

**Answer to:**

**Interactive comment on “Impact of the South Asian monsoon outflow on atmospheric hydroperoxides in the upper troposphere” by Bettina Hottmann et al.**

**Anonymous Referee #1.**

(black: RC, red: AC, blue: changed in manuscript)

This study presents observations of hydroperoxides during an aircraft campaign investigating the outflow of the south Asian summer monsoon and how it affects the composition of the Asian Monsoon Anticyclone (AMA). The observations of H<sub>2</sub>O<sub>2</sub> and ROOH are enhanced in the AMA, which the authors suggest is due to convective transport of these species. The authors compare these observations to steady state calculations constrained by observed OH, HO<sub>2</sub>, and photolysis frequencies as well as to the results of the EMAC global model. I have three major concerns regarding this study, which I summarize below, followed by more minor comments.

Major concerns:

*1) The inferred UHP is taken as the difference between measured ROOH and PSS MHP. The basis for this is not clear to me, as it assumes that MHP is accurately simulated by the PSS calculations. Given that the PSS H<sub>2</sub>O<sub>2</sub> calculation underestimates observed H<sub>2</sub>O<sub>2</sub> by a significant amount (up to a factor of 10!), there is no reason to believe that the PSS MHP doesn't suffer from the same problem. I found the use of UHP to be very confusing as it sometimes referred to as PSS UHP or calculated UHP or observed UHP. Given that what is measured is H<sub>2</sub>O<sub>2</sub> and ROOH, I suggest that the authors only use these two quantities throughout the manuscript and compare them to PSS H<sub>2</sub>O<sub>2</sub>, PSS MHP, EMAC H<sub>2</sub>O<sub>2</sub>, EMAC ROOH, thus removing any use of UHP.*

We are sorry for the confusion. As mentioned in the experimental section, the ROOH measurement is unspecific and due to the different solubilities of hydroperoxides only qualitative. In order to estimate the amount of MHP, which according to previous measurements is expected to be the dominant (if not the only) ROOH component, we calculated the amounts of MHP from a photo-stationary state calculation (as well as H<sub>2</sub>O<sub>2</sub>). The difference between ROOH and PSS MHP is unexplained or unaccounted for, thus we named it UHP. As discussed in the paper UHP can be due to an unidentified hydroperoxide (e.g. PAA), additional MHP due to advection or a combination of both. Since no specific ROOH measurements were made nor does the 3D-model indicate substantial amount of hydroperoxides other than MHP, we cannot finally decide on the nature (or composition) of the UHP. In the revised manuscript, we will more clearly define UHP and follow the referee in using PSS H<sub>2</sub>O<sub>2</sub>, PSS MHP, EMAC H<sub>2</sub>O<sub>2</sub>, EMAC ROOH in addition to EMAC MHP. Nevertheless we would still like to use UHP in the sense of an unaccounted for hydroperoxide either as additional MHP (exceeding PSS MHP) and/or a significant contribution by an organic hydroperoxide not simulated in EMAC (e.g. PAA).

Section 4.3.2 changed to:

Figure 14 shows histograms for the comparison between H<sub>2</sub>O<sub>2</sub>, MHP and UHP observations with EMAC simulations. Hydrogen peroxide simulations from EMAC cover a broader range of mixing ratios for both NH background (6 pptv up to 576 pptv) and AMA (8–714 pptv) compared to observations (NH background: 20–301 pptv; AMA 46–446 pptv). For the SH model simulations and observations indicate almost identical ranges of 15–409 pptv and 85–510 pptv, respectively. Median EMAC-H<sub>2</sub>O<sub>2</sub> values are similar for NH background (66 pptv) and AMA (71 pptv) conditions (Table 2), while observations indicate an enhancement of +64 pptv in the AMA relative to the NH background. For the SH the model simulated H<sub>2</sub>O<sub>2</sub> mixing ratios are four times higher than in the NH background (272 pptv), while the observations only show a median increase by 47 pptv to 211 pptv (Table 2).

EMAC mainly simulates MHP mixing ratios lower than 50 pptv for background and AMA, while PSS-MHP ranges from LOD–140 pptv. Again the model simulates highest MHP mixing ratios in the SH with values up to 502 pptv compared to up to 346 pptv in the PSS-MHP calculations. Similar as for H<sub>2</sub>O<sub>2</sub>, medians of EMAC-MHP for NH background and monsoon conditions are almost identical (11 pptv and 13 pptv respectively, Table 2) in the model simulations, while the observations show a small difference towards higher mixing ratios in the AMA (64 pptv and 70 pptv, respectively). In the simulations, southern hemispheric EMAC-MHP mixing ratios are almost ten times higher than NH background values, compared to two to three times higher ones in the observations.

