RC1: **'Comment on acp-2022-504', Anonymous Referee #1, 28 Aug 2022**

Review of "Diurnal variability of atmospheric O_2, CO_2 and their exchange ratio above a boreal forest in southern Finland" by Faassen et al.

In this paper, the authors present diurnal variations in $\delta(O_2/N_2)$ and CO_2 observed at two heights above the boreal forest. They calculated ER_{forest} and ER_{atmos} based on flux and concentration measurements, respectively, and found ER_{forest} and ER_{atmos} cannot be used interchangeably. The authors also applied the observed ER_{forest} to separate the NEE into GPP and TER, and they found comparable results to the commonly used eddy covariance approach. These findings supported and refined the discussion by Seibt et al. (2004) and Ishidoya et al. (2013, 2015) who reported differences between ER_{forest} and ER_{atmos} and its application to forest carbon cycle. There are only a few data sets of continuous measurements of both $\delta(O_2/N_2)$ and CO_2 over forests, and accurate estimate of ER_{forest} at various forests is highly important for not only forest but also global carbon cycle. This paper makes a valuable contribution in this respect. However, I find some issues in the observed variations in $\delta(O_2/N_2)$ which should be addressed before publication.

We thank the reviewer for their review and assessment of our manuscript. We will address the issues on the observed variations and other points below. Note that line numbers given refer to the line numbers in preprint version.

Main Points

The authors ascribed the temporal decreases of O_2 and CO_2 between 13:00-20:00 (P3b) in Figure 4 to a remaining artefact that could not be corrected for with the pressure correction associated with the instability of the MKS pressure regulator in 2019. If so, I think the artefact also superimposed on the O_2 data during the other periods (P1, P2, and P3a), and I am concerned about the unrealistic values of ER_{atmos} of 2.28±0.01 and 2.05±0.03 found in Fig. 5 are also attributed to the artefact. In my experience, larger ER_{atmos} than 2.0 has never been observed in a diurnal cycle at a forest in a growing season. I recommend the authors to create the aggregate day based on the periods other than 7-13 July, 2019, and calculate the ER_{atmos} for the average diurnal cycles. Especially, the ER_{atmos} in 2018, when the pressure correction was not applied, will be useful for comparison. If larger ER_{atmos} than 2.0 is also found in the average diurnal cycles in 2018, then the value will be reliable. However, if larger ER_{atmos} than 2.0 is found only in the diurnal cycles in 2019, then it may be due to the artefact and the ER_{forest} may also be affected by the artefact. To discuss differences between ER_{forest} and ER_{atmos} properly, it is important to rule out the possibility of the significant effect of the artefact.

We agree with the reviewer that the correction for the instability in the MKS pressure transducer is not sufficiently explained in the paper and that the effect of this correction on both the ER_{forest} and the ER_{atmos} signal can be explained more thoroughly. We address this as 3 different points: first, we give further details on the correction we made, secondly, we compare the 2018 ER_{atmos} signals, and finally, we discuss the possible explanations for the ER_{atmos} values higher than 2.0.

1) Further details on MKS pressure transducer instability correction

Figure 1 below shows how we determined the correction for the MKS pressure transducer instability. This figure shows the relationship between the four minute $\Delta(\Delta)O_2$ values of the three different calibration tanks (indicated each with a different symbol) per reference tank period (indicated by different colours) for 2018 and 2019 separately. The $\Delta(\Delta)O_2$ values are the deviations from the mean of each calibration tank. This figure clearly shows that the $\Delta(\Delta)O_2$ values in 2018 were not influenced by issues of the instability of the MKS pressure transducer. This is different for 2019, where the pressure difference of the MKS sensor shows a relationship with $\Delta(\Delta)O_2$. When the differential pressure values deviate further from zero, the $\Delta(\Delta)O_2$ values decrease. These pressure deviations are strongest for the period with the last used reference tank (#5) in 07-15 July 2019 and the aggregate day that we use in the paper is measured in this period. We derived the linear regression line for 2019, as shown in the figure, and used this to correct the 2019 $\Delta(\Delta)O_2$ measurements.

