Answer to: Interactive comment on “Hydrogen peroxide in the upper tropical troposphere over the Atlantic Ocean and western Africa during the CAFE-Africa aircraft campaign” by Hamryszczak et al.
Anonymous referee #1

Please note the used color code
(black: Referee Comments, red: Author Comments, blue: manuscript changes according to Referee’s recommendations and comments)

This paper presents H_2O_2 observations in the upper troposphere over the tropical Atlantic from the CAFE campaign and compares to photochemical steady state (PSS) values and to the EMAC model.

Overall assessment: The observations are interesting but the interpretation is routine, and as a result I don’t see any significant scientific advances coming out of this paper. This seems a missed opportunity because the observations could be used to lend new insights into several interesting questions: (1) the scavenging efficiency of H_2O_2 in deep convection, (2) whether H_2O_2 is directly injected or is produced following the injection of CH_3OOH, and (3) what time scales are involved in the evolution from fresh convective injection to PSS. These are questions that have been debated in the literature and for which this data set (it seems to me) could provide new answers. Instead, the comparison to model results is long and tedious but does not go beyond being descriptive and anecdotal, and I finished this paper without the impression of having learned anything. The PSS calculation is wrong – H_2O_2 has too long a lifetime to be in instantaneous PSS (it needs to be 24-h PSS). The convective influence on H_2O_2 in the upper troposphere is by itself not new – this has been shown in several previous aircraft campaigns.

I’m sorry to be so negative because I feel that the observations are valuable and could provide the basis for a good paper.

We thank the referee for the assessment and the helpful comments. The work gives a general overview of H_2O_2 levels over the tropical Atlantic and the impact of convective processes taking place in ITCZ on the total budget and the spatial distribution of hydrogen peroxide in the upper troposphere. To our knowledge, tropical hydrogen peroxide measurements and airborne-based analyses at altitudes above 12 km are scarce due to technical restrictions associated with aircraft measurements.

In our work, we show that additional H_2O_2 is not only injected into the UT (above 8 km) in the convection prone region of the ITCZ but further subsequently redistributed towards the subtropics. For this reason, other than in the free troposphere and upper troposphere below 12 km, which was shown during previous airborne studies, the levels of hydrogen peroxide do not display any significant latitudinal gradient corresponding with the inclination of the solar radiation. In our studies, we show that the levels of H_2O_2 seem to be far more dependent on additional sources than previously assumed.

We thank the referee for the valuable suggestions on analyses, which might provide significant insight to highly interesting studies on deep convection processes. As described in Sect. 2, the objective of the mission was to investigate large-scale distribution of trace gases, radicals and aerosols in the upper tropical troposphere. As displayed in the three-dimensional H_2O_2 distribution below, unfortunately only few vertical profiles were measured outside of the region of the base of operation on Cape Verde and the ITCZ. We believe that, due to a lack of statistical significance in other vertically performed flight legs, only the 30 take-offs and landings give sufficient information on the distribution of hydrogen peroxide throughout the tropospheric column. For this reason, based on the available dataset, the scavenging efficiency in deep convection and insights on injection processes and time scales cannot be considered, unfortunately.

As further described in the experimental Sect. 3.1, due to the instrumental technique, detailed characterizations of single organic peroxide species are not possible. The measurements obtain the total amount of organic hydroperoxides without distinction between the organic species in the sampled air. Thus, the measurement uncertainty of hydroperoxides other than H_2O_2 is about 40%. We believe, this high uncertainty factor does not serve well for any quantitative analyses on the organic hydroperoxide budget in the upper troposphere as well as on any related questions regarding convective transport.

The presented calculations of hydrogen peroxide under photostationary steady-state conditions are, as mentioned throughout the work, of local character and serve exclusively the characterization of atmospheric regions, where observed hydrogen peroxide levels deviate from the expectations due to potential additional sources and sinks (e.g. injections due to deep convection, cloud scavenging and rainout). We do not intend to compare the observations of hydrogen peroxide with PSS calculations beyond the aspect of the observed local imbalances between photochemical production and loss paths of the species.