Data for UHP in the model are calculated from the sum of simulated ethyl hydroperoxide (EHP) and peroxyacetic acid (PAA), which are the only non-methyl organic hydroperoxides in the free troposphere according to the model. EMAC-UHP mixing ratios range from 1–238 pptv in the NH background, 1–259 pptv in the AMA and 1–132 pptv in the SH. PSS-UHP based on the observations indicate lowest mixing ratios in the NH background (LOD–261 pptv), while in the AMA and the SH the ranges are quite similar (80–311 pptv and LOD–334 pptv). A comparison of median values emphasizes the large difference between model simulations and observation-based estimates. In the NH background, the median PSS-UHP mixing ratio from the observations is 70 pptv higher than EMAC simulations (78 pptv and 8 pptv respectively). In the AMA the difference is even larger, with about 200 pptv higher PSS-UHP levels compared to the EMAC simulations. The smallest difference with a factor of four was found for the SH (Table 2).

*2) Throughout the manuscript (including the abstract and conclusions) the comparisons between observations and model results (both PSS and EMAC) are described in very vague and qualitative terms (such as “observed concentrations are higher than model calculations”, “the model underestimates H<sub>2</sub>O<sub>2</sub>”, etc. . .). This lacks rigor and leaves the reader unsure about the magnitude of the misrepresentation of the models. I strongly encourage the authors to be more quantitative in their comparisons throughout the manuscript, using statistical measures, which could include mean bias, normalized mean bias, FAC2, RMSE, etc. . . The figures and tables should include these statistical measures.*

We added the ranges, averages and standard deviations for the in-situ and PSS comparison (Table 1). In addition we added more statistical information in table 2 (former table 1). The abstract as well as conclusion were changed so that they are more quantitative.



NH background	median range avg±sdev	66 6–576 102±110	100 20–301 110±53	11 2–408 28±58	64 21–202 75±42	8 1–238 18±31	78 LOD–261 103±77
monsoon	median range avg±sdev	71 8–714 84±92	164 46–446 167±69	13 2–216 18±28	70 37–220 92±49	12 1–259 18±34	208 80–311 199±59
SH background	median range avg±sdev	272 15–409 272±68	211 85–510 238±105	116 2–502 155±125	152 40–346 191±95	33 1–132 42±24	122 LOD–334 125±102

Title of Fig. 13 changed to: “Figure 13: Histograms of measured (top) and calculated (bottom) H<sub>2</sub>O<sub>2</sub> mixing ratios (bars) and the associated medians (lines).”

3) *The authors suggest that deviation between EMAC and observed H<sub>2</sub>O<sub>2</sub> and ROOH are due to uncertainties in the scavenging efficiencies of these species in the model. As described in line 430 “..sensitivity study with EMAC excluding scavenging”. This sentence seems to suggest that scavenging of all species is turned off, which seems like a rather brute force method as lack of scavenging of other species could in turn affect the photochemical evolution of H<sub>2</sub>O<sub>2</sub> and ROOH. A simulation in which scavenging of only H<sub>2</sub>O<sub>2</sub> and ROOH is turned off seems more appropriate. Also, is scavenging turned off only for the AMA region or the entire globe? If it is for the entire globe, then the difference between the simulations might not be related to processes associated with convection over India. It seems that the link between convection and peroxides could be investigated more carefully with EMAC, including a more targeted sensitivity simulation, and also examining correlations of modeled peroxides and NO/NO<sub>y</sub> ratio as well as acetone. Also, the authors do not discuss how well convection is represented in the model in the first place. For example how well does EMAC reproduce observations of species that are not scavenged (such as CO or some VOCs)?*

- CO in the upper troposphere is lower in EMAC due to weaker convective transport (possibly caused by the low resolution of the global model) as described in Tost et al. (2016) and Tomsche et al. (2019).