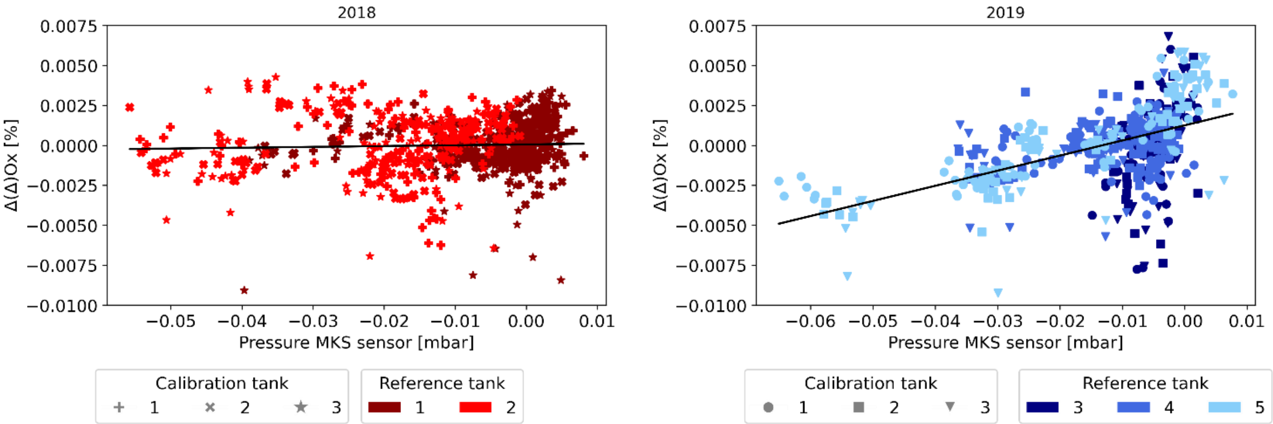

Figure 1 The relationship between the differential pressure measured by the MKS sensor and the 4 minute Δ(Δ)O2 values of the calibration tank values during the 2018 and 2019 measurement period. The Δ(Δ)O2 values are the deviations from the mean of the specific calibration tank.

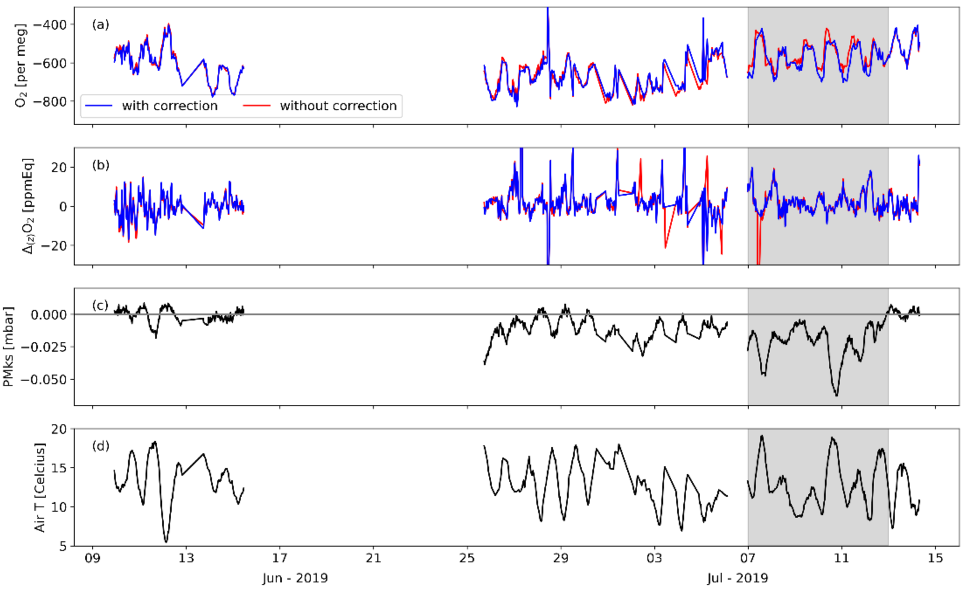

Figure 2 The corrected and not corrected 30-minute averaged O2 concentrations at 23 m for the PMKS deviations (a), together with the corrected and not corrected gradient of O2 (b). The time series for the 2019 measurement period of the PMKS (c) and the air temperature (d). Same as Figure B1 in the appendix.

