

Comment on acp-2022-119

Anonymous Referee #1

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_2^* is unclear. In the first sentence it sounds as if this is the sum of RO_2+HO_2 , but later it looks as if also OH is included. Please clarify and be precise and accurate with definitions.*

Answer:

The meaning of RO_2^* is now clarified. The RO_2^* is mentioned in the abstract in Line 19 of the revised manuscript:

“The measurements of RO_2^ on HALO were made using the in-situ instrument Peroxy Radical Chemical Enhancement and Absorption Spectrometer (PeRCEAS). RO_2^* is to a good approximation the sum of peroxy radicals reacting with NO to produce NO_2 .”*

In Line 127 in the main text, the meaning of RO_2^* is explained in more detail:

“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 .”*

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

Answer:

The sentence in Line 23 has been rewritten to prevent misunderstanding, as follows:

“Radical production rates were estimated using knowledge of the photolysis frequencies and the RO_2^ precursor concentrations measured on-board HALO, as well as the relevant rate coefficients. Generally, high RO_2^* were measured in air masses with high production rates.”*

- Abstract L23: RO_2 is not directly produced from the photolysis of ozone and HONO, but OH is that then further reacts to produce RO_2^* species. Please be accurate how you phrase this.*

Answer:

The sentence has been rephrased as follows:

“In the airmasses investigated, RO_2^ is primarily produced by the reaction of O^1D with water vapour and the photolysis of nitrous acid (HONO), and of oxygenated volatile organic compounds (OVOC, e.g. formaldehyde (HCHO), and glyoxal (CHOCHO)).”*

- 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.*

Answer:

The sentence in Line 27 in the revised manuscript has been extended for clarification:

“ Due to their short lifetime in most environments, the RO_2^* concentrations are expected to be in a photostationary steady state (PSS) i.e., it is assumed a balance between production and loss rates. The RO_2^* production and loss rates and the suitability of PSS assumptions to estimate the RO_2^* mixing ratios and variability during the airborne observations are discussed. The PSS assumption for RO_2^* is considered robust enough to calculate RO_2^* mixing ratios for most conditions encountered in the air masses measured.”

- *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.*

Answer

The text has been rephrased for clarification:

“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 . Above 2000 m, $HO_2 - HO_2$ and $HO_2 - RO_2$ reactions dominate the RO_2^* removal.”

- *L90: Reaction R25 should be mentioned as well.*

Answer:

The R25 has been included in Line 95 as suggested:

“R23 and R25 are two of the most important reactions in the troposphere as they lead to O_3 formation via the reactions R27 and R28.”

- *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.*

Answer:

The text from Line 99 has been modified for clarification:

“The sum of HO_2 and RO_2 that react with NO to produce NO_2 can be estimated by assuming that the interconversion of NO to NO_2 reaches a photostationary steady-state (PSS), in which production and loss are to a good approximation equal.

The PSS assumption for $[NO_2]$ in the following mechanism (R23 to R29) leads to Eq. 1



$$[HO_2 + RO_2]_{PSS} = \frac{k_{NO+O_3}}{k_{NO+(HO_2+RO_2)}} \left(\frac{j_{NO_2}[NO_2]}{k_{NO+O_3}[NO]} - [O_3] \right) \quad (Eq.1)$$

where j_{NO_2} is the photolysis frequency of NO_2 ; k_{NO+O_3} ($1.9 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ at 298K and 1 atm.) is the rate coefficient of the reaction of NO with O_3 and $k_{NO+(HO_2+RO_2)}$ is usually estimated for the most abundant peroxy radicals HO_2 and CH_3O_2 by assuming a 1:1 HO_2 to CH_3O_2 ratio and averaging the k_{NO+HO_2} ($8.2 \times 10^{-12} \text{ cm}^3$

molecules⁻¹ s⁻¹ at 298K and 1 atm.) and $k_{\text{NO}+\text{CH}_3\text{O}_2}$ (7.7×10^{-12} cm³ molecules⁻¹ s⁻¹ at 298K and 1 atm.) rate coefficients for the reaction with NO. As noted by Parrish et al (1986), the PSS assumption requires conditions with sufficient and stable solar irradiation, ensuring NO₂ stable photolysis rates (j_{NO_2}) “

- *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.*

Answer:

The text in Line 106 has been accordingly modified:

“ where j_{NO_2} is the photolysis frequency of NO₂; $k_{\text{NO}+\text{O}_3}$ (1.9×10^{-14} cm³ molecules⁻¹ s⁻¹ at 298K and 1 atm.) is the rate coefficient of the reaction of NO with O₃ (...). “

As stated now in S1 of the supplementary information, the reaction rate constants used for the RO₂* calculations along the flights were calculated for the ambient temperature and pressure measured on-board HALO.

- *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.*

Answer:

In Eq. 1 the $k_{\text{NO}(\text{HO}_2+\text{RO}_2)}$ is usually estimated for the most abundant HO₂ and CH₃O₂ peroxy radicals by averaging the $k_{\text{NO}+\text{HO}_2}$ (8.2×10^{-12} cm³ molecules⁻¹ s⁻¹ at 298K and 1 atm.) and $k_{\text{NO}+\text{CH}_3\text{O}_2}$ (7.7×10^{-12} cm³ molecules⁻¹ s⁻¹ at 298K and 1 atm.) rate coefficients assuming a 1:1 HO₂:CH₃O₂ ratio. The text in Line 107 has been accordingly modified:

“... and $k_{\text{NO}(\text{HO}_2+\text{RO}_2)}$ is usually estimated for the most abundant HO₂ and CH₃O₂ by assuming a 1:1 HO₂ to CH₃O₂ ratio and averaging the $k_{\text{NO}+\text{HO}_2}$ (8.2×10^{-12} cm³ molecules⁻¹ s⁻¹ at 298K and 1 atm.) and $k_{\text{NO}+\text{CH}_3\text{O}_2}$ (7.7×10^{-12} cm³ molecules⁻¹ s⁻¹ at 298K and 1 atm.) rate coefficients for the reaction with NO.“

- *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 RO₂*. My expectation would have been that this would allow to perform also full model calculations of RO₂* concentrations, which could be compare PSS calculations. Please explain in more detail.*

Answer:

The PSS radical calculated by Eq. 1 assumes that the NO₂ is in a steady state and has been shown in the past to be very sensitive to the accuracy of the NO₂ to NO ratio. The NO (in-situ) and NO₂ (miniDOAS remote) measurements during the EMERGe campaign would not enable a suitable calculation of PSS peroxy radicals with Eq. 1.

