Answer to: Interactive comment on "Distribution of hydrogen peroxide over Europe during the BLUESKY aircraft campaign" by Hamryszczak et al.
Anonymous referee #1

Please note the used color code
(black: RC, red: AC, blue: manuscript changes according to RC recommendations)

We thank the reviewer for her/his helpful comments.

Significance:
This manuscript describes airborne measurements of H_2O_2 and CH_3OOH during BLUESKY campaign, and compares the results to common atmospheric model predictions. The study was performed during Covid lockdown in Europe, and thus provides an interesting comparison to research performed previously without lockdown measures.
The manuscript offers an interesting view on the atmospheric peroxide chemistry. The authors seem to be experts in the field of airborne measurements, and the study is performed with previously introduced standard techniques. However, there seems to be some discrepancies with the previous data that could perhaps be caused by instrumental biases, and thus there are several issues I would like the authors to elaborate on, before I can recommend publishing the manuscript.
These concerns are detailed below.

Major comments:
Hydrogen peroxide and organic peroxide are known to decay on steel surfaces, yet the inlet here is made of steel. How much did this inlet system affect the overall results of this study? Is the 0.52 H_2O_2 sampling efficiency related to this fact? Does it account the steel part of the sampling? As the inlet system seems critical for understanding the results, it should be better described. A figure would help.

The inlet system used on the HALO aircraft is described in detail in the paper by Hottmann et al. (2020): Air was sampled from the top of the aircraft fuselage through a forward facing trace gas inlet (TGI) designed as a bypass, consisting of ½'' PFA (perfluoroalkoxy alkanes) tube inside the aircraft with an exit trough a second TGI. From this bypass ¼'' PFA tube with a flow rate of 2 slpm (standard liter per minute) was directed to HYPHOP. To obtain constant pressure at the HYPHOP inlet a constant pressure inlet (CPI) consisting of a dual stage membrane pump (Vacubrand MD1 VARIO SP, Wertheim, Germany) was used. Similar inlet designs were used for the measurement on the Lear-Jet during UTOPHIAN-ACT and HOOVER (Klippel et al., 2011).
Thus, the inlet system does not include any metal surfaces. Sampling losses are affected mainly by the surface of the ¼" PFA tube and the CPI. We assume that the smaller surface of the bypass which is maintained at a high flow has only a minor influence on H_2O_2 inlet losses. Therefore, the inlet efficiency due to losses in the CPI were measured every second day with a gas phase calibration device (for details see our answer to referee 2).

Figure 2: There seems to be very little variation in the obtained values. Is it possible that the instrument was not working correctly? Could you show us the relevant calibration plots, or any other data that shows a time-period where the signal varied considerably?
Additionally, was there a correction term / procedure included to the measurement methodology after the previous flight campaigns, or is the analysis of the peroxides exactly the same between the campaigns? The BLUESKY data seems to consistently report lower H_2O_2 than other campaigns.

As discussed in the manuscript, the enhanced presence of clouds within the middle troposphere and relatively high total precipitation rate can affect the levels of hydrogen peroxide and lead to a general decrease in their latitudinal variability relative to that observed in previous campaigns.
Due to the relatively high difference in the range of the means for each campaign dataset, the variability of the H_2O_2 values during BLUESKY appears to be lower in comparison to previous campaigns. Fig. S3 of the Supplement gives additional insight into the species variability in each tropospheric layer during the campaign with a higher resolution.
An exemplary signal variation during the measurement flight performed on 23.05.2020 is presented below. Please note that the measured mixing ratios of organic peroxides here were not scaled according to the MHP sampling efficiency of 0.6. In order to avoid data loss, the time consuming liquid calibration was performed prior to the take-off.