Figure 2 shows the impact of the correction on the measurements. This figure is now also included in the appendix of the paper. Figure 2a shows the effect of the pressure correction on the O_2 concentrations measured at 23 m, and the vertical gradient of O_2 during the 2019 measurement period. The figure shows that in the beginning of the measurement period, the pressure correction was minimal and at the end of the measurement campaign the correction increased, according to the increasing instability of the MKS pressure transducer. This corresponds to the data in Figure 1, where the period of reference tank 3, used in the period 07- 15 July, shows the strongest deviations in the PMKS. The shaded area indicates the period that we used to calculate the representative aggregate day.

The MKS pressure transducer instability correlated with air temperature. This is visible in panels c and d of figure 2. With higher temperatures, the PMKS deviated further from zero compared to lower temperatures, although the malfunctioning of the pressure transducer prevented the differential pressure to go to zero completely, even at night. We therefore find different impacts of the correction between day and night, with a larger correction needed during the day compared to the night, increasing the uncertainty of the day-time measurements, compared to the night-time measurements. Based on this analysis, we therefore do not include the period 13:00-20:00 in our calculation of ER_{atmos}.

Compared to the concentration measurements, the gradient is hardly affected by the PMKS correction (Figure 2b). Since the correction is applied at the two heights, the bias is cancelled in calculating the gradient as a difference between the two heights. ER_{forest} is therefore not affected by this correction as it is based on the gradient, in contrast to ER_{atmos} which is based on a single measurement height.

We have updated the text in lines 164, 320, 332 to further explain the correction.

2) Comparison of ER_{atmos} values between 2018 and 2019

To make sure that the high values for ER_{atmos} observed in 2019 are not caused by the pressure correction, we evaluated the ER_{atmos} signals of several days in 2018. In 2018 no pressure correction was applied, because there was no instability in the MKS pressure transducer at that point (Figure 1). We selected several days in 2018 that showed a clear diurnal cycle for CO_2 and O_2 for which we calculated ER_{atmos}. We calculated ER_{atmos} values for daytimes periods that include the entrainment process (between 5:00-13:00 LT). The obtained values of the daytime ER_{atmos} ranged between 1.5 to 2.7, based on aggregates that have reasonable diurnal cycles and gradients of O_2. From these 2018 ER_{atmos} values, we confirm that a value of 2.28 which we obtained for the aggregate day in 2019 is not uncommon and can be reproduced in a different year for a period in which pressure stabilization issues were absent.

Explanations for the high ER_{atmos} values

Next to reviewer 1, also the other 2 reviewers had concerns about the high ER_{atmos} values. We will therefore elaborate here on the possible explanations for these values. Three possible explanations were given by the different reviewers:
- The PMKS correction could have caused these high numbers (all 3 reviewers). We show above that high ER_{atmos} values were also found in 2018 when there were no issues with the MKS pressure stabilization.

- The lake could have affected the measurements (Reviewer #2). We analysed the footprint and the wind direction. In the answer to reviewer #2 we provide evidence that the dominant wind direction was between north and northeast. Therefore, the footprint of the concentration and flux measurements is not influenced by the lake and mainly influenced by boreal forest exchange.
- High ER_{atmos} values should be linked to fossil fuel combustion (Reviewer #3). The main fossil fuel sources are to the south of the measurement tower. As the main wind direction is from the north to northeast throughout the duration of the aggregate day, it is unlikely that fossil fuel combustion strongly influenced our signal.