Tost, H., Jöckel, P., and Lelieveld, J.: Influence of different convection parameterisations in a GCM, *Atmos. Chem. Phys.*, 6, 5475–5493, <https://doi.org/10.5194/acp-6-5475-2006>, 2006

-As described in Klippel et al., scavenging of all soluble species was turned off in the model, not only for the Indian sub-continent. Since the purpose of the sensitivity study is to calculate the maximum amount of H<sub>2</sub>O<sub>2</sub> that can be transported into the AMA, we believe that this is justified. Simultaneous wash-out of other soluble species (HNO<sub>3</sub>, organic acids etc) will not directly affect H<sub>2</sub>O<sub>2</sub> but might change HO<sub>x</sub> levels, thus affect H<sub>2</sub>O<sub>2</sub> through secondary chemistry. Also convective addition of H<sub>2</sub>O<sub>2</sub> in other regions (e.g. the West African Monsoon) will hardly affect H<sub>2</sub>O<sub>2</sub> levels in the AMA due to the limited lifetime of H<sub>2</sub>O<sub>2</sub>.

*Minor Comments*

*Sections 3.3, 3.4: Can the authors indicate the lifetimes of H<sub>2</sub>O<sub>2</sub> and MHP during flight conditions? This will be useful to assess the validity of the PSS assumption. In particular, the validity of PSS will also depend on time of day/SZA. For what conditions do the authors apply PSS?*

The lifetime of H<sub>2</sub>O<sub>2</sub> is around 4 days and MHP around 1 day. Major losses are the reaction with OH and photolysis by sunlight. No special conditions were applied to the calculations as the aim was to estimate local photochemistry. Measurements were only performed during daytime.

*Line 258. The authors mention that the data were averaged in 60 second intervals. It wasn't clear from the description what the frequency of the measurements were, in particular for H<sub>2</sub>O<sub>2</sub>, ROOH and the species used to calculate PSS.*

Data are from merged data sets which were calculated from the original data that were recorded with a higher resolution. For H<sub>2</sub>O<sub>2</sub> and ROOH we record 1 value per second, TRISTAR (CH<sub>4</sub> and CO) appr. 1 per second, OH and HO<sub>2</sub> appr. 4 per minute, NO and NO<sub>y</sub> 1 per second, J values 1 value per 1 or 2 seconds.

Changed to:

L272: Data were collected from a merged data set given as 60-second-means (calculated from the original data set obtained at higher resolutions) in order to get the same time resolution for all compounds.

*Figure 2. Can the authors indicate the number of days for which the back trajectories were calculated?*

Ten day back trajectories were used.

The title of the figure is changed to:

Figure 2: Track of flight 17 (black dotted line) and calculated 10-day-back trajectories (lines colored as a function of altitude) to show the origin of sampled air masses during the flight.

*Figures 3. It is unclear why the authors show the data on the timescale of the EMAC model, given that in the text (line 263) the authors say that the model was interpolated in time and space along the flight track. Given that the observations are likely available at a higher time resolution as can be seen in Figure 4, it might make more sense to show the observations at their original time resolution instead of the much coarser 10-15 minute resolution of EMAC.*

EMAC results are obtained at a temporal resolution of 12 min and spatial resolution of 2.8° x 2.8°, and interpolated in space along the flight track. Therefore, any interpolation to higher time resolution of this dataset would not provide any added value.

Changed to:

L253: For this study EMAC simulations were performed for the OMO flight tracks in 2.8°x2.8° grids with a time resolution of 12 minutes.

*Figures 6&7 (as well as Figures 10&11) and lines 295-3050. The authors discuss the correlation of UHP with acetone and NO/NO<sub>y</sub>, without mentioning the correlation with the other peroxides. First, given that*

*UHP is inferred based on the PSS calculation, it would make more sense to use observed ROOH. Also, based on looking at Figure 4, it seems that H<sub>2</sub>O<sub>2</sub> might also be correlated with acetone and NO/NO<sub>y</sub>. Correlations (or lack thereof) with H<sub>2</sub>O<sub>2</sub> should be discussed in the text.*

Following the suggestion, we have provided the requested relations. Please note that a positive correlation not necessarily indicates a relation to a precursor. It can also indicate a co-location of sources.