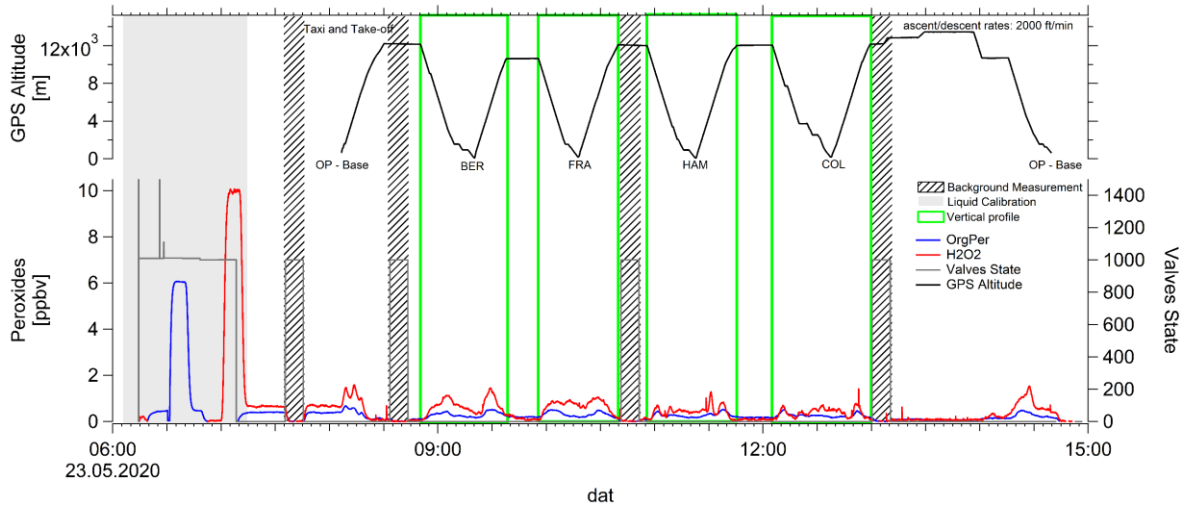

Figure 1: Temporal series of BLUESKY flight #1 performed on 23.05.2020. Data were plotted for observed hydrogen peroxide (red) and unscaled sum of organic peroxides (blue) mixing ratios in relation to altitude (top black). Liquid calibration, background measurements and vertical profiles are highlighted in gray, dashed and green boxes, respectively. Please note that the displayed peroxide data has a temporal resolution of 1 sec.

Additional exemplary signal variations during two flights are presented in Fig. 7a of the manuscript as well as in Fig. S10, indicating variations of H_2O_2 mixing ratios over almost an order of magnitude (0.1 ppbv to 1 ppbv).
The analysis of the peroxide data was performed analogously to previous campaigns. The measurement methods and instrumentation are based on the same principles.

Line 248: Also “intercomparison is dominated by the high variability of the mixing ratios”. They are not apparent from the provided figures. Could you explain what you men with this.

We apologize for the confusion. The mixing ratio means (± 1 sigma) and medians calculated for each campaign subdivided into the main tropospheric layers display a high variability relative to each other, as discussed in detail later in the paragraph. A corresponding overview on estimated means and medians is given in the Table S1 of the Supplement.

Line 254 (former 248) was changed to:

In both lower tropospheric layers (0 – 6 km) the hydrogen peroxide mixing ratios during BLUESKY differed significantly from those measured previously.

It seems from Figure 7a that there was hardly any influence from cloud scavenging or precipitation, as the H_2O_2 time trace is roughly constant, and both hydroperoxide signals significantly increase during the second cloud "scavenging" episode. This seems to be contradictory to what is discussed.
Could you clarify this. Also, it might be that the dimensions of Figure 7a are somewhat too complex (or too reduced?) and reduce its information content. Also, couldn't Fig 7b be interpreted so that the water content actually protects the H_2O_2 as its concentration steadily increases with altitude all the way to the top of the cloud cover, after which it starts decreasing? This is actually even commented by the authors "Previous studies on the possibility of mass transfer of H_2O_2 from rain water to the surrounding air indicate a possible release of hydrogen peroxide to the atmosphere (Hua et al., 2008; Huang and Chen, 2010; Xuan et al., 2020).", but the discussion seems a bit misplaced.

Fig. 7a shows a temporal series of the measurements over Frankfurt, where a vertical profile flight was performed. Please note that high resolution data reported by the instrument are shown. Due to the time resolution of the instrument (90 sec) individual data points are not independent from previous or following data points, leading to slow and small changes, that give the impression of rather constant mixing ratios. During the measurement the aircraft passed the cloud layer during the descending and ascending legs twice. Please note the plotted altitude in the upper part of the figure (black). As mentioned in the introduction of the manuscript the vertical distribution of hydrogen peroxide normally displays a characteristic inverted c-shaped trend. Based on the expected trend, decreasing hydrogen peroxide levels were expected with decreasing flight altitudes, as observed within the measured organic peroxides levels and H_2O_2 simulation by EMAC (blue and black plots in the lower part of the figure). Instead, here the measured hydrogen peroxide levels increased at low altitudes, contrary to the expected distribution.
The rise of hydrogen peroxide levels during the second cloud scavenging episode is due to the ascending character of the flight leg and the corresponding increase in altitude and corresponds with the levels of hydrogen peroxide measured during the descending through the cloud layer.
The levels of hydrogen peroxide within the cloud layer are decreasing with the increasing liquid water content towards the base of the cloud. The striking feature here is more likely the rapid increase of hydrogen peroxide concentrations directly below the cloud, which we assume is due to mass transfer from the falling rain droplets to the surrounding air.