These possibilities mentioned by the reviewers do not explain the high ER_{atmos} signals, but we do agree with the reviewers that such high values for ER_{atmos} of 2.05 for the entire day and of 2.28 for the period P2 are indeed questionable in the context of previous values reported in literature, based on ecophysiological relationships between respiration and photosynthesis.

Although we cannot fully rule out remaining artefacts in the calibration due to e.g. temperature changes in the measurement cabin, we suggest that the more plausible explanation is that ER_{atmos} is highly influenced by atmospheric processes. These processes are closely linked to the development of the atmospheric boundary layer dynamics.

We are currently working on extending the work presented in this manuscript with a modelling study, to support the data analysis. We use the Chemistry Land-surface Atmosphere Soil Slab (CLASS) model (Vilà-Guerau de Arellano et al., 2015) and have implemented the O_2 and CO_2 exchange. We are therefore able to disentangle which individual contributions determine ER_{atmos} and how such high values could have formed. Our preliminary results show that entrainment of air masses originated at the residual layer, with different characteristics of O_2 and CO_2, leading to the dominant contribution after sunrise (figure 3 between 04:00 – 09:00). During this period the signal of the measured O_2 and CO_2 concentration is more determine by atmospheric factors than by surface factors.

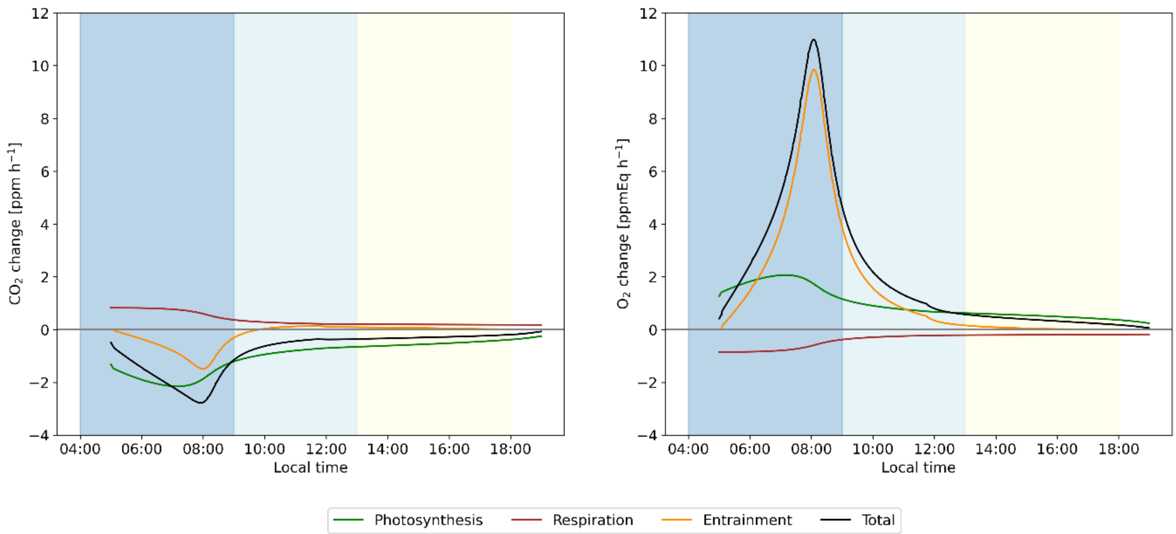

Figure 1 The change of O_2 and CO_2 over time, split into the different processes that contribute to the total signal, modelled with CLASS for the representative aggregate day (7-12 July). The shaded colours indicate the same time periods as indicated in Figure 4a in the paper.