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. We agree with the referee that this calculation is a good task for a model if available. In this study 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 RO₂* PSS with the RO₂* measurements on-board.

The text starting with “In contrast to other experimental deployments” has been modified for clarification:

“In contrast to other experimental deployments, the concentrations and/or mixing ratios of the majority of the key species involved in reactions R1 to R26 were continuously measured on-board HALO during the EMERGe campaign. This enables the use of a large number of measurements to constrain the PSS calculation of RO_2^* . Consequently, this data set provides an excellent opportunity to gain deeper insight into the source and sink reactions of RO_2^* and the applicability of the PSS assumption for the different pollution regimes and related weather conditions in the free troposphere.”

- *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.*

Answer:

The use of abbreviations has been kept to a minimum in the revised version, as proposed by the referee. However, a few abbreviations are required for the terms or definition which are often repeated, in order to facilitate the reading.

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

Answer:

“stable flight layers” refer to the fact that the altitude of the HALO aircraft was kept constant for the time probing at each level of the vertical profiles.

The text has been modified:

“Vertical profiles of trace constituents were typically made by keeping the HALO altitude constant at different flight levels upwind and downwind of the target MPCs.”

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

Answer:

The values have been calculated for 200 mbar which was the PerCEAS inlet pressure during the EMERGe campaign in Europe. This information has been added in Line 174.

- *L172: Why do you only refer to CH3O2 as RO2? Earlier you mention "weighted average rate coefficient" implying that you not only have CH3O2.*

Answer:

The calibration of PerCEAS in the laboratory is only made for HO_2 and for a 1:1 mixture of $HO_2 + CH_3O_2$ as described in George et al. (2020). The text from Line 176 has been extended for clarification and in order to include the details requested by RC2:

“The HO_2 and RO_2 detection sensitivity depends on the rates of loss of HO_2 and RO_2 by the R19 and R22 reactions. The latter depends on the concentration of the reagent gas NO added and the reaction rate coefficients, where k_{22} is larger than k_{19} . 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 $\pm 1\sigma$ standard deviation estimated from the reproducibility of the experimental determinations. Likewise, the ratio $\alpha = eCL_{CH_3O_2} / eCL_{HO_2}$ 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 their experimental errors.”

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

Answer:

The following text has been included in Line 189 of the revised manuscript, to provide quantitative information about the humidity effect on the eCL of PerCEAS, as suggested by the referee:

“The $[\text{H}_2\text{O}]$ in the DUALER inlet was lower than 1×10^{17} molecules cm^{-3} for 60 % of measurements during EMeRGe in Europe, for which the $\text{eCL}_{\text{wet}} = 76 \%$ of eCL_{dry} . At the highest humidity observed during the campaign, i.e., $[\text{H}_2\text{O}]_{\text{inlet}} = 2 \times 10^{17}$ molecules cm^{-3} , the eCL_{wet} is 55 % of eCL_{dry} (see Fig. S1 in the supplementary information).”

In addition, the Fig. S1 showing the ambient $[\text{H}_2\text{O}]$ versus $[\text{H}_2\text{O}]$ during the EMeRGe campaign in Europe has been included in the supplement together with an explanatory text:

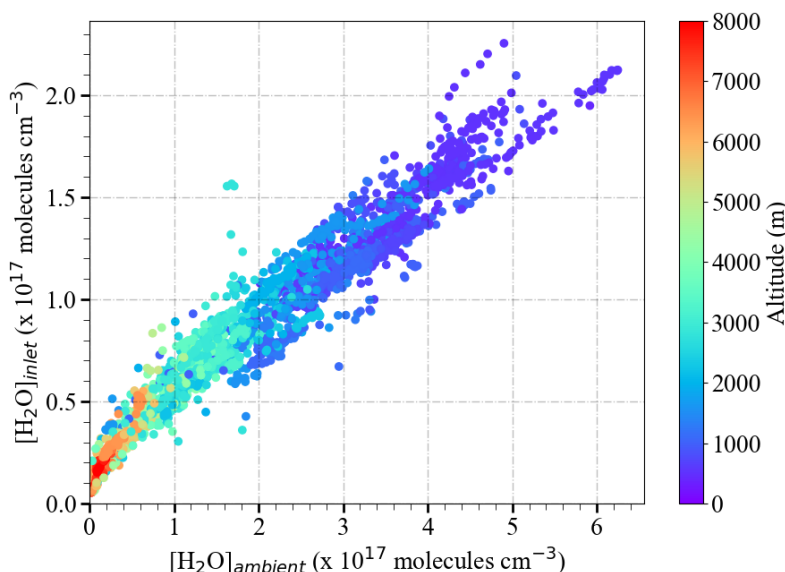


Figure S1: Ambient $[\text{H}_2\text{O}]$ versus $[\text{H}_2\text{O}]$ measured in DUALER during EMeRGe campaign in Europe, colour-coded with altitude.

