Responses to Referee 1

I think this is a good article and I'm happy with the authors response to my comments. As I was checking though this time I spotted a few typos that should be corrected, and I also think the final paragraph could benefit from being reworded. Other than that I think it can be published.

Thank you very much for your significant and useful comments on the paper "Measurement report: Method for evaluating CO_2 emissions from a cement plant using atmosphere $\delta(O_2/N_2)$ and CO_2 measurements and its implication for future detection of CO_2 capture signals" by Ishidoya et al. We have revised the manuscript, considering your comments and suggestions. Details of our revision are as follows. The line numbers denote those of the revised manuscript.

Line 10: I think "Continous observations of the atmospheric" should be "Continous observations of atmospheric"

Line 10: The words "Continuous observations of the atmospheric" have been changed to "Continuous observations of atmospheric", as suggested.

Line 18: I think "O_2 and CO_2 amount fractions changes" should be "O_2 and CO_2 amount fraction changes"

Line 18: The words "O_2 and CO_2 amount fractions changes" have been changed to " O_2 and CO_2 amount fraction changes ", as suggested.

Line 21: I'm pretty sure "OR" should be "ER"

Line 21: The "OR" has been changed to "ER".

Line 216: This line is missing a space "the7-months"

Line 229: The words "the7-months " have been corrected to "the 7-months ". Thank you for pointing it out.

Line 217: Should probably change "seven months" to "7 months" as the number is used everywhere else

Line 230: The words "seven months" have been changed to "7-months ".

Line 223/224: I think "If the short-term variations driven" should be "If the short-term variations were driven"

Line 236-237: The words "If the short-term variations driven" have been corrected to "If the short-term variations were driven".

Line 226: "biosperic" should be "biospheric"

Line 239: The typo “biosperic " has been corrected to “biospheric ".

Line 239: I think "(see 2.3 in details)" should be "(see details in section 2.3)"

Line 252: The words “see 2.3 in details" have been changed to “see details in section 2.3".

Line 259: "Februaty" should be "February"

Line 272: The typo “Februaty” has been corrected to “February”.

Line 263: I'm pretty sure "OR" should be "ER"

Line 276: The “OR” has been changed to “ER”.

Line 286: I think "which locates between" should be "which is located between"

Line 287: The words “which locates between” have been changed to “which is located between”.

Line 290: I think "also contributes to" should be "also contribute to"

Line 291: The words “also contributes to” have been changed to “also contribute to”.

Last paragraph: while I'm glad you've added in a limitations/next steps paragraph, I actually think it comes off as a bit negative, and that it could be improved with softer language, for example instead of saying "we need to do this" or "we should do this" say "this could be done". I rewrote this part to show what I mean.

Some of the more detailed variations in the CO2 amount fractions were not reproduced by the AIST-MM. This is at least partially due to the spatial resolution of the AIST-MM which limited its ability to reproduce air transport from a point source, such as the cement plant in the present study. In the future this work could be expanded on by using a higher resolution atmospheric transport model to improve the agreement between the observed and simulated CO2 amount fractions. An additional step could be developing a more accurate method for extracting y(CO2*) due only to cement production, especially for the period when air-sea O2 flux is substantial. This would improve the estimation of the amount of CO2 capture and/or CO2 leak around the observation site from an inversion analysis using the higher-resolution atmospheric transport model.

Lines 333-340: The sentences have been rewritten following your suggestion. Thank you for editing the sentences.

Appendix A title: I think "to evaluate an effect" should be "to evaluate the effect"

Line 358: The words “to evaluate an effect” have been changed to “to evaluate the effect”.

Figure 4b: The plot has "all" in the top right hand corner, which I don't think is necessary

Figure 4b: The word “all” has been removed.

Figure 4 caption: "μmol mol－1" isn't in bold and I think "both of data groups" should be "both of the data groups"

Figure 4 caption: Both words have been rewritten, as suggested.

Other point

Lines 30-31: We have added Liu et al. (2023) as a reference since they applied atmospheric O_2 measurements to evaluate urban CO_2 cycle recently.

