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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Diurnal variability, photochemical production and loss processes of hydrogen peroxide in the boundary layer over Europe” *by* Horst Fischer et al.

Anonymous Referee #2

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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 $\sim$ 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).

Specific comments:

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

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

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.

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

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

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?

P6/L5: Subscript x on NOx

P6/L6: Parentheses around Fig. S1-S5

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.

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?

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

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?

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

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.

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?

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?

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?

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

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

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

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

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.

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.

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?

P12/L1-2: It seems from your discussion of the differences between night and day deposition characteristics that using the noontime values would be a more realistic substitute for the morning than linear interpolation between night and day, considering that the morning will have substantial vertical mixing. How different an answer would you get if you just use the noontime values?

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

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?

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.

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.

P14/L4: "mourning" should be "morning"

P14/L18: "similar" should be "similarly"

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.

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

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