We hope the following clarifications and comments will improve the overall understanding of the analyses and results, which we are presenting in the scope of this work.

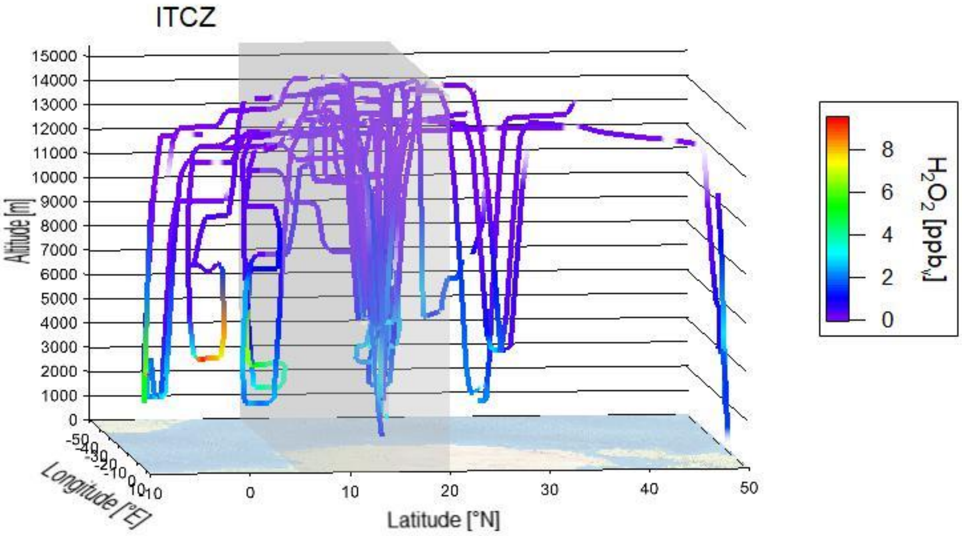

Figure 1: General overview of performed measurement flights with respect to the observed H_2O_2 levels (color-code) with the assumed region of ITCZ during the campaign highlighted in grey.

Specific comments (lines)

40-45, also 68-69: this summary of H_2O_2 chemistry is textbook wrong. HO_2 does not necessarily come mainly from CO+OH; any VOC+OH (for example CH_4+OH) will lead to HO_2. And the ‘competition’ between self-reaction of HO_2 and reaction with NO and O_3 (producing OH) does not actually affect H_2O_2 formation in a NO_x-limited regime because the OH will go back to HO_2.

We agree with the referee that in general, the most organic peroxy radicals also form HO_2 in secondary reactions Also, other primarily production paths, as in case of formaldehyde photolysis, might contribute to HO_2 production. Nevertheless, under the UT conditions, which were investigated in this work, HO_2 is expected to be mainly formed via reaction of carbon monoxide with OH radicals. Further, as shown by Tadic et al. (2021), the production rate of HO_2 via reaction of OH is on average a factor 5 higher than the production rate via photolysis of HCHO.

It is correct that the OH formed via the reaction of HO_2, NO and O_3 might regenerate HO_2. Nonetheless, in an NO_x rich environment both, OH and HO_2, also react with NO and NO_2 to form HNO_3 and HNO_4, the latter being mostly abundant in the upper troposphere. Thus, the literature (e.g. Reeves and Penkett 2003) reports about competition between these reactions.
Lines 40 – 45 (now L44 – 49) and L68 – 69 (now L74 – 76) were changed according to the referee's comment.

L44 – 49 (former L40 – 44): The most prominent pathway leading to H_2O_2 is the self-reaction of HO_2 radicals (R4). HO_2 can be formed by many pathways. Under the upper troposphere conditions investigated in this work, HO_2 is mainly formed via reaction of carbon monoxide with OH radicals which can be formed initially in the photolysis of ozone and the subsequent reaction of O^1D with water vapor (R1-R3). Moreover, OH can be recycled from HO_2 in reactions with NO or O_3. The budget of H_2O_2 is thus controlled by the steady-state concentration of HO_2 radicals and the main gas-phase loss processes photolysis and reaction with OH (R5-R6).