Responses to Referee 2

I would like to thank the authors for taking my comments into consideration and adjusting the paper accordingly. The paper has improved significantly. The validation of the model in Figure 4 strengthened the study, by showing that the transport model performs well. The addition of some examples in the main text and adding the equations to the method sections improved the readability of the paper. The analysis of mixing different signals with specific ER signals has also improved. However, on this last point still some improvement could be made. Therefore I would like to ask the authors to take the following points into consideration.

Thank you very much for your significant and useful comments on the paper "Measurement report: Method for evaluating CO_2 emissions from a cement plant using atmosphere $\delta(O_2/N_2)$ and CO_2 measurements and its implication for future detection of CO_2 capture signals" by Ishidoya et al. We have revised the manuscript, considering your comments and suggestions. Details of our revision are as follows. The line numbers denote those of the revised manuscript.

There is still some discrepancy on how the term Exchange Ratio (changed from Oxidative Ratio of the previous paper) is used. Now ER is used everywhere, however fossil fuel ER values are closely linked to OR signals. I would recommend to carefully evaluate when each term should be used. The ER should be used when describing measurements in the atmosphere and what is exchanged between the surface and the atmosphere, the OR is more related to the processes/oxidation of the fossil fuel burning itself.

Lines 37-41: Following sentences have been added considering your comments.

"It is noted that the words "Oxidative Ratio (OR)" has also been widely used in by the same definition as ER. Strictly speaking, there is a distinction in the terminology between ER and OR; the ER indicates the exchange between the atmosphere and organisms or ecosystems while the OR indicates the stoichiometry of specific materials (Faassen et al., 2023). We use the ER throughout the present study conveniently, but the distinction should be kept in mind."

Line 211 of track changes document: The budget of the amount fractions of O2 and CO2 at RYO are determined by adding up the terrestrial biosphere activity, fossil fuel combustion and cement production. By focussing on short time scales the authors exclude the ocean and the three previously mentioned processes should cover the complete budgets of O2 and CO2. However, because the authors look at hourly time scale I wonder if entrainment of air from the free troposphere into the atmospheric boundary layer makes the budget calculation of O2 more complicated. Entrainment of O2 is not linked to an ER signal of one of the three previously mentioned budget processes, but the ER is rather a result of the difference between the boundary layer (mainly biosphere) and the free troposphere (combination

of fossil fuel and biosphere). This would result in a decoupling of the ER signals between the boundary layer and the free troposphere and can create a difference in behaviour of O2 compared to CO2 of the entrainment flux that cannot be linked to one specific ER signal. I am not sure if this could be easily checked. Would it be possible for the authors to add the validation of O2 from the transport model with the observations and see if there is a mismatch during the morning transition? Or would it be possible to transport O2 by linking the ER signals directly to the surface fluxes of CO2? This should make sure that the budget of O2 at RYO is calculated correctly.

Lines 154-164 and 342-356, and Fig. A1a-d: Following sentences have been added considering your comments. Figures A1a-d have also been added.

"In this regard, it should be noted that Faassen et al. (2023) carried out continuous observations of $\delta(O_2/N_2)$ and the CO_2 amount fraction at a forest site in Finland, and they found higher ER (referred to as "ER_{atmos}" in their study) than 2.0 during the morning transition for the average diurnal cycle in summer. Such high ER cannot be obtained from summing up the contributions of fossil fuel combustion and terrestrial biospheric activities at the surface, so that they suggested the ER signal not only represented the diurnal cycle of the forest exchange but also includes other factors, including entrainment of air masses in the atmospheric boundary layer before midday, with different thermodynamic and atmospheric composition characteristics. Considering their results, we examined average diurnal cycles of $\delta(O_2/N_2)$ and the CO_2 amount fraction at RYO in October 2017 and August 2018 (Fig. A1a-d in Appendix A). We found the ER values are close to 1 throughout the day both for the observed and simulated diurnal cycles. Therefore, we consider the entrainment of air masses do not change the ER at RYO substantially, and the atmospheric transport processes in the AIST-MM is appropriate to compare the observational results in the present study."