The high values that we find for ER_{atmos} can therefore be explained by the entrainment process, and are influenced by a difference between CO_2 and O_2 in what we call the jump. The jump is the difference between the concentration inside the boundary layer compared to the free troposphere or the residual layer. A difference in the jump of O_2 and CO_2 can arise when different sources of background air are mixed. For example, ocean CO_2 and O_2 exchange are decoupled, so when an ocean CO_2 sink is present in the background signal, the air will be depleted of CO_2 whereas the O_2 concentration will be hardly affected. When sources of air mix with different ER signals, we cannot just simply average these ER signals as they could describe different states of the atmosphere (see line 570, or point 3 below). This would mean that the resulting mixture of O_2 and CO_2 could have an ER that is an 'unrealistic' value when we compared it to ER signals of single processes. The air in the troposphere is a mixture of air from different background sources. Our preliminary model results show (not shown here) that even a slight difference in jump between O_2 and CO_2 would result in a change in ER_{atmos}. This confirms our message that the ER_{atmos} signal is sensitive to entrainment, and that we should always look at ER_{forest} if we would like to indicate the surface ER. If no entrainment would occur, ER_{atmos} would be the same as ER_{forest}. ER_{atmos} could therefore be used to help quantify the relevance of the biosphere processes with respect to atmospheric driven processes.

This explanation of the entrainment processes dominating the values we find for ER_{atmos} does not directly explain why we get such high ER_{atmos} values compared to other studies. We think this can be explained to the measurement height. The studies of Seibt et al. (2004) and Battle et al., 2019 measure closer to the canopy compared to our study. The effect of entrainment on the measurements is less when measuring closer to or even inside the canopy. When looking at the ER_{atmos} values of the 125 m from our study we find an ER_{atmos} signal for P2 of 3.40. This number is even higher compared to the 23 meters value of 2.28. For the study of Ishidoya et al. (2015) it is not completely clear to us how high they measured compared to the canopy as they assume a range in canopy height. It seems that their highest measurement height is at a similar distance to the canopy compared to our lowest height (23 m). However, they find only a small difference between ER_{atmos} and ER_{forest}. A possible explanation for this could be the difference in background air that is entrained from the free troposphere or that surface exchange dominated over the atmospheric effects. Based on the different findings between these studies we suggest that more research is needed, especially focussing on measuring the

O_2 and CO_2 concentration also in the free troposphere and further modelling studies to better determine the drivers of O_2 and CO_2 by biosphere or atmosphere effects.

We have changed the text in line 481 to better clarify our explanation of the high values of ER_{atmos} linked to entrainment.

Other Specific Points

1) Line 175-178 and Table 1: What does "our own calibration" mean? Did the authors calibrate the target cylinder using the primary Scripps cylinders by themselves? I think the declared value with calibration in Groningen is based on SIO scale. Therefore, the values of target cylinder based on "our own calibration" should also be on SIO scale to calculate the mean of the difference.

We agree with the reviewer that this is unclear. We did not mean to say that we have used two different calibrations, what we meant was indeed that we use the values calibrated at Groningen using the SIO cylinders there. We have updated the text accordingly.

2) Line 190-192: Related to the main points, the period of 7 through 12 July 2019 to create the aggregate day is shorter than that by Ishidoya et al. (2015). I am concerned about the artefact during this period considering the very high ER_{atmos} found in Fig. 5.

We agree with the reviewer that we used indeed less days compared to the study by Ishidoya et al. (2015) and that by adding more days we could have made our results more robust. However, the reasons we used only these six days was because before and after this period the measurements were not showing clear diurnal cycles and gradients. We also wanted to use consecutive days and because our measurement period was relatively short, we used only these six days. These days were chosen based on their gradient of O_2 and the meteorological conditions, as is describe in lines 182-185. Furthermore, our measurements in 2018 also give high values for ER_{atmos}, which shows that the high values are not dependent on the artefact of the PMKS correction, but rather are explained by entrainment which we have further elaborated above in reply to the first major point.

3) Line 223-226: The authors calculated the ER_{forest} from means of the O_2 and CO_2 flux during night, day, and entire day. I think it can also be calculated by applying a linear regression between O_2 and CO_2 flux (or ΔO_2 and ΔCO_2) on the points as Ishidoya et al. (2015, 2020) did. Wouldn't this method reduce the uncertainty on ER_{forest}?

