Comment on acp-2022-693
Anonymous Referee #2

Referee comment on "Hydrogen peroxide in the upper tropical troposphere over the Atlantic Ocean and western Africa during the CAFE-Africa aircraft campaign" by Zaneta Hamryszczak et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-693-RC2, 2022

This paper presents results from the CAFÉ-Africa aircraft mission, focusing on the measurements of hydrogen peroxide (HOOH). HOOH is an important species that controls or is an indicator of the oxidative capacity of the troposphere. The authors compare the observed HOOH with global chemistry models and with photochemical calculations using the observations made during the flights. This is an important paper for the observations, but the model-measurement evaluation is confusing and not insightful. There are a lot of confusing comparisons and speculation. It needs some cleanup. The authors should come up with one or two major points and support them.

What is missing here is some idea of the variability of HOOH in the upper troposphere. We are shown 6 min averages binned into 2-degree latitude blocks (Fig. 3). The figure below shows all the ATom measurements of HOOH (from the 10s merged data) as a function of latitude. These are ~10,000 points and only include data above 8 km (comparable to the CAFÉ data here). The mean/median value of the points is 105/82 ppt. This is consistent with CAFÉ results (Fig. 2) but the large scatter, but with many (>10%) above 200 ppt indicates recent convective sources at almost all latitudes at some time or another (warning, this is all the 4 ATom deployments). It is hard to see a latitudinal pattern except for the much higher baseline values between 10S and 20N).

Figure: HOOH (ppt) vs. latitude. ATom-1234, above 8 km, Atlantic basin
L15: I would not describe this as a "uniform latitudinal distribution" from either Fig 3 or the ATom data. There are clear hot spots at several latitudes. Admittedly there is no clear latitudinal gradient from 40S-40N.

L19-20: This is too simple and wrong. I see in Fig 3 values > 1 at 25N and 30N. Likewise values <<1 are scattered all over including near the ITCZ (which is not that well defined). The question is: Are all the ratios > 1 associated with recent deep convection. Your pattern in Fig 3 seems patchy.

L21: are there not some <1 squares here?

L23: You talk about scavenging of HOOH but there is no evidence here to show it. What I read is that deep convection brings up high values of HOOH that are above the local PSS values, and that over time (How much time??) these go back to PSS. What this work does not explain is how this ratio drops below 1 for many palaces. Scavenging is not possible as there is no liquid water clouds up here. Perhaps our PSS model is wrong?

L25: I am not sure the "north and south" here is correct, the spreading of convective outflow could be east-west also.

L29: I would not call this 'uniform' but rather that it showa no clear gradient with latitude.

L30: I do not see how you can attribute this just to underestimated loss instead of overestimated production. The lifetime of HOOH up here is how long (about 2 days?) and you calculate PSS values based on instant measurements – what is the error/uncertainty in this? Your comparison with PSS misses out on the transient response.

Abstract: Overall, the abstract could be improved, and made to summarize the facts of the observations and then the surmises of the authors when comparing with models (PSS or EMAC).

I cannot easily understand what the authors have discovered from CAFE-Africa from this abstract.
L50: where is the heterogeneous cloud loss (wet scavenging at least?)

L56: the missing question is what is the HOx source > 8 km, OH is not mainly from HOOH, or is it? We know it is not acetone any more, but what else? O1D + H2O is operating, but ore slowly.

L59: not all wet scavenging leads to deposition, it can be released by virga, e.g.

L63a: Agreed, this is what ATom shows for the tropical Atlantic – but in models, part of this comes from the maximum in OH production (and hence HO2) above the MBL (950 hPa) because of clouds (Spivakovsky et al., 2000).

L63b: This only applies here to > 8km, and the previous sentence talks about 2-5 km and the MBL.

L79: 'might' to 'is expected to...'

L83: correct, what we are missing here is the 'vertical distribution'

L93: What does 'mean values' here refer to? The comparison with ATom here is odd. Why did you only compare with the Aug and Oct deployments? This is a tropical measurement and the seasonal differences are small and mostly related to variations around ITCZ or major biomass burning layers. I did a quick sampling of the ATom 1234 deployments over the tropical Atlantic above 8 km. There are about 1,000 10s points in each sample. I do not understand how your 'mean values' range from 0.05 to 0.25 ppb. The Allen et all. 2022 paper has mean and median tables, but their values for the Atlantic are much higher because they are not limited to >8km.

<table>
<thead>
<tr>
<th>20S-20N</th>
<th>Atom-1</th>
<th>ATom-2</th>
<th>ATom-3</th>
<th>ATom-4</th>
<th>Here (all Latitudes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean (ppb)</td>
<td>0.14</td>
<td>0.14</td>
<td>0.09</td>
<td>0.12</td>
<td>0.18</td>
</tr>
</tbody>
</table>
L113: 'probed area' is odd English usage. Can you give any info on vertical sampling?

L219: Did you check using your EMAC model if eqn6 really does produce the correct PSS when all reactions and missing species are accounted for. This should be an obvious check.

L221: This is odd. Why use EMAC to supplement observations. Then the comparison is corrupted. You need some independence. Also, Why is the data every 6 min when the HOOH is measured every 122 s = 2 min as stated above. These do not add up.

L241: Are the mean and median stats from the 1x1 degree averages? or from each measurement? This is not clear.

L243 – locally up to 0.67 ppb means what? You found one 122s observation with 0.67 ppb? [restricted to > 8km).

L263: Good point. If you flew at 15 km most of the time, the HOOH should be smaller. What is your sampling profile? The profile in Fig 3 is probably semi-uniform vertical sampling since it is limited to the LTO cycle above your airport. What are the densities for the rest of the observations?

L264: Agreed.

L266-269: This is an excellent way to express your 'latitude findings' rather what you have in the abstract. I am not sure they are dependent on latitude in the lower latitudes as tied to convection.

L290-291: I do not see this in Fig 3b at all. The for > 20N, the model:obs ratio varies from <0.3 to >3. How is this 'good'.

L293: I do not believe the cloud scavenging bit – it is totally speculation. It could also be
that EMAC has the wrong chemistry or photolysis. It might be scavenging, but really it could be anything.

L295: This is weird because one would have expected that Florence would have brought up lower HOH that was far from local PSS. Can you explain this?

L303: Yes, whichever side of PSS (high or low) one would expect that recent convection would NOT be in PSS. This is written incorrectly – the local PSS may be the only current P's and L's; but the amount deposited by convection is not in PSS. This section needs to be clarified.

L308-Fig4. I am not sure we get much from this that we did not see in Fig.3. It is close to the same information.

Try 'sampled' instead of probed.

L348: This trend with latitude is meaningless, I am not sure how it is calculated but it does NOT look like the PSS curve in Fig.5. Also, what does it mean?

I find this whole section up to L393 to be opaque, too much detail, and not convincing

L364: EMAC must be correct at all altitudes, particularly the convective source region. You cannot and do not address this issue. Did EMAC get the correct profile? why not compare with the Allen 2022 profiles of HOOH?

L408: These are the sub-tropical profiles at 23N, not in the region where deep convection comes from. Where are the comparisons of OH and HO2 profiles? Also, even at 23N EMAC shows the wrong profile with a peak ~ 1.5 km instead of 3 - 5km as observed. This is not great performance.

L426-427: Fig.7 excess mole fraction of HOOH w.r.t. PSS does NOT tell me transport rates.

L462: Correction – the ATom HOOH shows small latitudinal differences. However, the figure above is not published, so at least be specific as to which observations show a large latitudinal gradient.
Overall, this paper contains some reasonable conclusions, but spends too much time on weak points like the EMAC comparison.