"Appendix A: Additional figures to evaluate the effect of entrainment of air mass on the observed ER

As we described in 2.2, Faassen et al. (2023) found higher ER ("ER_{atmos}" in their study) than 2.0 at a forest site in Finland during the morning transition for the average diurnal cycles of $\delta(O_2/N_2)$ and the CO_2 amount fraction in summer. On the other hand, Ishidoya et al. (2013) reported ER values ("ER_{atm}" in their study) close to 1 at a Japanese forest site in summer, for the average diurnal cycles throughout the day. Considering the discrepancy between Faassen et al. (2023) and Ishidoya et al. (2013), we derive the average diurnal cycle of $\delta(O_2/N_2)$ and the CO_2 amount fraction at RYO. For this purpose, deviations of $\delta(O_2/N_2)$ and the CO_2 amount fraction from their 24-hr mean values were calculated, and the $\Delta\delta(O_2/N_2)$ were converted to $\Delta y(O_2)$ by multiplying $X(O_2)$ (=0.2094). Figures A1a-b show the average diurnal cycles of $\Delta y(O_2)$ and $\Delta y(CO_2)$ in October 2017, and their relationship. Those for August 2018 are also shown in Figs. A1c-d. As seen from the figures, the observed $\Delta y(O_2)$ took maxima in the daytime, and the ER values for the average diurnal cycles at RYO were close to 1 throughout the day. The corresponding diurnal $\Delta y(O_2)$ and $\Delta y(CO_2)$ cycles and their relationships obtained from the simulated results by AIST-MM were also shown in Figs. A1a-d. Similar to the

observations, it was found that the simulated $\Delta y(O_2)$ took maxima in the daytime and the ER were close to 1 throughout the day. These facts indicate the observed ER at RYO can be reproduced by the AIST-MM generally, including the period during the morning transition. Therefore, an entrainment of air mass to yield high ER during the morning suggested by Faassen et al. (2023) may be a characteristic phenomenon at their observational site."

Line 274 of track changes document: I would recommend to re-evaluate this sentence; 'Therefore, it is considered that the ER lower than 1.05 indicates CO2 flux from cement production mixes with the surrounding air that has already been influenced by terrestrial biospheric activities or fossil fuels combustion.' The number 1.05 seems like a hard limit for me, because combining different processes of the biosphere and fossil fuels could also produce ER values lower than 1.05 and it seems that Figure 3 and 5 also show this. I appreciate that the authors added the discussion that combing the processes of photosynthesis and respiration could create an ER that is lower than 1.05. However they argue that this is not the case because ER signals lower than 1.05 always show a correlation with high CO concentrations. Based on Figure 3 and 5, I would argue that ER signals lower than 1.05 could also indicate mixing of fossil fuels with the biosphere or even changes in the ER signal of the biosphere itself because of still high correlation coefficients (Figure 5) or no peak of CO (Figure 3) during some events where the ER drops below 1.05. Adding a fossil fuel signal to a dominant biosphere signal produced by the surface could also create low ER signals (and not an ER between 1.1 and 1.4) because of mixing processes with an opposite flux for O2 and CO2 (same explanation as given in line 270). The high CO concentration would then indicate a fossil fuel signal rather than a cement signal. I would recommend to add the criteria that the correlation coefficient between O2 and CO2 should be lower than a specific value in combination with an ER signal lower than 1.05 as an indication for a cement production signal.

Lines 215-221 and Fig. 3c: Following sentences have been added considering your comments. $\Delta y(CO_2)$ values have also been added to Fig. 3c.