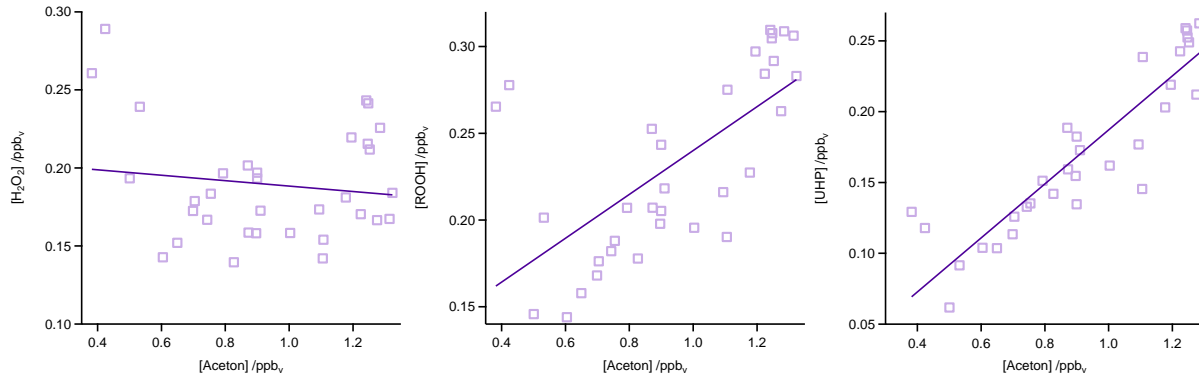
Section changed to:

L311: The PSS-UHP and acetone mixing ratios in this part of the flight are strongly correlated (Figure 6), with a slope of  $0.19 \pm 0.02$  (ppbv/ppbv) and an offset of  $(-0.003 \pm 0.02)$  ppbv. The regression coefficient  $R^2$  is very high (0.99). For H<sub>2</sub>O<sub>2</sub> and ROOH the correlation is not that strong with slopes of  $-0.02 \pm 0.02$  (ppbv/ppbv) and  $0.13 \pm 0.03$  (ppbv/ppbv), respectively, and offsets of  $(0.21 \pm 0.02)$  ppbv and  $(0.11 \pm 0.03)$  ppbv (Figure 6). The relation between ROOH mixing ratios and an air mass age tracer based on the ratio between [NO] to [NO<sub>y</sub>] shows higher values of ROOH at smaller ratios representing older or more processed air masses (Figure 7), since highest ROOH mixing ratios (>200 pptv) are found at the lowest [NO]/[NO<sub>y</sub>] ratios (all <0.19). Thus, most of the observed ROOH was measured in aged air masses transported within the anticyclone. The correlation with PSS-UHP shows that this effect is mainly due to PSS-UHP. For H<sub>2</sub>O<sub>2</sub> there are also some higher mixing ratios for high [NO] to [NO<sub>y</sub>] mixing ratios and thus fresher air (Figure 7).

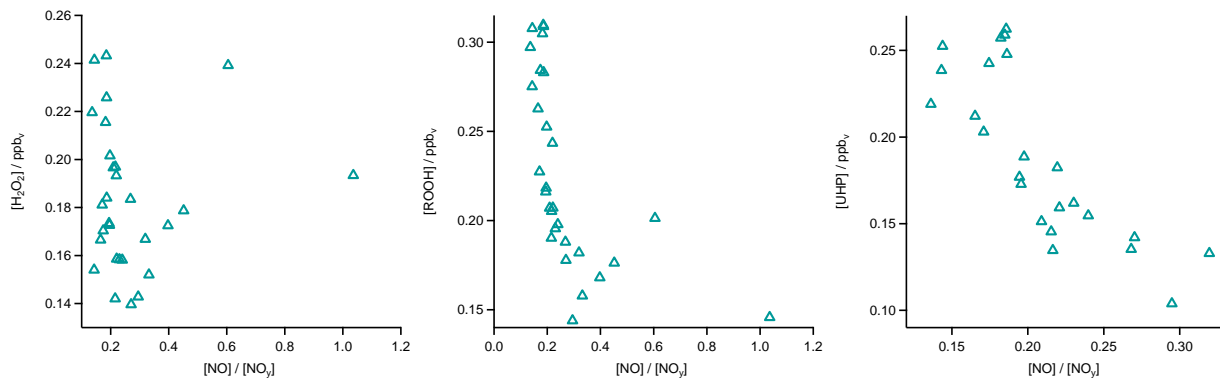
Section changed to:

L344: In the analysis of flight 17 we found a strong correlation between PSS-UHP and acetone (Figure 6) and an increase of PSS-UHP at the oldest air mass ages, represented by low [NO]/[NO<sub>y</sub>] (Figure 7). Extension of this analysis to all observations in the upper troposphere obtained during OMO yields similar results for the relation between PSS-UHP, in situ ROOH and in situ H<sub>2</sub>O<sub>2</sub> and acetone (Figure 10). Enhanced mixing ratios of hydroperoxides are typically associated with enhanced acetone mixing ratios, especially for PSS-UHP. A simple calculation of the production of MHP out of the photolysis of acetone and the reaction of acetaldehyde (from EMAC) with OH shows that per day appr. 40 pptv MHP can be formed within the AMA. The lifetime of MHP was calculated to be around 1.5 days. Thus not all of the PSS-UHP in the AMA (median 210 pptv) can be accounted for by MHP that was chemically produced from VOCs in the AMA. The scatter plots of the hydroperoxides vs. [NO]/[NO<sub>y</sub>] for the whole data set, show no clear correlation with a large spread of hydroperoxides mixing ratios at the lowest [NO]/[NO<sub>y</sub>] ratios, representing the oldest, i.e. chemically most processed air masses (Figure 11).

