

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

Anonymous Referee #2

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The paper describes aircraft measurements of hydroperoxide compounds and supporting observations taken during the Oxidation Mechanism Observation (OMO) mission. These measurements are analyzed alongside photochemical steady state calculations, trajectory modeling, and global model simulations to understand the source regions of the air sampled in the upper troposphere. The major findings are that hydroperoxide mixing ratios are enhanced in the Asian Monsoon Anticyclone (AMA) compared to the background Northern Hemisphere (NH) mixing ratios, but highest hydrogen peroxide (H_2O_2) and methyl hydrogen peroxide (CH_3OOH) mixing ratios were found in the background Southern Hemisphere (SH). The authors attribute the high mixing ratios in the AMA to upwind convection, using a sensitivity simulation with the global model EMAC

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to support this claim.

It is interesting to discover the higher-than-expected hydroperoxide mixing ratios in the Asian Monsoon Anticyclone, and then learn what caused these high mixing ratios. I find that the study provided hints as to the cause of the high mixing ratios, but did not provide complete attribution. The analysis would benefit from conducting box model chemistry calculations to fully understand the processes affecting hydroperoxide mixing ratios. In addition, there are a number of items that need further work as detailed below.

Specific Science Comments

1. The abstract should be more quantitative in their claim about enhancements in the AMA versus NH background. Line 22 states that observations show enhanced mixing ratios for H₂O₂, MHP (CH₃OOH), and UHP (unidentified hydroperoxides) in the AMA relative to the NH background. However, Figure 4 shows perhaps a small enhancement (10-20%) of H₂O₂, which is within the uncertainty (25%) of the measurements and no enhancement of MHP. There is only substantial enhancement (78%) of UHP. More convincing are the histograms in Figure 9 that show median values of H₂O₂ in the AMA to be 55% higher than those in the NH background, but MHP median values are quite similar between AMA and NH background. Again, the UHP median value is clearly enhanced in the AMA.

2. Introduction. Consider adding more information on the flow patterns of the Asian monsoon. A good resource for this information is Lawrence and Lelieveld ACP (2010).

3. Section 3.1 describes the hydroperoxide measurements. The method measures total peroxides which is the sum of H₂O₂, CH₃OOH, and other organic peroxides. The method uses a catalase to destroy H₂O₂ allowing the ability to infer H₂O₂ (i.e., total peroxides minus ROOH gives H₂O₂, where ROOH represents the sum of organic peroxides). ROOH is assumed to be mainly CH₃OOH. To determine CH₃OOH, a photostationary-state chemistry approximation is used based on measurements of OH, HO₂, CO, CH₄, NO, and photolysis rates. It is unclear why it is valid to estimate

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CH₃OOH from photostationary steady-state when the chemical lifetimes of CH₃OOH and H₂O₂ are a few days (as stated on line 381, page 13).

It would be better to describe the measurement technique as measuring total peroxides, inferring H₂O₂, and estimating MHP_PSS with the remaining ROOH being called unidentified hydroperoxides (UHP). Then, when the authors suggest that most of the UHP is CH₃OOH, then they can use MHP without further notation.

4. Lines 295-305. The correlation between UHP and acetone is very strong, but there's no explanation on what the cause and effect may be. I suggest further analysis on this result. Even stating acetone photolysis produces methyl peroxy radical which can react with HO₂ to form CH₃OOH is good, but more interesting would be box model calculations.

5. Section 4.3. I think assuming photostationary steady-state for H₂O₂ and CH₃OOH interferes with the comparisons described in Section 4.3.

a. While, it is useful to point out the large discrepancy between observed H₂O₂ and H₂O₂ estimated by photostationary steady-state, it needs an explanation of why there is such a discrepancy (Lines 333-340).

b. In Section 4.3.2, I do not find it useful to compare the ranges of the observations and EMAC results. For example, EMAC clearly underpredicts CH₃OOH mixing ratios most of the time, but the range of EMAC results overlaps with the observations. It may be better to discuss medians or simply describe that most EMAC CH₃OOH is < 50 pptv for NH background and AMA air, while most observations range from level of detection to 120 pptv.

c. The photostationary steady-state assumption interferes with the comparisons of the MHP and UHP observations with EMAC. If H₂O₂ and CH₃OOH are not in photostationary steady-state, then it would make more sense to compare total organic peroxides between observations and EMAC results. The differences between model results and

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observations need an explanation of why they are different.

d. Shouldn't a conclusion be that assuming photostationary steady-state can be inappropriate?

6. Lines 379-385. This discussion, to me, is not well supported and contains a lot of suppositions. This manuscript is relying on one paper (Bozem et al., 2017) to say H₂O₂ is enhanced in convective outflow regions compared to the background upper troposphere. Yet Bozem et al. (2017) found an unusually high H₂O₂ mixing ratio in convective outflow (1.25 ppbv) which is not found in other studies. Snow et al. (2007) and Barth et al. (2016) both show that H₂O₂ is depleted in convective outflow compared to background upper troposphere. We do not know what H₂O₂ mixing ratios are like in convective outflow near the convection that transports constituents into the AMA, but we can make use of the array of literature from past studies to guide us for what to expect and what further analysis is needed. This leads to my next comment.