“Figure S1 shows the humidity measured in the DUALER during the EMeRGe campaign in Europe. As the pressure in the DUALER inlet is lower than the ambient, $[\text{H}_2\text{O}]_{\text{inlet}} < [\text{H}_2\text{O}]_{\text{ambient}}$. However, the humidity is still significant and affects the eCL in the DUALER. Therefore, the eCL was corrected using the equation $\text{eCL}_{\text{wet}} = \text{eCL}_{\text{dry}} \times A^{([\text{H}_2\text{O}] \times 10^{-16})}$ obtained from the laboratory characterisation of the eCL water dependence, where $A = 0.973$ for the NO number concentration added to the DUALER inlet during EMeRGe campaign in Europe (George, 2022, PhD thesis).

The $[\text{H}_2\text{O}]$ in the inlet was lower than 1×10^{17} molecules cm^{-3} for 60 % of measurements during EMeRGe in Europe, for which the $\text{eCL}_{\text{wet}} = 76 \%$ of eCL_{dry} . At the highest humidity observed during the campaign, i.e., $[\text{H}_2\text{O}]_{\text{inlet}} = 2 \times 10^{17}$ molecules cm^{-3} , the eCL_{wet} is 55 % of eCL_{dry} .”

- *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.*

Answer:

Table 1 includes references for detailed descriptions of the instruments on-board HALO used in this study. In addition to adding further important details of PerCEAS, the objective of the section 3 is on the remote-sensing instruments to understand the shortcomings of combining results of in-situ and remote sensing instruments. With this purpose further details on the conversion of column densities measured by remote sensing instruments into mixing ratios or number concentrations as provided by in-situ instruments are given. To improve clarity the following sentences have been rephrased:

“The remote sensing instruments used on HALO during EMeRGe were the mini Differential Optical Absorption (miniDOAS) and the Heidelberg Airborne Imaging DOAS Instrument (HAIDI). The miniDOAS observes the atmosphere using six telescopes: two being optimised for the ultraviolet, two for the visible, and two for the near infrared. Three telescopes observe in nadir viewing and three in limb viewing. The three limb scanning telescopes point to the starboard side perpendicular to the aircraft fuselage axis. They are rotated to compensate for roll relative to the horizon. A variant of the DOAS retrieval technique uses least square fitting of the measured and radiative transfer modelled absorption along the line of sight to retrieve the differential salt column density, dSCD, of the target gas and a scaling reference gas. The latter is the dimer of molecular oxygen (O_4). As the vertical profile of the concentrations of O_2 and thus O_4 are known then the mixing ratios of the target gas at the flight altitude obtained from the target gas and O_4 dSCDs (for more details see Stutz et al., 2017; Hüneke et al., 2017; Kluge et al., 2020; Rotermund et al., 2021). The HAIDI nadir observations are used to retrieve the dSCDs below the aircraft. The dSCDs from HAIDI are then converted to the mixing ratios using knowledge of the aircraft altitude and the corresponding geometric Air Mass Factor (AMF), calculated by a radiative transfer model under a well-mixed NO_2 layer assumption. As a result of this assumption, the calculated mixing ratios for HAIDI target gases are lower limits and similar to the actual values observed while flying within and close to a well-mixed boundary layer. In spite of the differences in the sampling volume, temporal sampling and spatial resolution between the in situ and remote sensing techniques, the concentrations of the gas HCHO measured by both techniques were in good agreement and the concentrations of the NO_2 (remote sensing) and NO_y (in situ) were consistent (for more details see Schumann, 2020).”

- *L186: Please explain RT modelling.*

Answer:

RT stands for radiative transfer and has now so been included in the rephrased paragraph beginning at the Line 192

- *L187: Please explain the abbreviation HAIDI.*

Answer:

HAIDI is the abbreviation for the name of the instrument: The Heidelberg Airborne Imaging DOAS Instrument (HAIDI). This has been included in the text.

- *L191: Please explain what you mean with “common and related species”.*

Answer:

The text has been modified for clarification:

“In spite of the differences in the sampling volume, temporal sampling and spatial resolution between the in situ and remote sensing techniques, the concentrations of the gas HCHO measured by both techniques were in good agreement and the concentrations of the NO_2 (remote sensing) and NO_y (in situ) were consistent (for more details see Schumann, 2020).”

- *L202: I would avoid a conclusion about the reason for high RO_2 in specific regions before doing the analysis. Your arguments are plausible but there are also other plausible explanations giving the contrary conclusion.*

Answer:

The sentence in Line 202 “This is attributed to the higher insolation and temperatures favouring the rapid production of RO_2^* from the photochemical oxidations of CO and VOCs.” has been modified and moved to Line 335, as suggested by the referee.

“Photochemical processing is expected to be enhanced over Southern Europe due to the prevailing conditions of high insolation and temperatures during the EMeRGe flights, which might lead to the rapid production of RO_2^* from the photochemical oxidations of CO and VOCs.”

- L210: I do not understand the argument "comparable". What is exactly compared here? Calculating RO_2^* 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.

Answer:

The emphasis of this sentence in Line 210 in the original manuscript (“Provided that insolation conditions and a sufficient number of key participating precursors are comparable, the air mass origin is irrelevant for calculating RO_2^* concentrations and mixing ratios.”) is on the fact that the RO_2^* are dominated by fast photochemistry. The local conditions and chemical composition of an airmass rather than its origin should determine the variability and variations of RO_2^* concentrations. Therefore, the air trajectories are not considered in this analysis.