Figures 6 and 7 changed to:

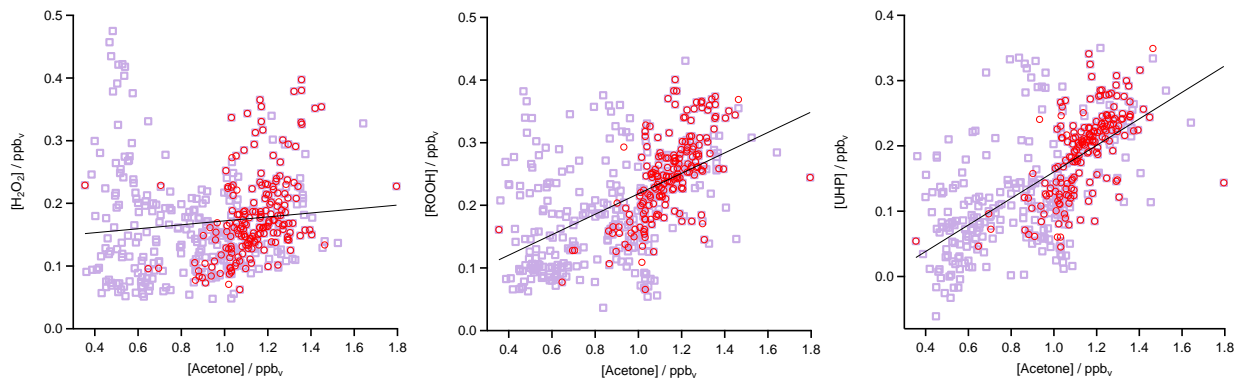


**Figure 6:** Scatter plots of measured acetone and in situ H<sub>2</sub>O<sub>2</sub> (left), in situ ROOH (middle) and PSS-UHP (right) during flight 17. The black lines represent the least orthogonal distance fits with regression coefficients of 0.99, 0.98 and 0.99.

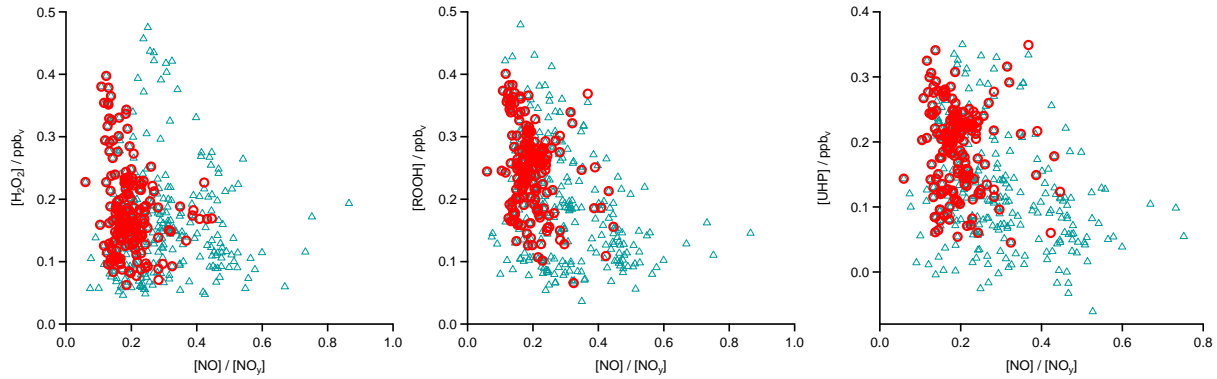


**Figure 7:** Scatter plots of in situ H<sub>2</sub>O<sub>2</sub> (left), in situ ROOH (middle) and PSS-UHP (right) and NO/NO<sub>y</sub> ratio during flight 17.