It is indeed not obvious from previous literature how to correctly infer ER_{forest} from the O_2 and CO_2 flux data. We explain here how we arrived to our approach, after considering 1) the slopes of the gradients and 2) the slopes of the fluxes.

1) Slope of the O2-CO2 vertical gradients

We first considered the methods that Ishidoya et al. (2015, 2020) use, which derives ER_{forest} from the gradients alone. In figure 3a below the vertical gradient of O_2 is shown against the gradient of CO_2. The slope of a linear regression through all the points (24 hours) is -1.028.

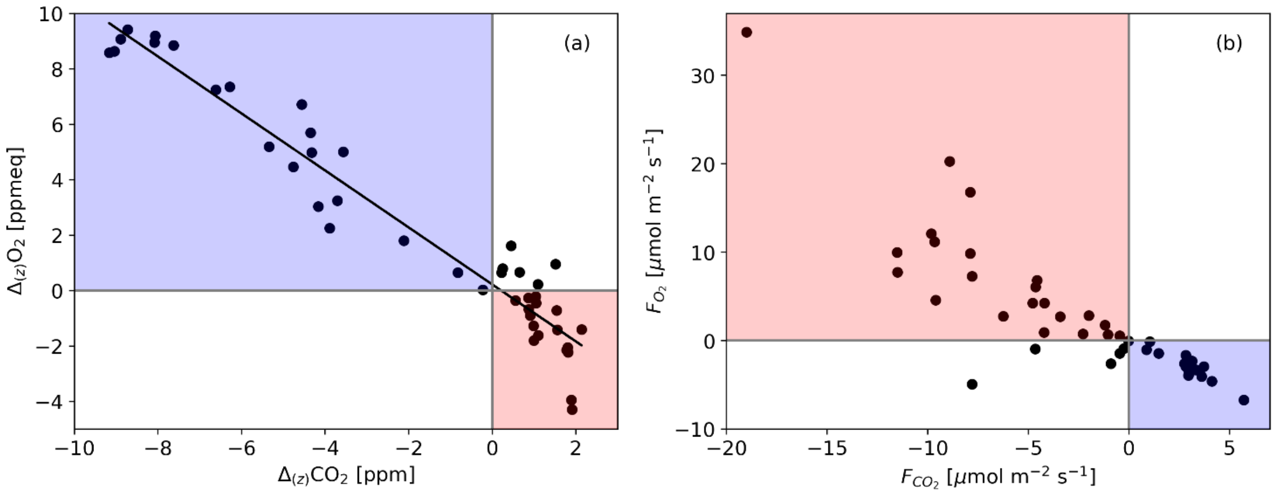

Figure 2 the vertical gradient of O_2 against the vertical gradient of CO_2 (a), together with the surface flux of O_2 against the surface flux of CO_2 (b) of the aggregate day. The shaded blue part is the period that indicates the night and the shaded red is the period that indicates the day.

However, by looking only at the gradients, the size of the flux itself is not taken into account. The size of the flux is calculated as a combination of the vertical gradients and the turbulence of the atmosphere is (K in equation 6). To get the correct ER values that represent the complete forest, the fluxes need to be weighted according to their contributions.

For example, during the night, the gradient is relatively large, and changes rapidly (blue area in Figure 3a) compared to the daytime (red area in Figure 3a). These large gradients during the night, are mainly caused by strengthening of the thermal stratification and somewhat by the surface fluxes. If we would focus on the gradient changes, we would therefore focus on the periods where the stability of the atmosphere changes fast and not focus on the periods where the surface fluxes are the largest (during mid-day). When determining the ER_{forest} of an ecosystem it is important to take into account the size of the flux as the largest flux contributes the most to the final ER_{forest}. However, during the day, the gradients are very small due to the more active turbulent mixing, while the fluxes are larger than during the night. Also, the transition periods (from gradient-dominant stable nocturnal conditions to flux-dominant convective diurnal conditions) takes place during the day. During these transitional periods it is recommended to be careful in using the vertical gradient.