The text from line 222 has been modified for clarification:

“The origin and thus the composition of the air sampled during the seven flights over Europe were different and heterogeneous. Typically, the air masses measured were influenced by emissions from MPCs and their surroundings, and sometimes by biomass burning transported over short or long distances. The concentration and mixing ratio of RO_2^* rather depends on the insolation and the chemical composition of the air probed, particularly on the abundance of RO_2^* precursors, than on the origin of the air masses. Since RO_2^* are controlled by fast chemical and photochemical processes, the air mass origin and trajectory are not used in the calculation of RO_2^* concentrations and mixing ratios, but are of interest as the source of the RO_2^* precursors. Thus, the RO_2^* variability and its production rates provide valuable insight into the photochemical activity of the air masses probed.”

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

Answer:

The figure 3 has been modified as proposed by the referee.

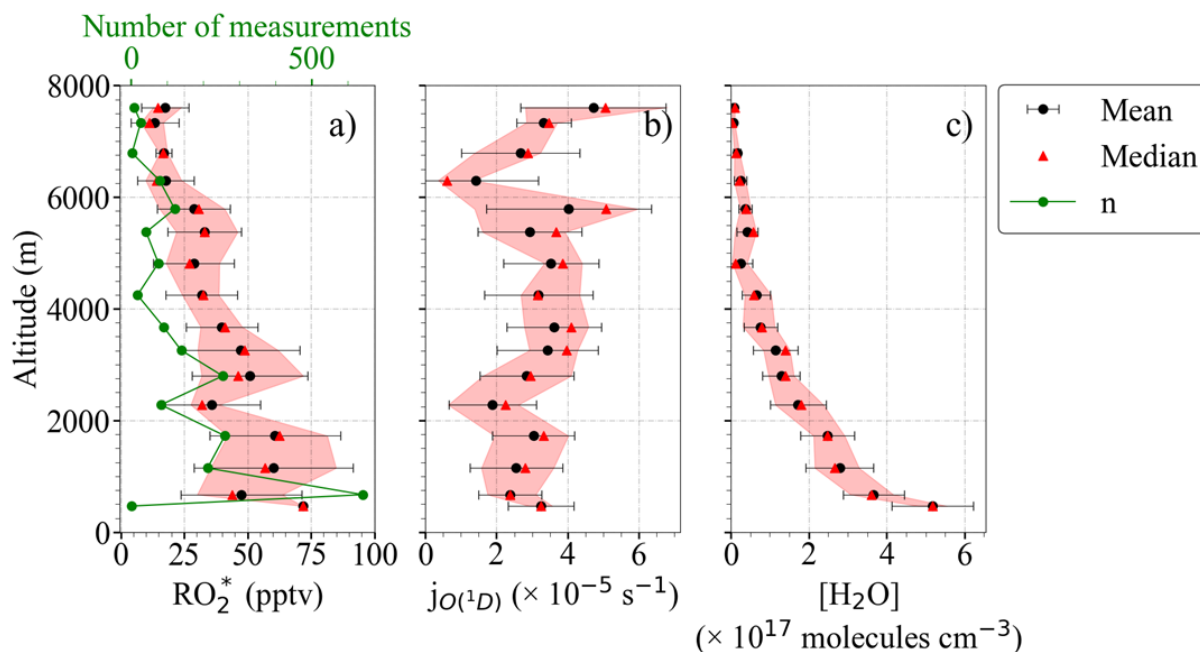


Figure 3: Composite average vertical profiles of a) RO_2^* , b) $j_{O(^1D)}$ and c) $[H_2O]$ observations. The measurements are binned over 500 m altitude. The error bars are the $\pm 1\sigma$ standard deviation of each bin. Median values (red triangles) the interquartile 25-75% range (red-shaded area) and the number of individual measurements, n , for each bin (in green) are additionally plotted.

- 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.

Answer:

In agreement with the last two comments of the referee the Figure 3 has been changed and the sentence in Line 224 has been removed.

- *Line 235: "becomes" instead of "become"*

Answer:

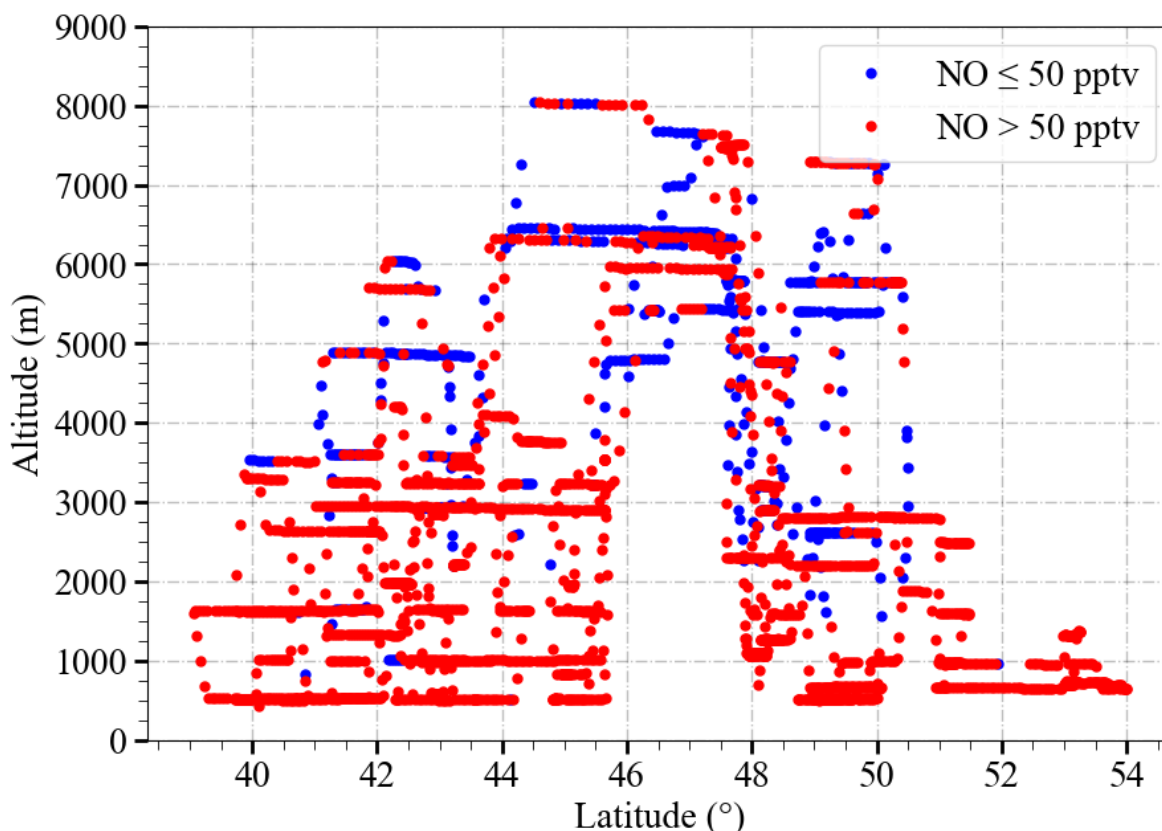
This has been corrected

- *L235: Please clarify what you mean with "low NO_x conditions" and why this impacts the significance of H₂O₂ photolysis.*

Answer:

The results of Tan et al., (2001) during the PEM-Tropics B campaign show that in the case of low concentrations of NO_x, the rate of the reactions HO_x with NO_x decreases. All other conditions being the same, this increases the concentration of HO₂ and RO₂ and thus the rates of production of the concentrations of the peroxides H₂O₂ and ROOH. These peroxides photolyse and react with OH to form HO_x. At higher mixing ratios of NO_x, the reactions of HO_x with NO_x dominate. Tan et al., 2001 investigated clean chemical conditions, which are defined as "low NO_x conditions", with 95% of the measured NO values below 50 pptv and 76% below 20 pptv, and median O₃ values below 20 ppbv.

As can be seen in the figure below, in most of the air masses measured during EMERGe in Europe, NO were higher than 50 pptv, in ~75 % of the airmasses probed. Therefore, the conclusions from Tan et al.(2001) are applicable to the present work.



The text has been modified to clarify this aspect (starting at Line 251):

“In this study, Eq. 2 has been applied to the measurements taken within the EMERGe campaign in Europe. There were no H₂O₂ measurements available for EMERGe. However, the measurements reported by Tan et al. (2001) indicate that the rate of OH production from the H₂O₂ photolysis is not significant except when the NO_x is low. To be more precise, for conditions having NO < ~50 ppt, the partitioning of HO_x is strongly shifted to HO₂, which then predominantly reacts with itself or RO₂ to form peroxides, which can in turn photolyse. For conditions with NO > 50 pptv, the rates of reactions of HO₂ or RO₂ with NO_x are faster than those of HO₂ with HO₂ and RO₂. As the NO mixing ratio was higher than 50 pptv in 75 % of the air masses probed in Europe, the rate of the photolysis of H₂O₂ was, as a first approximation, assumed not to be significant source of OH for the EMERGe dataset considered in this study.”

- *L238: Please define OVOC before using it in Eq 2*

Answer:

OVOC has been defined with the Eq. 2 in Line 250 as :

“where OVOC stands for oxygenated volatile organic compounds.”

- *L237. This statement 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 RO₂* 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.*

Answer:

The text has been modified to clearly distinguish between primary radical production and propagation reactions in Eq. 2. Furthermore, it has also been clarified, that the terms without measurements are not considered in the analysis. This is the case of the ozonolysis of alkenes and the photolysis of H₂O₂.

“The rate of production of RO₂* from the reactions R1 to R13 is given by:

$$P_{RO_2^*} = 2jO_D^1 [O_3] \frac{k_{O_D^1 + H_2O} [H_2O]}{k_{O_D^1 + H_2O} [H_2O] + k_{O_D^1 + O_2} [O_2] + k_{O_D^1 + N_2} [N_2]} + j_{HONO} [HONO] + 2j_{H_2O_2} [H_2O_2] + 2 \sum_i j_i [OVOC_i] + \sum k_{O_3 + alkenes_k} [O_3] [alkenes_k] \quad (\text{Eq. 2})$$

where OVOC stands for oxygenated volatile organic compounds.

In this study, Eq. 2 has been applied to the measurements taken within the EMERGe campaign in Europe. There were no H₂O₂ measurements available for EMERGe. However, the results reported by Tan et al. (2001), indicate that the rate of OH production from the H₂O₂ photolysis is not significant except when NO_x is low. To be more precise, for conditions having NO < 50 ppt, the partitioning of HO_x is strongly shifted to HO₂. HO₂ then predominantly reacts with itself or RO₂ to form peroxides, which can in turn photolyse. For conditions with NO > 50 pptv the rates of reactions of HO_x with NO_x are faster than those of HO₂ with HO₂ and RO₂. As the NO mixing ratio was higher than 50 pptv in 75 % of the air masses probed in Europe, the rate of the photolysis of H₂O₂ was as a first approximation assumed not to be a significant source of OH for the EMERGe dataset considered in this study.

Formaldehyde (HCHO), acetaldehyde (CH₃CHO), acetone (CH₃C(O)CH₃), and glyoxal (CHOCHO) were the OVOCs measured in EMERGe forming directly radicals through photolysis. They are produced in the photolysis and oxidation of VOCs and are likely the most abundant and reactive OVOCs present. In this study they were assumed to be the dominant VOCs in the air masses probed.

There were no measurements of alkenes provided in EMeRGe. Consequently, the ozonolysis term in Eq. 2 was not included in the analysis.”