L74 – 76 (former L68 -69): In urban areas, the formation of hydrogen peroxide is diminished by the increased mixing ratios of NO_x ($NO_x = NO_2 + NO$) derived from anthropogenic sources, as the self-reaction of HO_2 to H_2O_2 is competing with the much faster reaction of HO_2 with NO (Lee et al., 2000; Reeves and Penkett, 2003).

126: the instrument measures ROOH as well as H_2O_2, and I would have expected the ROOH data to be brought into the analysis, in particular as diagnostic of fresh convective injection and chemical aging in the upper troposphere. This seems like a missed opportunity.

The ROOH data are measured as a sum of the different species, and a detailed characterization of each sampled organic peroxide compound using the measurement technique is not possible. Given a TMU of 40% as stated in the work, the data lacks further relevance to reliably quantify any convective injection or chemical aging of hydrogen peroxide in the upper troposphere.

201: H_2O_2 has a lifetime of days and therefore cannot be assumed to be in instantaneous PSS. PSS would have to be calculated over a 24-h diurnal cycle with periodic boundary conditions.

We agree with the referee on the extended H_2O_2 lifetime in the troposphere. Nonetheless, as discussed above, the presented calculations under PSS conditions are of local character and serve exclusively to identify the atmospheric regions, where observed hydrogen peroxide levels deviate from the expectations.

207: what would be the 'other gases producing H_2O_2'? According to current knowledge HO_2+HO_2 is the only source.

We apologize for the confusion. Former L207 was removed from the work according to the referee's comment.

222: what does 'supplement' mean? It is not clear to me if HO_2, OH, and JH_2O_2 come from the measurements or from the model.

We apologize for the confusion due to the wrong choice of words. The results generated by the model EMAC were compared with the observations in order to analyze the accuracy of the model's performance, especially regarding non-photochemical processes in the troposphere.

L236 (former L221): For the purpose of the present study, we used measured H_2O_2, OH, HO_2, water vapor, $j(H_2O_2)$, temperature, and pressure and compare these with the concurrent spatially interpolated EMAC simulations. To synchronize the time resolution of the simulated data with the measurement output, we calculated a mean of the measurement data with a matching temporal resolution of 6 min (equivalent to model output).

244: why continental? Couldn’t it be marine?

L259 (former L244) was changed according to the referee’s comment.

L259 (former L244): These maxima are most likely due to atmospheric transport of H_2O_2 into the upper troposphere.

259-263: SONEX was also in the fall when H_2O_2 would be lower. The authors may be right that the higher values in ATom (not just ‘slightly’) could be due to lower-altitude sampling but that would affect the other campaigns as well that used the NASA DC-8. It would be good to show the vertical profiles (Figure 6) earlier in the paper to make that point.

We thank the referee for the comment. Since, as mentioned in Sect. 3.5, the vertical profiles are restricted to the take-offs and landings at the base of operation at Sal, the shown vertical trends serve rather the purpose of the comparison between the observations and the EMAC simulations as well as to point out in detail, where deviations from the PSS are expected in the sampled region at the base of operation. Surely the trends in deviations are expected to be quite different especially in the southern part of the domain, where the air masses are known to be highly impacted by biomass burning emissions, as can be seen in the plots accounting the whole data set (e.g. below 8 km of altitude).

267-268: ‘hydrogen peroxide in the upper troposphere seem to be far less dependent on latitude than those at lower altitudes’. I don’t see the evidence for this. The lack of latitudinal gradient here is likely because the campaign was in summer.

As described in Sect. 2, the measurement flights were performed between August and September, not in the summer alone. Additionally, the campaign took place over the tropical Atlantic, which by means of the region and the meteorology does not show important seasonal dependencies. The main seasonally driven difference would apply to measurements in the boundary layer and the free troposphere in the southern hemisphere due to differences in biomass burning emissions. Nonetheless, as the works clearly shows, there is no evidence of biomass burning emissions affecting hydrogen peroxide levels in the upper troposphere in the ITCZ and towards the subtropics.

291: shouldn’t ‘decreasing’ be ‘increasing’?

We apologize for the confusion. L307 (former L291) changed according to the referee’s comment.

