We thank the referee for her/his comments that we will address in the following.

Summary:

This study seeks to construct budgets of hydrogen peroxide (H2O2) in the planetary boundary layer based on in situ observations at five surface sites throughout Europe. The sites represent a diverse range of elevations, latitudes, and biomes, with four observational periods in the summer and one in the winter. Half-hourly binned observations at each site are classified by campaign-wide medians and 25th/75th percentile windows, to represent typical conditions and variabilities without being skewed (as the mean would be) by outliers such as rainy periods and measurements below detection limits.

Based on these median values, and particularly periods of increasing (morning) and steady (midday) median values, the authors construct a budget of H2O2 and diagnose the relative importance of photochemical production/loss, deposition, and transport at each of the sites. First, they use measured HO2, OH, and J(H2O2) to estimate rates of photochemical production and destruction. Depositional losses are estimated in two ways: first by assuming all H2O2 loss at night is due to deposition, and second by assuming that net photochemical production is balanced by deposition during midday hours when d[H2O2]/dt 0. Resulting daytime estimates are substantially higher than those derived from nighttime H2O2 loss. Finally, all d[H2O2]/dt not attributable to net photochemical production and deposition is attributed to transport. At four of the five sites, morning photochemical production is approximately balanced by deposition; the contribution of transport is therefore approximately equal to the total morning H2O2 increase.

General comments:

The authors propagate errors and uncertainties throughout the paper, but do not go on to discuss what this error means, e.g. how certain we can be (probabilistically) of the conclusions they come to about the relative importance of photochemical production/loss, deposition, and transport, and how variable these contributions are on a day-to-day basis. It would be helpful in the discussion to extend the brief description of uncertainties that focuses on HUMPPA to a wider scope, and especially to add error bars and/or daily variability to Figure 6. There are also a number of places throughout the manuscript where potential confounding factors and limiting assumptions are listed (e.g. not accounting for alkene ozonolysis, assumptions of photostationary steady state at midday) and the validity of these assumptions or the potential biases introduced are not described quantitatively, which makes it difficult to assess the total potential error from all sources in these analyses. More detail on specific occurrences of this are listed below.

A number of other concerns about the methods and their descriptions within this manuscript are provided below within the specific comments. Most notably, I think more discussion of the use of median values and 25th/75th percentiles for the entirety of the analysis is needed. While it is clear that using medians instead of means avoids some difficulties associated with outlier values, it is not clear that the day-to-day variability can be ignored when calculating photochemical production and loss, or that this is particularly useful when the calculations could just as well be performed on un-averaged data. It would help to provide some analysis of how the calculations might change if they were not performed exclusively on campaign-wide medians. Additionally, some aspects of the calculations performed herein are not entirely clear, especially on the deposition estimates, where two complementary methods are used but the descriptions of each are intertwined. Finally, the figures could use substantial clarification; conversion of UTC to local time would help, axis titles should be added to Figure 5, axes on Figure 3 should go to zero, consistent color-coding between Figures 3-5 would be nice, and error bars should be included on Figure 6 (as well as 25/75 percentile ranges on Figure 5).

As indicated in Table S1 the data coverage for the different campaigns varies strongly. In particular, missing HOx values make it difficult to analyze the time series of individual campaigns. Therefore, we decided to analyze diurnal variations. This can be done by using mean values and standard deviations, which are both strongly affected by values below detection limits due to e.g. cloud presence that will reduce photochemical activity. Median and inner quartiles are less sensitive but still provide a measure of the variability, excluding extreme events. The error propagation includes measurement uncertainties and atmospheric variability, with the latter being the dominant term. Exclusion of the atmospheric variability would results in errors an order of magnitude smaller. Therefore the stated values for net-production, deposition and transport are best estimates for the median values, while the error bars reflect atmospheric variability and are thus a very conservative measure of the uncertainty.

Specific comments:

P2/L11: Why does the rate coefficient depend on water vapour concentration separately from pressure?