- *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.*

Answer:

The present study uses only the measurements on-board as input for the RO_2^* calculations. The 4 OVOCs species mentioned were the only VOCs measured in most of the flight legs. OVOCs are the most abundant and reactive VOCs and are therefore considered to be representative for the sum of VOCs. There were taken as a surrogate because it cannot be ruled out that the air masses contain other non-measured OVOC species. As mentioned in the answer above, the text has been modified to clarify this:

“Formaldehyde (HCHO), acetaldehyde (CH₃CHO), acetone (CH₃C(O)CH₃), and glyoxal (CHOCHO) were the OVOCs measured in EMeRGe forming directly radicals through photolysis. They are produced in the photolysis and oxidation of VOCs and are likely the most abundant and reactive OVOCs present. In this study they were assumed to be the dominant VOCs in the air masses probed.”

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

Answer:

This is true. The word “estimated” has been replaced by “calculated”.

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

Answer:

The text has accordingly been modified to avoid redundancy.

- *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.*

Answer:

As explained above in the answers for Line 91 and Line 126, the PSS radical calculation in Eq. 1 assumes the NO₂ steady state and in the present paper, the approach bases on the assumption of PSS for peroxy radicals. As the NO₂ steady state has usually been used in the past for the calculation of peroxy radicals, the Eq.1 is written in the introduction as a reference and to emphasise the difference with this work. The text at these positions has already been modified and potential confusion is hopefully by now clarified.

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

Answer:

We agree with the referee about this intrinsic redundancy. The initial idea was to emphasise the “competition between reactions”. The sentence has been reworded as:

“The R5 to R7, R12, R16b, and R23 to R26 are interconversion reactions between OH, RO, HO₂ and RO₂ and do consequently occur without radical losses. Solving Eq. 4 leads to Eq. 5 if RO₂* – RO₂* reactions are assumed to be the dominant radical terminating processes.”

- *L298 ff: Please justify that you can calculate the loss of RO₂* -RO₂* reaction by an weighted average rate coefficient? What do you use as weights? Without knowing the distribution between HO₂ and RO₂ 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 [HO₂] and [RO₂] concentrations. If you assumed e.g. [HO₂] = [RO₂] = 0.5 [RO₂*], this should be clearly said and written down what this means for the equation. The assumption of [HO₂] = [RO₂] would be expected if the loss of [HO₂] and [RO₂] 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 RO₂* due to the reaction of NO₂+OH? Could this have been significantly contributed to the RO₂* loss? Your analysis between differences, if you divide data sets between North and South may hint that this loss process was relevant.*

Answer:

Figure 7 does not involve any kind of mathematical calculations but rather provides a first qualitative glance on the relationship between the RO₂* measured and the square root of the production rate of RO₂* calculated using Eq.3. In spite of the spread around the 1:1 line, the obtained plot indicates a linear relationship. According to Eq. 5, the slope of this linear relationship should represent a total loss rate coefficient (called in the text “an effective RO₂* self-reaction rate coefficient”), i.e., a kind of weighted rate coefficient including the effect of HO₂ – HO₂, HO₂ – RO₂ and RO₂ – RO₂ reactions. As mentioned by the referee, it is challenging to calculate this rate mathematically without further details about the distribution between HO₂ and RO₂ and the RO₂ speciation. This was also included in the text on Line 306 (now Line 333):

“Apart from this, the spread in the diagram confirms that the effective RO₂* self-reaction rate $k_{RO_2^*+RO_2^*} [RO_2^*]^2$ varies widely in the air masses probed likely due to the effect of changes in HO₂ and $\sum RO_2$ concentrations in the individual loss reaction rate coefficients”

From this point in the analysis, the Eq. 5 is modified to include stepwise different mechanisms and assumptions aiming at the calculation of realistic RO₂*. This is the case e.g. of radical reactions with NO_x as mentioned by the referee.

The text has been modified for clarification:

In Line 326: “where $k_{RO_2^*+RO_2^*}$ represents an effective RO₂* self-reaction rate coefficient comprising HO₂ – HO₂, HO₂ – RO₂ and RO₂ – RO₂ reaction rates.”

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

Answer:

The sentence “Note that these results are only valid for the data set acquired over Europe during EMeRGe and do not yield a relationship between [RO₂*] and $\sqrt{P_{RO_2^*}}$, which is generally applicable for these two latitude windows.” points out that the data used are only a snapshot of the atmosphere during the flights and flight legs and under the particular encountered conditions of EMeRGe. Therefore, the concentration levels and radical production rates calculated in this work for Northern and Southern Europe are only an example but are not meant to be applicable under all conditions to these latitude windows.

The sentence has been revised.

“Please note that these results are only valid for the data set acquired over Europe during EMeRGe flights and do not yield a relationship between $[RO_2^*]$ and $\sqrt{P_{RO_2^*}}$, which is generally applicable under all conditions for these two latitude windows.”

- *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 RO2 consist only of CH3O2 is only, in order to have one RO2 species and therefore not considering differences in RO2+RO2 and RO2+HO2 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.*

Answer:

The names of the photolysis rates in Eq. 5 and Eq. 6 are consistent with the list of reactions in the introduction. Since Eq. 5 is the first equation in the text for the balance between radical production and losses in the PSS analysis, the name of the photolysis rates specifies the species being photolysed to emphasise visually the species and processes considered. As the Eq. 6 gets more complicated, the names of the photolysis rates are shortened by numbering them according to the reaction list in the introduction and in the Table 1 in the supplement.

A sentence has been included to explain this in Eq.5:

“where J_{HCHO} , J_{CH_3CHO} , $J_{CH_3C(O)CH_3}$, J_{CHOCHO} are respectively j_8 , j_9 , $j_{10a,b}$ and j_{11} , as in Table 1 in the supplementary information”

Starting by the simplified Eq.5 enables first showing the spread in the linear relationship between measured data and photolysis rates before proceeding with the calculation of RO_2^* by taking into account the dominant individual processes involved in the formation and destruction of radicals.

