Answer to: Interactive comment on “Distribution of hydrogen peroxide over Europe during the BLUESKY aircraft campaign” by Hamryszczak et al.

Anonymous referee #2

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.

The manuscript presents in situ aircraft measurements of hydrogen peroxide and organic peroxides during the BLUESKY campaign in May and June of 2020. The time period coincides with reduced emissions associated with shutdowns driven by the COVID-19 pandemic. The authors use a series of models to make the case that cloud scavenging and rainout processes over the region had a greater impact on reducing ambient peroxide levels than a reduction in emissions. The analytical methods used are sound. The data set is a valuable contribution and the manuscript is well written, and may be ready for publication with the following clarifications.

Line 137 states the CPI inlet sampling efficiency for hydrogen peroxide was determined to be 0.52. It would be helpful to know how this was determined and the frequency. Was the inlet cleaned during the campaign, and did this impact the transmission efficiency? Was the transmission efficiency examined for organic peroxides?

As mentioned in the manuscript (Line 164), the sampling efficiency was determined using gas phase calibration source, consisting of a LDPE permeation device filled with 30% hydrogen peroxide in a temperature-controlled oven at 35 °C flushed with synthetic air at a rate of 60 standard cubic centimeters per minute which was further diluted with approximately 2300 sscm purified air. The sampling efficiency was measured every second day during the field campaign by attaching the permeation source in front and behind the CPI inlet and calculated from the difference between the measured hydrogen peroxide levels with and without the CPI inlet implemented to the gas flow. Please note that the CPI and the ¼” PFA tubing connecting it to the ½” bypass line (also PFA) represent the largest surface of the whole inlet design, so that we assume that surface losses dominantly occur in this part of the inlet, while the high flow in the bypass minimizes surface losses there. The whole inlet was regularly flushed with purified dry air at rates of approximately 10,000 sscm. No impact on the transmission efficiency was observed based on single measurements. Due to lack of adequate organic peroxide permeations sources during the campaign the transmission efficiency of organic peroxides was not examined.

Line 164 (former 160) changed to:
In order to estimate the sampling efficiency, a calibration gas was analyzed every second day during the field campaign. The calibration gas was created by a LDPE permeation source filled with 30% hydrogen peroxide embedded in a temperature-controlled oven at 35 °C and flushed with synthetic air at a rate of 60 standard cubic centimeters per minute (sccm). The defined amount of hydrogen peroxide gas was diluted with approximately 2300 sccm purified ambient air. The sampling efficiency was calculated based on the difference between the measured hydrogen peroxide levels with and without the CPI inlet implemented into the calibration gas flow. The permeation gas is calibrated by bubbling the gas through a water-filled flask followed by photometric examination via UV spectroscopy using the $TiCl_4$ method described by Pilz and Johann (1974).

Line 150, notes an assumption that organic peroxides that pass the inlet are unaffected by any further losses and assumes a stripping efficiency for MHP from Lee et al., 2000. The manuscript would be strengthened if loss of organic peroxides in the sampling system were characterized. However short of that details regarding the stripping system should be provided to establish whether adopting the Lee et al stripping efficiency is appropriate.

As mentioned above, gas phase calibration devices for organic peroxides were not available. We expect that individual ROOH will have a different sampling efficiency depending on wall losses in the inlet and solubility into the scrubbing solution. Assuming that MHP is the dominant component of ROOH, we scale the scrubbing efficiency relative to H_2O_2 by using the Henry's law constant of those species. The sampling set-up, with respect to the sampling coil, the used sampling solution, the residence time and the temperature are similar to the design used in Lee et al. (2000) (gas flow rate of approximately 2300 sccm, scrubbing glass coil continuously flushed with precooled buffered sampling solution consisting of 41 g potassium hydrogen phthalate, 185 mL 1 M NaOH, 0.1 g EDTA and 1 mL of 37% HCHO at a flow rate of 0.000508 L/min (pH 6) (Lazrus et al., 1986)). Therefore, we assume a similar sampling efficiency as used in Lee et al. (2000).

Line 152 (former 150) changed to:
For this study we assumed that MHP is the sole component of organic hydroperoxides that passes the inlet and is unaffected by any further losses and scaled the signal of Channel B with the sampling efficiency for MHP based on the stripping efficiency by a precooled buffered sampling solution at a flow rate of 0.000508 L/min in accordance to previously reported sampling efficiencies.