"On the other hand, when photosynthesis signal is larger than respiration signal, ER for the combination fluxes could be variable and potentially even become lower than 1.05. Therefore, we consider the observed low ER values with high $\Delta y(CO)$ and $\Delta y(CO_2)$ are attributed to substantial CO_2 flux from cement production, of which ER value is 0, rather than the photosynthesis signal. These characteristics can be seen from the typical ER, $\Delta y(CO)$ and $\Delta y(CO_2)$ in August 2018 plotted in Fig. 3c. Therefore, it is considered that the air mass having ER lower than 1.05 and $\Delta y(CO)$ and $\Delta y(CO_2)$ higher than 0 simultaneously indicates CO_2 flux from cement production mixes with the surrounding air that has already been influenced by terrestrial biospheric activities or fossil fuels combustion"

Figure 3c and Figure 5 bottom: The authors explain in the text that the ER signals in these figures are based on regression lines of successive 24-hour periods. It is not entirely clear to me what this means and what kind of implications this would have for the ER signals in the figures. Does successive mean a linear regression of the previous 24 hours of each point? If that is the case, then figure 3c and the bottom figure of 5 would give a false idea of an hourly ER signal because this figure looks at a 24 hour signal. Could this be clarified?.

In the manuscript, I did not write these figures give an hourly ER. The ER signals were 24 hour signal, obtained as slopes of the regression lines to the observed data during successive 24-h periods (before and after 12-h of each point). Therefore, the words "24-h periods (before and after 12-h of each point)" have been added to the caption of Fig. 3c.

Figure 4a: I highly appreciate the addition of this figure that validates the transport model. A minor recommendation would be to put 2017 on top of 2018 in the legend.

Figure 4a: The legends have been modified, as suggested.

Figure 6 and 7: There seems to be a circularity in the validation of the modelled CO2 cement amount fractions with the observed cement CO2 amount fractions. For the observed cement CO2 amount fractions the ER signals of only the biosphere and the fossil fuel signal is used (ER(bio+ff)). However, to acquire this signal a model is needed and therefore the authors attain this ER value from the model that they try to validate. I understand that this was the only way to get the ER(bio+ff) signal, however I would recommend to add a discussion about this as this circularity could falsely improve the validation results. Especially because the modelled total ER signal does not match well with the observed total ER signal (Figure 5 bottom). Could the authors add a discussion on this?.

Figure 7 and line 615: Based on figure 7 the statement is made in line 615 that either an ER(bio+ff) of 1.1 or 1.4 could be used to estimate the observed contribution of cement. I would argue that is only on the monthly timescale is analysed in the figure, but it is still debatable on shorter time scales. The previous analysis of the paper showed that the cement signals are visible on hourly or diurnal time scales. The paper also showed that on hourly and diurnal time scales both the total CO2 amount fraction and the total ER can change drastically. When moving from a hourly/diurnal to monthly time scale, the CO2 and ER signal could smoothen and therefore the variation in the ER signal does not matter that much. On these shorter time scales it could therefore still be important to have a variable ER signal. I would therefore recommend specifying clearly for which time scales the statements apply here.

We consider following revisions will answer above 2 comments simultaneously.

Lines 300-303 and 374-378, and Figs. B4a-b: Following sentences and figures have been added to clarify that we do not need to use any simulated value to calculate $y(CO_2^*)$ for the model validation,

and this is also applicable on shorter time scales.

"This is also applicable on shorter time scales (Figures B4a and B4b in Appendix B). Therefore, we can derive the observed $y(CO_2^*)$ at RYO is without using any simulated value by an atmospheric transport model, and the observed $y(CO_2^*)$ can be used to validate hourly to annual average CO_2 fluxes from cement production simulated by a fine-scale atmospheric transport model."

"Figures B4a and B4b show the bottom panels of Fig. 6 and A2a, respectively, but for adding the $\Delta y(CO_2^*)$ calculated by using the α_{B+F} values of 1.4 and 1.1. As seen from the figures, several hours to day-to-day variations in the $\Delta y(CO_2^*)$ did not change substantially depending on the α_{B+F} value used to calculate $y(CO_2^*)$. Therefore, the contribution of cement production to the atmospheric CO_2 amount fraction at RYO can be estimated from the observed $y(CO_2^*)$ by assuming an α_{B+F} value of 1.1 or 1.4, not only for monthly time scale but for shorter (hourly to day-to-day) time scale."

Other point

Lines 30-31: We have added Liu et al. (2023) as a reference since they applied atmospheric O_2 measurements to evaluate urban CO_2 cycle recently.