L307 (former L291): With decreasing latitude, the model tends to significantly overestimate hydrogen peroxide; H_2O_2(EMAC)/H_2O_2(measurement) ratios are increasing from approximately 2 to 4 with decreasing latitude.

293: why would EMAC underestimate cloud scavenging? That’s generally not considered an issue in the upper troposphere where precipitation is infrequent.

Fig. 4 as well as in Fig. S2, present the respective information regarding the presence of clouds in the upper troposphere. Since generally the clouds are highly variable and complex and may consist of ice and supercooled liquid water, an uptake of hydrogen peroxide in all type of clouds should be assumed. In fact, to our knowledge, there is so far no evidence for hydrogen peroxide scavenging exclusively within the rain or liquid water phases of the clouds. H_2O_2 could be temporarily or permanently absorbed by ice particles in clouds as well.
As discussed further in the work L379 – 390 (former 365 – 384) and L426 – 428 (former L414 – 416) due to the rather minor differences between the measured and simulated H_2O_2 precursors (HO_2, OH and $j(H_2O_2)$), we assume the chemistry and photolysis not to be the major reason for the deviations between the model and the observations. From our past analyses we have learned that EMAC has difficulties to accurately simulate cloud scavenging (Klippel et al. 2011; Hottmann et al. 2020; Hamryszczak et al. 2022).

L309 (former L293) was changed.

L309 (former L293): Locally, most likely due to underestimated cloud scavenging as will be further discussed in this work, EMAC simulates highly elevated hydrogen peroxide with a factor of up to 14 in excess of the measurements (4.5°N, -9.5°E).

389: the departure from PSS seems to be only above 12 km. Is this because deep convective outflow was above that altitude? It seems from the comparison with the EMAC vertical profile that EMAC may release outflow at 10-12 km and thus underestimate the depth of tropical convection, which is a common problem in models.

That is correct. As discussed in L423 – 426 (former L411 – 414), the increased H_2O_2(EMAC)-to-H_2O_2(measurement) ratio, which is based on observed and simulated H_2O_2 levels, might indicate the simulated depth of the convective outflow in the model at 10 – 12 km.

404-405: if deposition is important below 2 km, how come PSS underestimates observations there?

As discussed in the work (L429 – 435, former L417 – 423), the comparison of the vertical profiles indicates a missing source or an overestimated sink below altitudes of 5 km. The difference between the measured and calculated mixing ratios can be associated with air masses affected by Saharan dust, which were often sampled during take-offs and landings at Sal. Due to deposition of HO_2 on desert dust particles, the production term of PSS-H_2O_2 (Eq. 2) is affected and thus, the PSS calculation underestimates the levels of hydrogen peroxide relative to the observations (Eq. 6).

423: I thought HO_2 was directly measured? In any case, this dust uptake explanation would not help explain the PSS underestimate in the MBL.

As described in the experimental Sect. 3.2, HO_2 was measured using a laser-induced fluorescence-based method (LIF; additional chem. conversion for HO_2) with the instrument HORUS. Fig. S7 presents a direct comparison between the measured HO_2 and PSS-based HO_2 calculated using the observed levels of H_2O_2. As stated above, HO_2 was most likely removed by deposition on dust particles, which affects the production term of PSS-H_2O_2 (Eq. 2, 6). Based on the decreased mixing ratios of HO_2 up to 5 km altitude relative to the PSS-HO_2 a direct correlation with the underestimation of H_2O_2 under PSS conditions can be assumed. Here, the production of H_2O_2 is underestimated relative to the measurements due to decreased levels of HO_2.

431: Figure 7 doesn't seem to add anything.

Figure 7 displays the local absolute amount of excess or lost H_2O_2. The presented spatial resolution indicates the imbalance between the sources and sinks and the respective regions, where processes of non-photochemical origin are impacting the budget of H_2O_2. The calculated excess hydrogen peroxide levels quantify the impact of transport processes due to convection in the ITCZ and due to the subsequent redistribution towards the subtropics. Further the estimated levels show the amount of H_2O_2, which is missing due to cloud scavenging on a local scale, where enhanced presence of clouds was observed (Fig. S2).

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