Section 4.3. changed to:
The distribution of hydrogen peroxide above, in and below clouds at Frankfurt Airport (50° 1′ 59″ N and 8° 34′ 14″ O) was measured during the BLUESKY-flight #1 and showed untypical increases in hydrogen peroxide mixing ratios at low altitudes.
Based on NOAA HYSPLIT backward trajectory analysis (model duration of 24 h), the probed airmasses originated from the North Atlantic, passing northern France and were nearly uniformly affected by rainout during 6 hours prior to the measurement time. During the measurement the aircraft passed a cloud layer at approximately 2 – 6 km during descending and ascending legs of the vertical profile. The descent and ascent into and out of Frankfurt took place between 9:00 and 11:00 UTC. Fig. 7 displays the time series of the approach to Frankfurt. Mixing ratios of H_2O_2 from observations and EMAC are shown.
The relative humidity (RH) of 100% (grey areas in Fig. 7) indicates the presence of clouds. Rain was mainly observed below the clouds at low altitudes (light blue areas) at slightly lower RH. ERA 5 reanalysis (Fig. S11a) confirmed the presence of clouds at altitudes of 2 – 6 km (Flight #1). Based on local meteorological reports, light

rain started approximately one hour prior to the vertical profile measurement and lasted until approximately half an hour.

Minor comments:

Add the instrument used to measure the peroxides already to the abstract. Any other details missing that were crucial for doing the study and/or obtaining the results?

The information on the used instrument was added to the abstract. No other details of importance are missing.

Abstract was changed to:

Abstract. *In this work we present airborne in situ trace gas observations of hydrogen peroxide (H_2O_2), and of the sum of organic hydroperoxides over Europe during the Chemistry of the Atmosphere – Field Experiments in Europe (CAFE-EU, also known as BLUESKY) aircraft campaign using a wet chemical monitoring system, HYdrogen Peroxide and Higher Organic Peroxide monitor (HYPHOP).*

The campaign took place in May/June 2020 over *central* and *southern* Europe with two additional flights dedicated to the North Atlantic Flight Corridor. Airborne measurements were performed on the High Altitude and LOng-range (HALO) research operating out of Oberpfaffenhofen (*southern* Germany). We report average mixing ratios for H_2O_2 of 0.32 ± 0.25 ppbv, 0.39 ± 0.23 ppbv and 0.38 ± 0.21 ppbv in the upper and middle troposphere and the boundary layer over Europe, respectively. Vertical profiles of measured H_2O_2 reveal a significant decrease in particular above the boundary layer, *contrary* to previous observations, most likely due to cloud scavenging and subsequent rainout of soluble species. In general, the expected inverted c-shaped vertical trend with maximum hydrogen peroxide mixing ratios at 3 – 7 km was not found during BLUESKY. This *deviates from* observations during previous airborne studies over Europe, i.e., 1.64 ± 0.83 ppbv during the HOOVER campaign and 1.67 ± 0.97 ppbv during UTOPIHAN-ACT II/III. Simulations with the global chemistry-transport model EMAC partly reproduce the strong effect of rainout loss on the vertical profile of H_2O_2. A sensitivity study without H_2O_2 scavenging performed using EMAC confirms the strong influence of clouds and precipitation scavenging on hydrogen peroxide concentrations. Differences between model simulations and observations are most likely due to difficulties in the simulation of wet scavenging processes due to the limited model resolution.

Consider chopping the first paragraph of introduction into several smaller ones.

The first paragraph of the introduction was modified as recommended in the RC.

Line 35: There's an error in describing HOx as "peroxy radicals (HOx),"

The error has been corrected.

Line 35 was changed to:

Furthermore, gas-phase hydroperoxides are a reservoir for hydrogen oxide and peroxide radicals (HO_x), which are well known for their contribution to the self-cleaning properties of the atmosphere (Levy, 1971; Lelieveld and Crutzen, 1990; Crutzen et al., 1999).

”However, the underestimation of the photolysis frequencies by the model can be partly explained by the use of different absorption cross sections of H2O2 (Hottmann et al., 2020)” à Why were different cross- sections used here? Was this explained?

As reported by Hottmann et al. (2020), the H_2O_2 absorption cross sections were extrapolated up to 370 nm based on the recommended wavelength range of 280 – 350 nm in order to capture the whole photolytic activity range of the species.

Line 379 changed to:
However, the underestimation of the photolysis frequencies by the model can be partly explained by the use of additional extrapolated absorption cross sections of H_2O_2 in order to reproduce the entire photolytic activity range of the species (Hottmann et al., 2020).