Line 154, change "…to a lesser extend of…" to "…extent PAA…"

Line 154 changed according to the recommendation.

Line 157 (former 153) changed to:
Based on previous studies, HMHP (hydroxymethyl hydroperoxide) and extent PAA (peroxyacetic acid) and EHP (ethyl hydroperoxide) contribute significantly to the total amount of organic hydroperoxide mixing ratios at low altitudes (Fels and Junkermann, 1994; Slemr and Tremmel, 1994; Valverde-Canossa et al., 2005; Hua et al., 2008).

The analytical method used measures H_2O_2 and organic peroxides (RO_2H). The case is made that the RO_2H is likely, largely MHP. However, the technique does not distinguish the different organic peroxides. I recommend using RO_2H in figure 3 and through out the manuscript. This will not detract from the arguments presented in the manuscript and will not lead to an impression that MHP was a measured species.

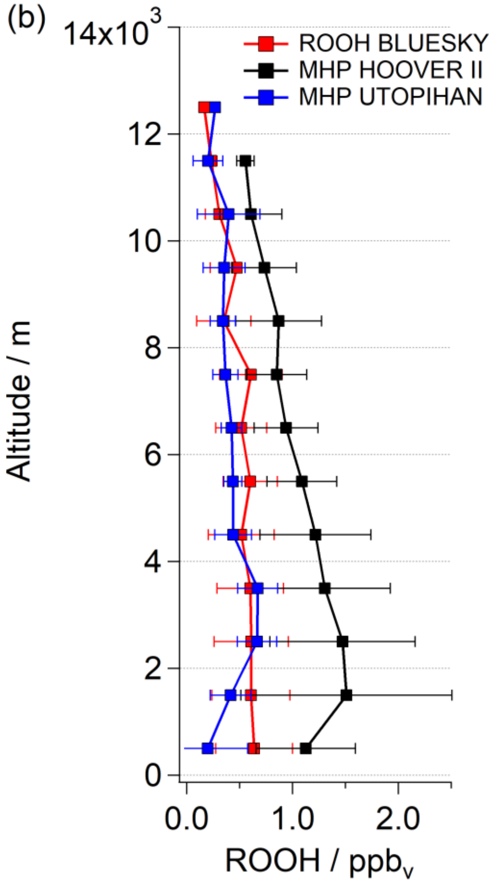
Notation changed according to the recommendations.

Line 10 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).

Line 149 (former 146) changed to:
This measurement technique does not provide mixing ratios for individual organic hydroperoxides. Previous studies indicate that methyl hydroperoxide is the most prominent free tropospheric component of organic hydroperoxides (90 – 100 %; Heikes et al., 1996a; Jackson and Hewitt, 1996; Walker et al., 2006; Hua et al., 2008). For this study we assumed that MHP is the sole component of organic hydroperoxides that passes the inlet and is

unaffected by any further losses and scaled the signal of Channel B with the sampling efficiency for MHP based on the stripping efficiency by a precooled buffered sampling solution at a flow rate of 0.000508 L/min in accordance to previously reported sampling efficiencies. Thus, ROOH used in this paper is scaled to an upper limit for the actual MHP in the free troposphere.

Figure 3b changed to:



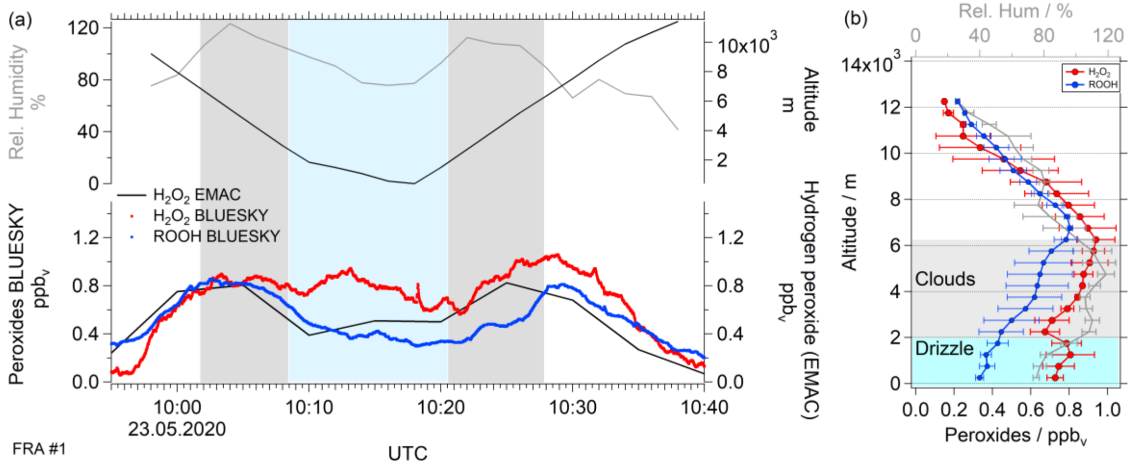
Caption of Figure 3 changed to:

Figure 3. Comparison of vertical hydrogen peroxide profiles (a), ROOH (b) and ROOH/H_2O_2 ratio (c) during BLUESKY (red) with outcomes of the earlier campaigns, HOOVER II (black) and UTOPIHAN-ACT II/III (blue). The data was plotted as mean ± 1 sigma.

Line 276 (former 272) changed to:

Generally, the presence of clouds has a marked impact on H_2O_2 but a much smaller effect on the majority of organic peroxides. ROOH are less sensitive to wet deposition due to lower Henry's law coefficients (for instance $2.2 \cdot 10^4$ mol $L^{-1} \cdot atm^{-1}$ at 298 K for MHP in contrast to $7.4 \cdot 10^4$ mol $L^{-1} \cdot atm^{-1}$ at 298 K for H_2O_2). Therefore, the

concentration ratio of the species can be an indicator of cloud presence (Heikes et al., 1996b; O'Sullivan et al., 1999; Snow, 2003; Snow et al., 2007; Klippel et al., 2011). The assumption of cloud processing via ratio comparison is derived from the fact that highly soluble species are transferred into the aqueous phase of clouds, where they are removed by reactions with other soluble species or by precipitation (Crutzen and Lawrence, 2000). Consequently, an increase in the ratio between ROOH and hydrogen peroxide of ≥ 1 can ensue as a result of deposition processes within clouds. Please note that due to the characteristics of the measurement technique, which derives the estimated ROOH mixing ratio as its tropospheric upper limit (Sect. 3.1.), the vertical trend of ROOH and therefore also the ROOH/H_2O_2-ratio are expressed as qualitative comparisons. Vertical profiles of ROOH measured during the BLUESKY and UTOPIHAN-ACT projects are comparable, while HOOVER II found higher values (Fig. 3b). However, the vertical trends of peroxides during HOOVER II can be assumed to be about equal, leading to an ROOH vs. H_2O_2 ratio of approximately 1. Thus, the two previous campaigns over Europe show corresponding trends with decreasing ROOH/H_2O_2-ratios above the boundary layer, where H_2O_2 mixing ratios are at their maxima (Fig. 3c). In contrast, increasing ratios of ROOH vs hydrogen peroxide at altitudes of 3 – 7 km were observed during the BLUESKY campaign. These increases during the BLUESKY campaign can be attributed to the lower mixing ratio of H_2O_2 and are indicative of more pronounced cloud scavenging.
Figure 7 changed to:

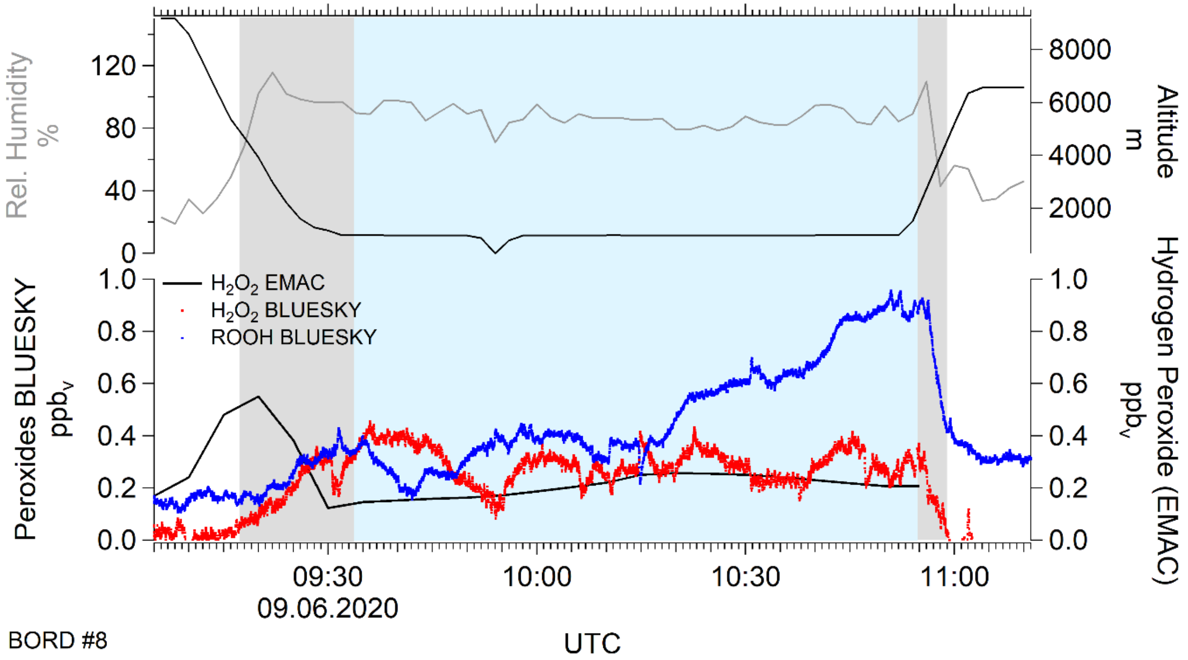


Caption of Figure 7 changed to:

Figure 7. Temporal series of BLUESKY flight #1 over Frankfurt (50° 1′ 59″ N and 8° 34′ 14″ O; left) and vertical distribution (right) of hydrogen peroxide impacted by cloud and rain scavenging. Data were plotted for observed (red) and simulated (black) hydrogen peroxide mixing ratios, and the observed ROOH mixing ratio (blue) in relation to altitude (top black) and relative humidity (light gray). Cloud scavenging and precipitation are highlighted in gray and light blue shading, respectively. Please note that the displayed peroxide data has a temporal resolution of 1 sec in contrast to the model resolution of 5 min.

Line 412 (former 407) changed to:
However, this assumption is not supported by the simultaneous ROOH mixing ratio observations (Fig 7b). In contrast to hydrogen peroxide, ROOH mixing ratios display a decreasing trend below 2 km.

Figure S10 changed to:



Caption of Figure S10 changed to:

Figure S10: Temporal series of peroxide mixing ratios over the Bordeaux area on 09.06.2020 (red: observed H_2O_2; blue: observed ROOH; black: simulated H_2O_2, grey: relative humidity; top black: GPS altitude). Cloud scavenging and precipitation are highlighted by gray and light blue shading, respectively. Please note that the observed peroxide data displayed has 1 sec time resolution in comparison to the model resolution of 5 min.

Line 173 notes an instrument interference caused by hopcalite contamination during the campaign. Can the authors discuss this interference? Was this interference dependent only on ozone concentrations? Did this have an impact on the RO_2H channel?

Hopcalite contains of a variety of metal oxides used to purify the ambient air from the majority of trace gases during background measurements. Since peroxides are sensitive to metal oxides, a lowered signals and therefore decreased levels of the species due to the contamination were observed. To our knowledge, the interference is not dependent on the ozone levels, but rather on the amount of metal oxides causing the contamination. Since the amount of the released hopcalite was not quantified, the impact of the negative interference could not be estimated separately and the ozone interference was extended by the hopcalite interference as a rough estimate relative to the calculated total measurement uncertainty.

Line 179 (former173) changed to:

Due to instrumental issues caused by hopcalite contaminations during the campaign, the uncertainty of the ozone interference was further extended by the hopcalite interference and estimated as 27% at 0.16 ppbv hydrogen peroxide.

Section 4.3 discusses the fate of peroxides below clouds. This section could benefit from providing some information and discussion about whether the airmasses sampled above and below the cloud deck have different trajectories and exposure to rain out. When did drizzle begin in the boundary layer relative to the measurement time?

Based on NOAA HYSPLIT (Stein et al., 2015) backward trajectories and GFSQ meteorological data analysis above, in and below the cloud layer (500 m, 300 m and 8000 m) with a duration of 24 h, the majority of the airmasses originated from North Atlantic passing North France. The analysis confirmed further a comparable exposure to rainfall in all layers. The drizzle begin was reported approximately 1 hour earlier and lasted until 11:00 UTC where the precipitation rate increased for another 2 hours.

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. During the measurement the aircraft passed a cloud layer at approximately 2 – 6 km during descending and ascending lags 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.