During the night, the surface fluxes are relatively constant (Figure 6 in paper), and the slope of the gradients as in figure 3a would give a value of -1.028, which is close to the ER_{forest} value we derived for the night with the methods described in our paper. Applying this method during the night would not per se reduce our uncertainty, as our surface fluxes are already quite certain during the night.

We added additional information in lines 226 and 559 to further explain this, and to better highlight the difference to the methods of Ishidoya et al. (2015).

2) Slopes of the O_2-CO_2 fluxes

The other option is to apply a linear regression to the O_2 and CO_2 fluxes, as was suggested by the reviewer (Figure 3b). However, this approach also has three issues that we discuss here below, showing that this approach does not necessarily reduce the uncertainty.

First, we cannot combine the day and night measurements and calculate one average from all the values. This is because the surface fluxes of O_2 and CO_2 change sign between the night and day because the processes that happen, both biosphere and atmospheric, are different. By changing sign, the ER for the day and the night indicate different processes by which the surface is affecting the atmosphere. Where for example during the night, the surface fluxes deplete atmospheric O_2 and during the day increases atmospheric O_2. We therefore cannot average the ER signals. This also shows in the ER_{forest} values in table 3, where the ER_{forest} value of 24 hours is not the average of the day and the night value. This is the reason why we first average the surface fluxes over the entire day and then use these averaged surface fluxes to calculate the ER_{forest}.

Second, the linear regression between the O_2 and CO_2 flux should give a correct ER when there only one process active, which is the case during the night (blue area in figure 3b). However, during the night the surface fluxes are quite constant in time, and it is therefore difficult to derive the linear regression, as most data points are close together. The derived slope (and resulting ER) becomes then sensitive to outliers.

Third, when two processes occur at the same time (during the day: red area in figure 3b), a linear regression would result in an average ER for the period we selected but ignores the fact that there are time steps with larger fluxes and thus should have a larger impact on the final ER. This is the same problem as described for the gradients above. Linear regressions for the day-time period (09:00-17:00) for the gradients (figure 3a) and the fluxes (figure 3b) would roughly give the same value for the slopes: -1.85 and -1.87 respectively. However, this should not be the case, as we showed above that the gradients and fluxes do not represent the same information.

Based on these arguments, we have chosen our method as described in the paper to calculate the ER_{forest} based on the average of the fluxes, giving, giving a weighted value of the ER_{forest} signal. We have elaborated more on this point and therefore added some text in lines 398 + 552 + 559.

4) Figure 4: Do the error bars indicate standard error? Please specify.

We agree with the reviewer that it is unclear throughout the text how exactly we determine the error bars in the figures and the resulting uncertainty values of the different ER signals. We therefore added extra information to the methods section that explains how we determined the error bars and the uncertainties of our data, see lines 166 + 192, and the added equation 4 after line 192.

We also added this extra information to the caption of figure 4 on how the error bars in figure 4b are determined, together with extra text in lines 332, 380 and 401.

5) Figure 7: The ER_{forest} is negative value in this figure, although it is defined as positive value throughout the paper. Please be consistent with the terms you use.

We agree with the reviewer that we were indeed not completely consistent with the negative or positive values of the ER_{forest} signals. We therefore changed figure 7, and updated the text accordingly where necessary.

6) I think it would be better to add the references and/or brief description of the EC method and temperature-based function used in this study, since comparison of EC method and O_2 method in Fig. 8 is an important topic.

We agree with the reviewer that we should elaborate a bit further how the data that we use from ICOS and how they approached the EC method. We therefore added the reference of Kulmala et al. (2019) and more text in lines 271.

7) The words "Eddy Covariance (EC)" appears repeatedly at line 30, 131, 227, and "Eddy Covariance fluxes" and "eddy-covariance CO_2 flux" also appear at line 429 and 634, respectively. I think it's better to use "EC" throughout the paper after the definition at line 30.

We agree with the reviewer that we can use only the term EC after introducing it in the introduction and do not have to write it completely out anymore after that. Therefore, we made sure that throughout the paper only EC is used to refer to the eddy covariance technique.

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