Line 105: Please remove citations to unpublished work (it’s not even mentioned in the reference list).

The citation was updated and added to the reference list.

Line 107 (former 105) changed to:
The reduced pollution levels gave rise to anomalous blue skies, hence the name “BLUESKY” (Voigt et al., 2022).

Line 158: What do you mean by “prior to the measurement at 0.95 – 0.98”?

We apologize for the confusing choice of words.

Line 161 (former 158) changed to:
The catalase efficiency for the destruction of H_2O_2 in Channel B was determined via liquid calibration of the instrument at 0.95 – 0.98.

Line 172: Why do you assume ambient H2O2 is zero above tropopause? How valid is this assumption? Could you elaborate.

We believe the assumption is justified by general trends in the atmospheric distribution of water vapor and photolytic activity, which are the limiting factors of hydrogen peroxide production at high altitudes. Above the tropopause, the concentration of water vapor decreases drastically due to dehydration processes occurring at the tropopause (Schoeberl and Dessler, 2011; Park et al., 2021). At the same time photolytic activity simultaneously increases, and the role of hydroperoxides as a source of HO_x becomes more prominent, leading to a decrease in hydrogen peroxide levels close to zero.

Line 176 (former 172) was changed to:
The interference was derived by plotting hydrogen peroxide mixing ratios vs. ozone mixing ratios in the lower stratosphere, assuming that ambient H_2O_2 is close to zero above the tropopause based on the decreased availability of water vapor for the H_2O_2 precursor production and simultaneously increased photolytic activity of H_2O_2.

“Consequently, an increase in the ratio between MHP and hydrogen peroxide of ≥ 1 can ensue as a result of deposition processes within clouds.” Is this enough? Why?

The levels of MHP are generally lower than the levels of H_2O_2, which leads to a MHP-to-H_2O_2-ratio of <1, as displayed in Fig.3c during the HOOVER and UTOPIHAN campaigns. As discussed in Line 272, both campaigns were performed under nearly cloud-free conditions. A significant increase in the ratio, as observed during the BLUESKY campaign, indicates highly decreased levels of H_2O_2 relative to MHP. As further discussed in Line 276 MHP is far less sensitive to wet deposition processes than H_2O_2 due to a much lower Henry's coefficient. Consequently, as H_2O_2 decreases within a cloud layer due to scavenging, MHP remains nearly unaffected. Thus, we believe MHP-to-H_2O_2-ratio of ≥ 1 serves as a valid indicator for meteorological changes in terms of clouds and rain in this context.

Seems a tad bit weird that the peroxide measurements are not mentioned in Table 1.

We apologize for the confusion. Table 1 gives a brief overview on significant information of instrumentation providing the supplementary information used in this study.

Table 1 caption was changed to:
Table 1. Overview of other observed species with corresponding measurement method, total measurement uncertainty (TMU) and references regarding the supplementary instrumentation.

Line264: Awkward reference. Also, in Figure 5 and Line 415, at least.

Reference was changed upon the request.

Line 264 (now Line 271), Figure 5 and line 415 (now Line 424) were changed to:
(Hersbach et al. 2018)

References

Hottmann, B., Hafermann, S., Tomsche, L., Marno, D., Martinez, M., Harder, H., Pozzer, A., Neumaier, M., Zahn, A., Bohn, B., Stratmann, G., Ziereis, H., Lelieveld, J., and Fischer, H.: Impact of the South Asian monsoon outflow on atmospheric hydroperoxides in the upper troposphere, Atmos. Chem. Phys., 20, 12655–12673, https://doi.org/10.5194/acp-20-12655-2020, 2020.

Park, M., Randel, W. J., Damadeo, R. P., Flittner, D. E., Davis, S. M., Rosenlof, K. H., Livesey, N., Lambert, A., and Read, W.: Near-Global Variability of Stratospheric Water Vapor Observed by SAGE III/ISS, Geophys Res Atmos, 126, https://doi.org/10.1029/2020JD034274, 2021.

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M., Holanda, B. A., Jöckel, P., Kaiser, K., Krüger, O. O., Lucke, J., Marsing, A., Martin, A., Matthes, S., Pöhlker, C., Pöschl, U., Reifenberg, S., Ringsdorf, A., Scheibe, M., Tadic, I., Zauner-Wieczorek, M., Henke, R., and Rapp, M.: Cleaner skies during the COVID-19 lockdown, Bulletin of the American Meteorological Society, https://doi.org/10.1175/BAMS-D-21-0012.1, 2022.