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Comment on acp-2022-119

Anonymous Referee #3

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-RC3>, 2022

Review of 'On the understanding of tropospheric fast photochemistry: airborne observations of peroxy radicals during the EMeRGe-Europe campaign'

The manuscript presents airborne RO₂* 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 RO₂* 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 RO₂*. Some details on the % breakdown of the primary sources of RO₂* are provided, but there is little discussion on the main sinks for RO₂*, 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 RO₂* because, not only are there unknowns relating to VOCs present, which impact the calculated RO₂*. The VOCs present also affect the ambient HO₂:RO₂ 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

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

Figure 4, 5 and 6: I don't see the value in binning $p(\text{RO}_2^*)$ as a function of production rate. I think total production rate as a function of altitude and observed $[\text{RO}_2^*]$ would be easier to visualise and take information from. I suggest $p(\text{RO}_2^*)$ 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_2^* precursor species as shown in figure 2 (there is no need to break these profiles down into $p(\text{RO}_2^*)$ production rate. In figure 6, I would focus on HONO, OVOC and O_3 altitude profiles as $\text{H}_2\text{O}(\text{v})$ and $j(\text{O}1\text{D})$ profiles are provided in figure 2.

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 $[\text{RO}_2^*]$. 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 $P(\text{RO}_x)$ and $D(\text{RO}_x)$ 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.

Section 4.3: This section begins with a series of correlation plots of RO_2^* measured vs the square root of the primary production of 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 HO_2 on $p(\text{OH})$ (or $j\text{O}1\text{D}$) using the following expression: $[\text{OH}]$ or $[\text{HO}_2]$ or $[\text{RO}_2^*] = (a \times j\text{O}1\text{D}^b + c)$. Where 'a' represents the influence of all chemical sources and sinks, 'b' accounts for the effect of combining all photolytic processes that produce OH, HO_2 or 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.

Section 4.3: It would be useful to show the breakdown of the termination pathways of RO_2^* as a function of altitude in this section; similar to the primary production pathways presented earlier.

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. Looking at fig. 12c, the calculated RO2* over-predicts the measured RO2* under high VOC loading. This, however, directly contradicts what is written on line 420, where the authors state 'RO2*m is systematically underestimated for ΣVOCs 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 RO2*m/RO2*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.

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 RO2* from methylglyoxal photolysis, leads to RO2*c systematically overestimating the measured RO2*m.

Assuming RO2*m is underestimated by RO2*c in regions of high VOC loading (see comment above on fig 12c), it would be useful to gauge how much additional p(RO2*) is needed in the calculation to bring RO2*c into agreement with the observations.

Specific comments:

Abstract: 'measurements of the sum of hydroperoxyl (HO2) and organic peroxy (RO2) radicals that react with NO to produce NO2, i.e. RO2 *' to measurements of the sum of hydroperoxyl (HO2) and organic peroxy (RO2) radicals (i.e. RO2 *) that react with NO to produce NO2'

Ln 103: 'kNO+(HO2+RO2) 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.

Ln 202: From figure 3, j(O1D) increases with altitude, so the highest RO2* concentrations (below 3000m) cannot be attributed to higher insolation alone. Rather the net j(O1D)*[H2O] leads to the greatest primary production of OH below 3000 m.