The formation of H2O2 by the self-reaction of HO2 is strongly promoted by water vapor, which – as mentioned in the manuscript – can significantly enhance the production rate (see e.g. the data sheet for the reaction of HO2 + HO2 from IUPAC (iupac.pole-ether.fr)).

P2/L11: Does "in general" signify that this positive dependence isn’t always the case? Why not?

We erased the phrase.

P2/L23: Reaction 3 does not appear to recycle the HOx from H2O2; it produces only one equivalent on HO2, and thus a cycle with R1 results in the loss of both 1OH and 1HO2.

We changed the manuscript to “partly recycling HOx”

P3/L33: Not a big deal, but the comparison with literature values seems to be spread through sections 3 and 4.

The literature review in section 3 lists previous H2O2 measurements in Europe comparing them to mixing ratio levels for this trace gas. The comparison to the literature in section 4 (discussion) deals with a comparison to other budget calculations.

P5/L6: What does the 10-90% represent?

This is a measure of the time resolution of the measurements. It is determined from calibration increasing from 10 % to 90 % of the signal.

P5/L23-27: How are these ranges and interferences (10-30% conversion, 12-15% RO2 interference) taken into account when calculating the HO2 and the uncertainty? Do you assume a constant fraction of the HO2 to be RO2?

As discussed in the manuscript the early HO2 measurements (100% conversion) suffered from an unquantified RO2 interference, mainly caused by biogenic alkenes. For HUMPPA 2010, which was conducted in a boreal forest, Hens et al., 2014 estimated an uncertainty of 30 % of the HO2 data due to the uncorrected RO2 interference. Crowley et al., 2018 found in a constrained box model study of the HUMPPA dataset 30% interference during noon by RO2, confirming the finding by Hens et al. but estimated for the nighttime and early morning hours a contribution of the RO2 interference of up to 100 % to the HO2 signal. In this study, we consider for the calculating the H2O2 production rate during HUMPPA a weighted all day interference of 50 % on the HO2 dataset. As discussed in section 4 around noon this leads to HO2 mixing ratios that are approx. 10 % lower than simulated values. The consequence of this uncertainty is discussed in section 4.

P6/L5: Subscript x on NOx

P6/L6: Parentheses around Fig. S1-S5

Changed.

P6/L15 and elsewhere: I don’t think it helps at all to use UTC instead of local time. It requires an extra step of thinking for the reader without adding any particularly useful opportunity for comparison between the campaigns. I would recommend converting everything to local time for clarity’s sake.

Since local time depends on time zone and season and is only weakly related to the soar cycles, we prefer to stick to UTC. Solar zenith angles in Fig.2 and JNO2 in the supplement should make it easy to identify sunrise, noon and sunset.

P7/L6: Why the specific cutoff of J(NO2) > 10ˆ(-3) sˆ(-1) for daytime conditions? Are the results quantitatively sensitive to the choice of cutoff?

This is an often used cutoff value to differentiate between night and day.

P7/L12: "where" instead of "were"

Changed

P8/L14-15: Visual inspection does not suggest linearity; at best I think this can be described as a visible positive dependence. I also find it misleading and unhelpful to use the uncorrected HUMPPA point in the figure, and to describe the linear regression as a better fit than the initial quadratic fit, when you go on to base your analysis on the corrected value and the resulting (better) quadratic fit. We already know from your discussion of R1 above that a quadratic dependence would be expected (not taking into account other processes and dependencies). But it's also confusing to apply this analysis to overall daytime medians; the direct quadratic dependence would really only be expected on the timescales of photochemical production of H2O2. How different would this analysis be if the quadratic fit were imposed on the un-averaged data from each campaign?

Figures 3 and 4 are not classical correlation plots. Instead, we use them to place the individual campaigns in a parameter space (observed H2O2 vs. HO2 and NOx, respectively). Since HO2 values during the night are generally close to zero, we restricted this analysis to daytime values (including nighttime would reduce the HO2 values by a factor of 2). An analysis of un-averaged data suffers from the low data coverage as mentioned above, and is therefore not practical. We will remove the term "linear" when describing the data in Figure 3.