Figures 10 and 11 changed to:



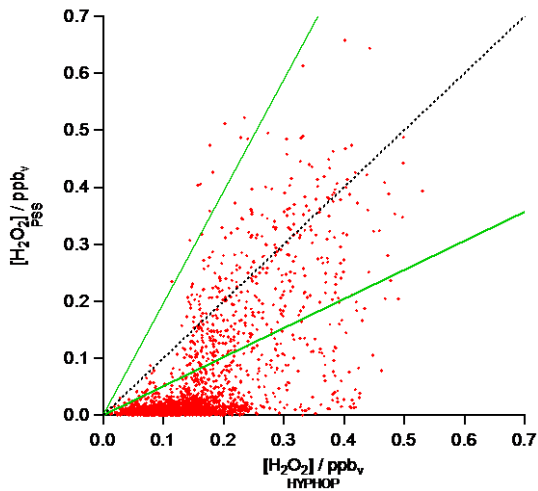
**Figure 10:** Scatter plots of in situ acetone and in situ H<sub>2</sub>O<sub>2</sub> (left), in situ ROOH (middle) and PSS-UHP (right) in the UT (purple squares) and especially in the AMA (red circles). The black lines represent the least orthogonal distance fit with linear regression coefficients of 0.96 (H<sub>2</sub>O<sub>2</sub>), 0.97 (ROOH) and 0.96 (UHP).



**Figure 11: Scatter plots of NO/NO<sub>y</sub> and in situ H<sub>2</sub>O<sub>2</sub> (left), in situ ROOH (middle) and PSS-UHP (right) in the UT (blue triangles) and especially in the AMA (red circles).**

Line 336 “The deviations from unity in the slope are within the combined uncertainties of measured and steady-state estimations of H<sub>2</sub>O<sub>2</sub> (51%, 1  $\sigma$ )” Looking at Figure 12, it looks like most points are outside the +/- 51% range. Can the authors be more quantitative and state the number of points outside the uncertainties?

82% of points are outside the range of the uncertainties of  $\pm 51\%$ .



Section 4.3.2 In the comparison to EMAC, the authors tend to focus on the range of modeled and observed values, which is not very informative. It would be more useful to discuss means or medians and provide statistical measures of the model/observations mismatch (such as mean bias, mean normalized bias, mean normalized gross error, etc. . .). Also to put the comparison of EMAC to peroxides in perspective, it would be useful if the authors could discuss the comparisons to other tracers (acetone, O<sub>3</sub>, H<sub>2</sub>O, CO, NO<sub>x</sub>, NO<sub>y</sub>, aerosols, etc. . .), which might shed light on whether the mismatch is an issue related to emissions, transport, scavenging, or chemistry.

Table 2 was changed (see above). In addition we want to refer to Lelieveld et al., 2018 where a detailed comparison of observed and modelled data is shown.



Line 379. Many other studies before Bozem et al. (2017) have shown the role of deep convection as a source of peroxides in the upper troposphere, including Prather and Jacob (1997), Jaeglé et al. (1997), Mari et al. (2002) among others.

Line 404 (former 379) was changed to

In contrast, other studies found that deep convection can be a source of H<sub>2</sub>O<sub>2</sub> in the upper troposphere (e.g. Jaeglé et al., 1997; Prather and Jacob, 1997; Mari et al., 2003; Bozem et al., 2017).

Lines 386-390. The authors fail to mention the very large underestimate of EMAC ROOH compared to observations.

Here we focus on the qualitative analysis of the longitudinal gradients and thus on the trends along the longitude. Including the additional information, the difference between in situ data and the EMAC model is discussed quite elaborately now.

References:

Jaeglé, L., et al.: Observed OH and HO<sub>2</sub> in the upper troposphere suggest a major source from convective injection of peroxides, *Geophys. Res. Lett.*, 24, 3181–3184, <https://doi.org/10.1029/97GL03004>, 1997.

Mari, C., et al., On the relative role of convection, chemistry, and transport over the South Pacific Convergence Zone during PEM<sup>2000</sup> RTropics B: A case study, *J. Geophys. Res.*, 107, 8232, doi:10.1029/2001JD001466, 2002. C4 ACPD Interactive comment Printer-friendly version Discussion paper Prather, M. J. and Jacob, D. J.: A persistent imbalance in HO<sub>x</sub> and NO<sub>x</sub> photochemistry of the upper troposphere driven by deep convection, *Geophys. Res. Lett.*, 24, 3189– 3192, <https://doi.org/10.1029/97GL03027>, 1997. Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2020-93>, 2020.