- *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.*

Answer:

The Eq.5 is not used to calculate $[RO_2^*]$ as it is done with Eq.6. With the help of Eq. 5 the relation between RO_2^* measured and the square root of $P_{RO_2^*}$ is investigated. In contrast, Eq. 6 is solved as a quadratic equation to obtain the $[RO_2^*_c]$, i.e., RO_2^* calculated, that are subsequently compared with the $[RO_2^*_m]$, i.e., RO_2^* measured.

The text in the revised version has been reworded for clarification.

- *L342: The effect that RO2* measurements can be affected by differences in the detection sensitivity of RO2 and HO2 should have been discussed for the results with delta=0.5 (Equation 5).*

Answer:

The text has been modified to improve clarity. The Eq. 8 and 9 in the original manuscript are now Eq.6 and Eq.7 and the information in Section 4 has been improved.

The text has been extended in Line 352 for the explanation of the detection sensitivity of RO_2 and HO_2 :

“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., $[HO_2] = \delta[RO_2^*]$ and $[CH_3O_2] = (1 - \delta)[RO_2^*]$, in the analysis. As a first

approach, RO₂ is assumed to consist only of CH₃O₂ to reduce the complexity of the calculations by considering only CH₃O₂ 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).”

- *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 RO₂, if you do not assume that all RO₂ is CH₃O₂?*

Answer:

If we do not assume that all RO₂ is CH₃O₂ in the calculations, we need to consider the impact of:

- a) Differences in the rate for the reaction of other RO₂ with NO. With the exception of CH₃CO₂O₂ the k(RO₂+NO) (listed in JPL) range within ≤15% and are <10% of the k(HO₂+NO). Only in the case of abundances in the air mass of CH₃CO₂O₂ or other RO₂ of similar reactivity with NO higher than CH₃O₂, the effect of a) would be significant.
- b) The branching ratio of the pressure dependent channel of the reaction of RO₂ with NO to form alkyl nitrates RONO₂, R= CH₃, C₂H₅, etc. that increases as R becomes larger. The studies of Carter and Atkinson, and more recently Butkovskaya et al. (see references below). These studies show that generally the yield of alkyl nitrates for the reaction of alkylperoxy radicals with NO increases from ca. 4% for C<3 to ca. 30% for C>8. If we assume that 10-20% of RO₂ have R larger than CH₃, the effect in the calculation of the pressure dependent channel forming alkyl nitrates is estimated to be within the experimental error of the measurements. For higher amounts, the RO₂* ambient would be underestimated. However, this quantification is not possible without knowledge of the RO₂ composition of the air mass.
- c) Differences in the rates of HO₂+RO₂ and RO₂+RO₂ reactions. The quantification of this effect is also challenging without knowledge of the RO₂ composition of the air mass. There is a limited number of reaction coefficients available for these reactions. Modelling studies such as Carter, (2010), use active peroxy radical operators such as MEO₂ + HO₂ = HCHO + O₂ + H₂; MEO₂ + MEO₂ = MEOH + HCHO + O₂ and MEO₂ + MEO₂ = #2 {HCHO + HO₂} for their simulation.

A quantitative estimation of the overall effect of a) b) and c) for the calculations is beyond the scope of this study.

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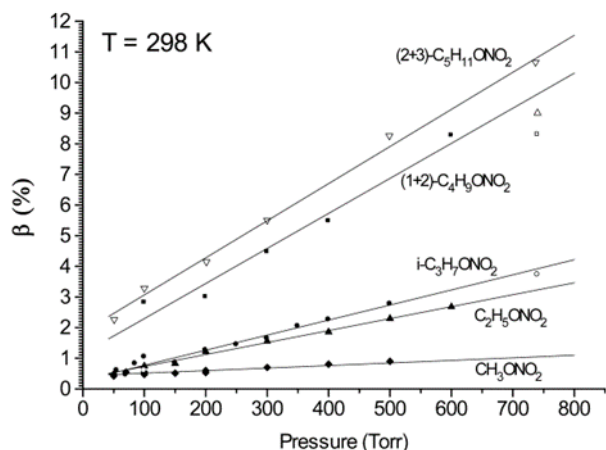


Figure 4. Comparison of the branching ratios k_b/k_a of alkyl nitrate formation in $\text{RO}_2 + \text{NO}$ reactions for small alkylperoxy radicals: ∇ , ref 14; \blacksquare , this work; \bullet , ref 18; \blacktriangle , ref 17; \blacklozenge , ref 16; atmospheric pressure data for propyl nitrate (\circ) and butyl nitrate (\square) are from ref 10, and those for *n*-pentyl (Δ) nitrate are from ref 43. The open circle at 100 Torr is the branching ratio for isopropyl nitrate from ref 44.

(from Butkovskaya et al., 2015)

- *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.*

Answer:

As mentioned above whole text in section 4 has been shortened and modified for clarification.

- *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.*

Answer:

As for the previous comment, this part of the text has been thoroughly modified to improve clarity and the whole manuscript has been checked for consistency.