P8/L23: If the HUMPPA-corrected quadratic fit provides the best correlation, why is it not shown?

As discussed above the HUMPPA HO2 data have not been corrected for the RO2 interference. Instead, the stated uncertainty includes this bias. Therefor throughout the manuscript, we show the original data set (Fig. 3 and Fig. S2). The discussion of Fig. 3 includes a sensitivity study to motivate the correction of the HUMPPA HO2 data for the subsequent analysis of the H2O2 production rates.

P8/L24-25: I think this requires further explanation as to why you expect this quadratic relationship to hold across environments with very different transport and deposition patterns and for median daytime values rather than instantaneous measurements of HO2 and H2O2. Figure 5 suggests that deposition and transport are highly variable and important for these locations.

The mixing ratio of H2O2 at a given location depends on transport and local photochemistry. Since the production term is proportional to the square of HO2, and the H2O2 can be expected to be dependent on its production rate, one would expect to find such a relationship.

P8/L26-27: If the biogenic VOCs were still quantified at DOMINO, why not correct for them in the same way even if they were low?

As mentioned above, a correction for the RO2 bias of the HO2 measurements for DOMINO and HUMPPA is not possible, but instead the effect is summarized through a larger uncertainty. It is expected that this has a stronger effect during HUMPPA due to generally higher alkene concentration. During DOMINO alkene concentrations are much

smaller and thus the HO2 mixing ratios are less likely be affected by such an interference.

P8/L30-32: Why are nighttime data included in this analysis? If the results are the same either way, it would be better to at least be consistent between the two figures. What if you used day and night for the H2O2 vs HO2 analysis?

As mentioned above HO2 during the night is zero, while this is not the case for NOx (as is H2O2). Limiting the plot to daytime values does not change the relation.

P9/L12-13: "Median values and 25 and 75 % percentiles do not include such events" - does this mean the points with rain or clouds were screened out entirely, or just that they always fall below the 25th percentile threshold? If they were screened, how so? Is this where the J(NO2) comes into play?

The data were not filtered for rain or cloud effects and the JNO2 filter was only used to differentiate between night and day. Under cloudy conditions or rain the photochemical activity is strongly reduced due to less insolation, which results in lower radical levels and thus H2O2. Since cloud/rain periods were rare during the campaigns they fall indeed below the 25th percentile threshold.

P9/L32-33: The implication above was that RO2 interferences had been corrected for; does this imply that there might be additional interferences?

According to the model results of Crowley et al (2018), the contribution of the interference by RO_2 on the HO_2 signal was much greater during nighttime than during the day, which results from the large (modelled) organic peroxy radical mixing ratios at night compared to the (modelled) HO_2 at night. Hence, the nighttime production of H_2O_2 during HUMPPA is likely to be an artefact, as mentioned. We shall extend the text to clarify this.

P10/L6: In the subsequent lines, this appears to be a factor of 15, not 10

Changed to "by an order of magnitude"

P10L10: Percent contributions of OH and photolytic losses would be more helpful here than "the same order of magnitude"

Changed to "are of similar magnitude"

P10/L10-13: This sentence has two verbs in one clause ("is"/"yields") - either missing a conjunction or remove the "is"

Changed

P10/L14: You define NPR three times, which are also the only times you use it aside from in a table. It is probably not necessary as an acronym.

Changed

P10/L14-15: It would be nice to see the NPR as part of a figure. Figure 5 could potentially include NPR on the production panel. It should also have axis titles, and might be improved with log-scale y axes to better distinguish the shapes of the curves with smaller magnitudes.

The production term is generally an order of magnitude larger than the photochemical loss. Therefore, the net production is equivalent to the production term. We will change Figure 5 by adding axis title and we will check whether a log scale will improve the readability of the graph.

