl glyoxal was therefore calculated to be 7.5 ppbv. The plot on the right indicates that methyl glyoxal\* was  $\leq 25$  ppbv in 80 % of the measurements. Model calculations beyond the scope of this work would be required to investigate the effect of methylglyoxal accounting for the high level of uncertainty in the calculation of the methyl glyoxal mixing ratios from the observations of methylglyoxal\*.

*Specific comments:*

- *Abstract: 'measurements of the sum of hydroperoxyl (HO<sub>2</sub>) and organic peroxy (RO<sub>2</sub>) radicals that react with NO to produce NO<sub>2</sub>, i.e. RO<sub>2</sub>\*' to measurements of the sum of hydroperoxyl (HO<sub>2</sub>) and organic peroxy (RO<sub>2</sub>) radicals (i.e. RO<sub>2</sub>\*) that react with NO to produce NO<sub>2</sub>'*

**Answer:**

Actually, PerCEAS and the PERCA technique only measures those RO<sub>2</sub> that react with NO to produce NO<sub>2</sub> while HO<sub>2</sub> always react with NO to produce NO<sub>2</sub>.

- *Ln 103: 'k<sub>NO+(HO<sub>2</sub>+RO<sub>2</sub>)</sub> is the weighted average rate coefficient assumed for the reactions of peroxy radicals with NO' the authors should state the rate that has been used.*

**Answer:**

The text has been extended for clarification (Line 107):

“.. and k<sub>NO+(HO<sub>2</sub>+RO<sub>2</sub>)</sub> is usually estimated for the most abundant HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> by assuming a 1:1 HO<sub>2</sub> to CH<sub>3</sub>O<sub>2</sub> ratio and averaging the k<sub>NO+HO<sub>2</sub></sub> (8.2×10<sup>-12</sup> cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> at 298K and 1 atm.) and k<sub>NO+CH<sub>3</sub>O<sub>2</sub></sub> (7.7×10<sup>-12</sup> cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> at 298K and 1 atm.) rate coefficients for the reaction with NO.”

- *Ln 202: From figure 3, j(O<sub>1</sub>D) increases with altitude, so the highest RO<sub>2</sub>\* concentrations (below 3000m) cannot be attributed to higher insolation alone. Rather the net j(O<sub>1</sub>D)\*[H<sub>2</sub>O] leads to the greatest primary production of OH below 3000 m.*

**Answer:**

This sentence intended pointing out in a qualitative manner the latitudinal differences in RO<sub>2</sub>\* concentrations below 3000 m. Following the comments of other referees, the sentence has been changed and moved to the discussion to prevent confusion.