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Atmospheric Chemistry and Physics Discussions

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

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This study presents observations of hydroperoxides during an aircraft campaign investigating the outflow of the south Asian summer monsoon and how if affects the composition of the Asian Monsoon Anticyclone (AMA). The observations of H2O2 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, HO2, 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.

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Discussion paper

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 H2O2 calculation underestimates observed H2O2 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 H2O2 and ROOH, I suggest that the authors only use these two quantities throughout the manuscript and compare them to PSS H2O2, PSS MHP, EMAC H2O2, EMAC ROOH, thus removing any use of UHP.

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 H2O2", 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.

3) The authors suggest that deviation between EMAC and observed H2O2 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 H2O2 and ROOH. A simulation in which scavenging of only H2O2 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/NOy 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)?

Minor Comments

Sections 3.3, 3.4: Can the authors indicate the lifetimes of H2O2 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?

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 H2O2, ROOH and the species used to calculate PSS.

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

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.

Figures 6&7 (as well as Figures 10&11) and lines 295-3050. The authors discuss the correlation of UHP with acetone and NO/NOy, 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, nased on looking at Figure 4, it

seems that H2O2 might also be correlated with acetone and NO/NOy. Correlations (or lack thereof) with H2O2 should be discussed in the text.

Line 336 “The deviations from unity in the slope are within the combined uncertainties of measured and steady-state estimations of H2O2 (51%, 1 σ)” 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?

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, O3, H2O, CO, NOx, NOy, aerosols, etc...), which might shed light on whether the mismatch is an issue related to emissions, transport, scavenging, or chemistry.

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.

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

References:

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Prather, M. J. and Jacob, D. J.: A persistent imbalance in HOx and NOx photochemistry of the upper troposphere driven by deep convection, Geophys. Res. Lett., 24, 3189–3192, https://doi.org/10.1029/97GL03027, 1997.

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