7. There will always be some variability in peroxides scavenging efficiencies and uncertainty in these scavenging efficiencies due to the complex processes associated with convection and chemistry. However, there were also 100s km (multiple days) of transit between the convection in northern India and the measurements over the Arabian Sea. What chemistry occurred during this transit? If it is true that the observations are reflecting chemistry in convective outflow, then one would also expect other volatile organic compounds, CO, and CH₄ to have been lofted in the convection. I would recommend conducting a number of box model calculations (e.g. Pickering et al., JGR, 1992; Apel et al., ACP, 2012, etc) to learn what chemical transformations are affecting the peroxides. Further, this box model can more definitively provide information on what unidentified hydroperoxides are.

8. Lines 405-409. I do not think the typhoon Mireille case is suitable to compare to this paper's results. Typhoon Mireille occurred over the Western Pacific ingesting air from Oceania (Preston et al., JGR, 2019) in the early 1990s and not the South Asia region

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of the mid 2010s.

9. I am surprised there is no mention of past literature on peroxides, peroxy radicals and convection and how these current results compare to those previous findings. Some papers to discuss are Jaeglé et al., GRL, 1997, Prather and Jacob, GRL, 1997, Crawford et al., JGR, 1999).

Organization, Clarity, Technical Comments

1. Line 140 should include a list of all species measured. It should state OH and HO₂ instead of HO_x, and include NO.

2. Lines 192-195. Shouldn't pressure and temperature measurements also be listed? These state parameters must be needed for calculating rate constants and air density.

3. Line 209. It would be good to explain why the CH₃O₂ to HO₂ ratio is needed. It would also be good to define P(HO₂) and P(CH₃O₂).

4. Line 217. Why is a scale height needed? Why not use pressure measurements from the aircraft along with temperature to get air density that can then be translated to N₂?

5. Line 221. Isn't there a H₂O dependence to the self-reaction of HO₂? See, for example, JPL (2015). <https://jpldataeval.jpl.nasa.gov/>

6. Line 229. Can you show or quantify the contribution of CH₄+OH and CO+OH to the total CH₃O₂ and HO₂ production, respectively? If the hypothesis is that the higher AMA mixing ratios are due to convective transport, then HCHO, CH₃OOH, and other VOCs will be elevated compared to background mixing ratios and their chemistry may be more important than assumed here.

7. Lines 245-248. What grid spacing is used for EMAC? Perhaps a short summary of the configuration could be given in supplemental material. Further, how do the authors analyzed EMAC output to provide comparisons to aircraft observations? Are the model

results interpolated in time and space to the aircraft location? Or are values from the nearest grid point and model output time (which, I assume, is every hour)?

8. Lines 249-255. What is the procedure when the back-trajectory encounters convection? Does FLEXPART have a means to represent convective transport? Or are the trajectories stop when convection is encountered?

9. Line 253-254. Since methane and its use for identifying AMA air via a threshold value is discussed on these lines, it would be useful to combine the first paragraph of section 4.1 with this information. Or move lines 252-255 to section 4.1.

10. Line 262. It is not clear which species concentrations are binned into 10 pptv segments. Please specify which species.

11. Line 265. “Case study: flight 17” is not very descriptive to the general audience. Consider using a heading that mentions the date and location of the flight.

12. Line 266. There should also be a short description of the flight, again mentioning date, but perhaps adding weather conditions (cloudy anywhere?) and location of the anticyclone, etc. You might want to add this description to section 2.

13. Line 272. → Tomsche et al. (2019) and on line 273, remove (Tomsche et al. 2019).

14. Line 274. State what EMAC time step is. I imagine this is the frequency of model output.

15. Line 279-280. Clarify that it is EMAC model data.

16. Line 282. → last period of the flight at the higher altitude,

17. Line 293. I think it would be better to say “temporal pattern” rather than “evolution” as there is no following an air parcel in time in the figure.

18. Line 318. → is found. Air masses

19. Line 333. → photostationary steady-state

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20. Line 372. It should be degrees E (not O), and please mention the red box in the figure.

21. Line 373. The observations are in orange (not yellow).

Figures and Table

1. Consider putting some figures into one with panels.
2. Figure 2. Please add number of days for back trajectories to caption. It would be helpful to mark each hour (text box of time) along the flight track so one can connect the map to the time series.
3. Figure 3 and others. It would help to say “EMAC modelled” for clarity. And “data-constrained calculated” should be “photostationary steady state calculated”. At least be consistent from figure to figure and figure to text with nomenclature.
4. Figure 4. Purple triangles look red in my version.
5. Figures 5, 6 and 7 could be combined. The lilac colored squares should be darker.
6. Figure 8. Please note in the figure caption that you are showing data only at <300 hPa.
7. Figures 10, 11, and 12 could be combined. The lilac colored squares should be darker.
8. Figure 12 figure caption should say “photostationary steady state calculated”.
9. Figure 14 axes labels and legends need to be larger. Please explain what vertical lines are in the caption.
10. Figure 15. Please explain what the red box is in the caption.
11. Figure 16. The photostationary steady state calculated markers are purple not blue.

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12. Figure 17. The MHP mixing ratios look more like pink than purple.

13. Table 1. Are these values from all flights? Please say so in the caption. "calc." is not a good heading. I suggest PSS estimate.

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