

1. In my (anonymous ref #2) original comments I pointed out that there is a considerable amount of text in the introduction regarding the NO-NO₂-O₃ photostationary state equation (Eq. 1), and yet it does not appear later in the text. In their response document they note “This ratio calculated from the NO (in-situ) and NO₂ (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 [HO₂+RO₂]”, and in their revision have only added ““The PSS radical calculation made on the assumption of the NO₂ steady state is very sensitive to the accuracy of the NO₂ to NO ratio and the O₃ measurements.” Yet, the considerable amount of text and equation 1 remain in the revision. This is very confusing for the reader. If the authors insist on keeping it then they should be much more explicit that this approach is not used (e.g., at least they could add that same sentence from their response document into the manuscript). Furthermore it would be useful to the reader if they clarified that there are two HOx radical calculation methods discussed here: 1. The NO-NO₂ interconversion photostationary state, described by equation 1, discussed from lines 96 – 120, and 2. The pseudo-steady state analysis presented in section 4.3 “**PSS estimation of the RO₂* mixing ratios**”, including equation 4: $P(\text{RO}_2^*) = D(\text{RO}_2^*)$

2. Another comment of mine that was not adequately addressed:

The original manuscript contains ““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”. In my original review I noted “reactions of RO with NO_x are rare and not discussed at all later in the manuscript”. The revision now includes this text: “The dominant terminating processes for RO₂* in the pollution plumes measured up to 2000 m are the formation of nitrites and nitrates from radical reactions with NO_x.”

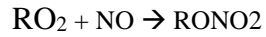
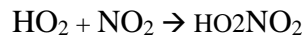
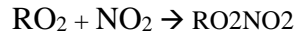
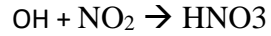
They have not understood my main point: formation of nitrites is not thought to be a major RO₂* removal process. I am unaware of supporting data from their study or from the literature that indicates that formation of **nitrites** can be a major RO₂* sink. In their *instrument* a large amount of CH₃O₂ is lost by the reaction $\text{CH}_3\text{O} + \text{NO} + \text{M} \rightarrow \text{CH}_3\text{ONO} + \text{M}$, i.e. formation of methyl nitrite, but these types of reactions are thought to be quite minor in the atmosphere. If the statement that formation of nitrites is a major RO₂* sink is to be kept in the manuscript it needs to be supported (which would be difficult). Moreover, it is not clear if they are including HNO₃ as a nitrate. I suspect the correct course of action is to simply change the sentence to “The dominant terminating processes for RO₂* in the pollution plumes measured up to 2000 m are the formation of nitric acid and organic nitrates”

3. Section 4.4.1. In my initial review I objected to the formulation of eq 11 (now eq 9 in revised manuscript). While I understand that the authors are referring to the analysis by Cantrell et al. (2003b), it is still very confusing:

$$P_{\text{RO}_2^*} = k_{\text{RR}} [\text{HO}_2 + \text{RO}_2]_2 + k_{\text{RN}} [\text{HO}_2 + \text{RO}_2] [\text{NO}_x] \quad (\text{Eq. 9})$$

“The first term on the right hand refers to radical radical reactions and the second term to RO₂*-NO_x reactions where RO₂* is considered to be the sum of HO₂+ RO₂ and K_{RR} and K_{RN} are effective rate coefficients”

The authors (and Cantrell) are calculating P(RO₂*) by equating it to L(RO₂*) (very safe assumption), and then calculating the L(RO₂*) terms. For the last term, the relevant RO₂* loss reactions that need to be summed in that term are the following:



While the 2nd and third reactions can be combined with an effective rate constant, I simply do not see how all four terms can be combined into the single term $k_{RN} [\text{HO}_2 + \text{RO}_2] [\text{NO}_x]$. The OH concentration does not necessarily scale with the $[\text{HO}_2 + \text{RO}_2]$ concentration.

Wouldn't it be simpler to calculate $P(\text{RO}_2^*)$ more directly based on RO_2^* formation reactions rather than the loss processes? ie, from photolysis of HCHO, $\text{O}_3/\text{H}_2\text{O}$, etc.

Figure 16 is a nice figure btw: I am not trying to suggest this entire section is bad, but its formulation is still problematic.

Equation 2, last term is $\sum k_{\text{O}_3+\text{alkenesk}}[\text{O}_3][\text{alkenesk}]$ – the ROx yield from this reaction should be included (i.e., $2 \times$ the OH yield).