P10/L17: The next couple paragraphs appear to go back and forth between which method is being described (day vs. night) in a very confusing manner. I think the differentiation within the paragraphs either needs to be a lot clearer or they should be separated entirely. E.g. In the first sentence on P11, when table 2 is mentioned, it's not clarified that it's just night.

P10/L19-21: The limitations mentioned here of estimating dry deposition at night and extrapolating to the day seem like major potential sources of bias. Can you provide any estimate of the extent to which this method might underestimate deposition? Were there vertical wind speed measurements?

P10/L23: Similarly, it would be useful to estimate the extent to which this assumption of a fully established daytime boundary layer is safe or might cause bias

P10/L24-27: This is not clear. You're focusing on times when dH2O2/dt is near zero, and then calculating k(d) from dH2O2/dt, despite saying that NPR and horizontal advection also contribute. Are you subtracting those terms off? Or does this only apply to night?

P11/L11: Again, do you have any estimate of how substantial this source of error (the neglect of alkene ozonolysis in your analysis) might be?

P11/L13: Compared to the literature values for dry deposition that you go on to list, yours are much lower. What insight do we get from this?

P11/L20-23: The assumptions described here (photostationary steady state and the balance between NPR and dry deposition) require more discussion of their validity and potential introduction of uncertainty/error/bias. Do you have any estimate of what role horizontal advection might play, if air masses are coming from somewhere with different chemical characteristics?

Since the above eight comments deal with the determination of the deposition velocity, we will address them together. The dry deposition of a trace gas depends on its loss on a surface (described by a surface resistance) and transport to the surface, mainly due to turbulence. During the night, the transport is small due to low turbulence. This leads to a small deposition velocity. During the day solar irradiation forces turbulence and thus stronger transport to the surface. In addition, the leave stomata are closed during the night, but are opened during the day and reduce the surface resistance. Both effects lead to higher deposition velocities. During the morning, the deposition velocity changes from low to high values, mainly with the increase of turbulence. Therefore, we use an

interpolation instead of the maximum value for noon. These interpolated values are similar to the cited values in the literature that were obtained during daylight hours. The assumption of a well-established boundary layer around noon is based on observations (e.g. Figure 4 in Ouwersloot et al., 2012). Based on aircraft observations, horizontal gradients in H2O2 mixing ratios are generally small (e.g. Klippel et al., 2011) so that we do not expect a strong influence of advection.

The text will be amended to remove any confusion related to how the Vdep was calculated.

P12/L12-13: These percent uncertainties should be added to the discussion below and to Figure 6.

See above for a discussion about uncertainties and atmospheric variability.

P13/L20-23: More detail on the variability of this analysis would be useful. Is the model always 50% lower, or does it fluctuate? Does the variance in the modeled HO2 match that of the measured HO2?

A detailed discussion of the comparison between modelled and observed HO2 can be found in the paper by Crowley et al., 2018.

P13/L24: It's my understanding from the previous sentence that the "good agreement" is largely because the measurements are corrected with the modeled RO2 to match the modeled HO2.

Correct

P13/L29-31: Do you have the necessary measurements to correct for this, or at least to weigh in on how much of a difference it makes, across your campaigns? It seems like this 33% increase (0.6 to 0.8) when considering terpene ozonolysis isn't necessarily negligible, especially if it influences the shape of the diurnal profile.

Since we interpolate between night- and daytime deposition velocities this small absolute difference in the nighttime deposition velocity is insignificant.

P14/L4: "mourning" should be "morning" P14/L18: "similar" should be "similarly"

Changed.

P15/L17: This statement that "the early morning rise if H2O2 mixing ratios is significantly influenced by dynamical processes" seems central to your conclusions, but given that it is based on prior estimates of net photochemical production and deposition with high uncertainty, it's not clear to what extent this statement can be supported within error estimates. What are the uncertainties on the subsequent numbers reported for each campaign? Error bars on Figure 6 would also help with this.

We will change the text to “is significantly influenced by dynamical processes”.

P15/L18-19: The sentence starting "Smaller contributions..." is missing a preposition
Changed.