- *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 $\text{HO}_2 + \text{NO}$ and $\text{HO}_2 + \text{O}_3$, it is not clear to me, what for example the product of $\text{HO}_2 + \text{O}_3$ would be. The factor rho associated with this term is explained as OH loss during the OH- RO_2^* 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 $\text{RO}_2 + \text{RO}_2$ 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.*

Answer:

The equations 5 to 9 have been modified to improve clarity and in the revised manuscript the Eq.5 is only modified to Eq. 6. The Eq. 6 is solved as Eq.7 and used for all the calculations. Some more text has been introduced to describe and clarify the terms of Eq. 6 (Line 358 onwards):

“The Eq. 5 is additionally extended to include RO_2^* effective yields from VOC oxidation and radical losses through HONO, HNO_3 , and organic nitrate formation:

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

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, $1 - \rho$ 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:

$$\rho =$$

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

Measurements of CH_4 , HCHO, CH_3CHO , CHOCHO, CH_3OH , and $CH_3C(O)CH_3$ on-board HALO are available and implemented in Eq. 6. These comprise the most abundant and reactive OVOCs and are considered to be a representative surrogate for the VOCs that act as RO_2^* precursors through oxidation and photolysis. During the EMERGE campaign in Europe, $k_{12a} \times HCHO$ and $k_{12b} \times CH_3CHO$ have the highest contribution to the $1 - \rho$ from all the OVOC measured. Their impact on the RO_2^* budget is found to be similar because their respective concentrations compensate the difference in the rate coefficients of their reactions with OH ($k_{12a} = 8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{12b} = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298K and 1 atm.). Despite its high mixing ratios measured, $CH_3C(O)CH_3$ is less important in the $1 - \rho$ term. This is because the rate coefficient $k(T)_{12c}$ is significantly slower than k_{12a} and k_{12b} (see Table S1 in the supplement). Similarly, the contribution of CHOCHO and CH_3OH is an order of magnitude lower than that of HCHO and CH_3CHO .

Concerning the term $\delta[RO_2^*](k_{23}[NO] + k_{24}[O_3])\rho$ on the right hand side of Eq.6, the HO_2 reaction with O_3 has a negligible effect as k_{24} is almost four orders of magnitude smaller than k_{23} and the NO concentrations remained about three orders of magnitude smaller than the O_3 measured during the campaign.”

- *L367 ff: It sounds as if you state that the reaction of OH+ HCHO and OH+ CH3CHO 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.*

Answer:

This has been addressed with the answer above.

- *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.*

Answer:

The sentence has been reworded and extended for clarification:

Line 382: “Concerning the term $\delta[RO_2^*](k_{23}[NO] + k_{24}[O_3])\rho$, the HO_2 reaction with O_3 has a negligible effect in Eq. 6 as $k_{HO_2+O_3}$ is almost four orders of magnitude smaller than k_{HO_2+NO} and the NO concentrations remained about three orders of magnitude smaller than the O_3 measured during the campaign.”

- *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 HO₂/RO₂ ratio in the case, when VOCs concentrations were high?*

Answer:

The overestimation of loss processes cannot be excluded. The text starting in Line 452 has been reworded and extended for clarification:

“RO₂^{*}_m is both underestimated and overestimated for Σ VOCs mixing ratios greater than 7 ppbv. The composition of these air masses is very different, as reflected by the Σ 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 RO₂^{*}_m and RO₂^{*}_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) RO₂^{*} production from the photolysis of carbonyls, which were not measured and/or c) RO₂^{*} production from the ozonolysis of alkenes or unidentified biogenic terpene emissions and/or d) overestimation of the loss processes. For VOC < 2ppb and Σ VOCs/NO < 20, RO₂^{*}_m is systematically overestimated. This might indicate underestimation in the radical losses through nitrite and nitrate formation.”

The uncertainties related to the presence of RO₂ other than CH₃O₂ has been discussed in the answer to L344. In the text starting in Line 506, the effect of changes in the HO₂ to RO₂ ratio on the PerCEAS accuracy during the E-EU-03 flight is discussed.

“Taking CH₃O₂ as a surrogate for all RO₂ might lead to uncertainties in the RO₂^{*} calculations in the presence of OVOCs with larger organic chains. On the experimental side, changes in the HO₂ to RO₂ ratio affect the accuracy of the PerCEAS retrieval of the total sum of radicals. As noted in section 3, in this study RO₂^{*} = HO₂ + 0.65 × RO₂, and the eCL is determined for a 1:1 mixture of HO₂:CH₃O₂, i.e. $\delta = 0.5$ is used for the RO₂^{*} retrieval. However, the HO₂ to CH₃O₂ ratio is not expected to remain constant in all the air masses probed. For a 3:1 ratio of HO₂:RO₂, the RO₂^{*}_m would decrease by 10 %. Similarly, a HO₂:RO₂ ratio of 1:3 would lead to an increase of 10 % in the reported RO₂^{*}_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 RO₂^{*}_m and RO₂^{*}_c in particular cases. A complete explanation of the variability of RO₂^{*} 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”

- *L422: Why would OH recycling processes increase the calculated RO₂^{*}, if radical regeneration terms cancel out in the calculations for the sum measurement of RO₂^{*}?*

Answer:

The use of “recycling processes” was not adequate. This part of the text has been rephrased to prevent confusion.

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

Answer:

The uncertainty of the HCHO measurements is $\leq 40\%$ in 95 % of the measurements considered in this study. The impact of this HCHO uncertainty on the RO₂^{*}_c depends on the relative contribution of the HCHO photolysis to the total RO₂^{*} production rates. For the measurements below 4000 m, where the HCHO photolysis contribution is < 40 %, the HCHO uncertainty contributes $\leq 15\%$ of the total uncertainty of RO₂^{*}_c. For the measurements above 6000 m with 80 % of the RO₂^{*}_c formed from HCHO photolysis, the HCHO measurement uncertainty contributes up to 35 % of the total uncertainty of RO₂^{*}_c.

- *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.*

Answer:

The whole paragraph has been deleted as proposed by the referee.

- *Section 4.4.1. / Equation 11: Again the definitions of the effective rate coefficients is not clear. Also the use of NOx 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 NOx 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.*

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 $\text{HO}_2 + \text{RO}_2$ 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 results indicate that the simplified approach of Cantrell et al. (2003b) is not applicable to the more complex non-linear processes involved in the air masses investigated within EMERGe.

The text has been partly reworded for clarification.