Responses to Referee 2

The objective of this paper is to examine if it is possible to detect a CO2 signal at a measurement station that is coming from a cement plant 6 km away, and to extract this specific atmospheric signal using continuous O2and CO2 measurements. It is important to have the ability to distinguish between different contributors to the atmospheric signal of CO2, which gives the opportunity to study different carbon sources and sinks separately and verify CO2 emissions. This paper studies the short term relationship between O2 and CO2 and their resulting OR to detect a signal from the cement plant. The low OR signals that originate from air with a high CO concentration show that indeed a CO2 signal of the cement plant at this measurement location can be detected. By subtracting the CO2 signals of fossil fuel combustion and the biosphere from the total atmospheric CO2 signal, based on their combined OR signals, the variations in the CO2 signal caused by only the cement plant were shown with both the measurements and a regional atmospheric transport model. These results show the ability to use the relationship between O2 and CO2 to validate CO2 fluxes from a cement plant in a transport model and to use O2 as an indicator of possible leakages of carbon capture and storage locations.
This paper shows interesting and innovative results on how O2 can be used in this context and to validate models. This work is very relevant, as studies using atmospheric O2 are scarce and therefore there is much to be learned about this tracer. This study builds on previous work by e.g. Keeling et al. (2011), van Leeuwen and Meijer (2015) and Pak et al. (2016) and gets a step closer to understanding how the ratio between O2 and CO2could be used to detect leakages from carbon capture storage locations. This is done by combining data with models, which has not often been done before with atmospheric O2. I therefore find this study of importance and would recommend it for publication, taking into account the comments below. These are mainly focussed on clarification of the results, figures and the assumptions that are made in the paper.
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.

Major comments:
In line 31 the term exchange ratio (ER) is introduced as oxidative ratio (OR). However, OR is not correctly in all contexts used in the manuscript, as for example it does not apply to photosynthesis as O2 is produced there. I would recommend using ER instead. Note that there are several terms in use in the O2 community that all indicate the link between CO2 and O2 but on a different scale/process (e.g. ER, OR, alpha_B, ARQ).

The word "oxidative ratio" and "OR" have been changed to "exchange ratio" and "ER", respectively, throughout the paper, following your suggestion.

Furthermore, I would recommend to add further clarification about combining OR signals of different processes where the flux sign of O2 and CO2 are opposite. For example, in line 150 it is stated that a lower ER than 1.1 is observed and therefore shows an influence of the cement plant (which as an OR of 0). As this is probably the case, because the CO concentration is also high with these lower OR signals, I still think it is important to discuss what could happen when fluxes with different ER mix and that a ER lower than 1.1 does not directly indicate that a process is contributing with an ER lower then 1.1. When for example air from the biosphere (depleted in CO2, high in O2 and ER of 1.1) mixes with air that is mainly influenced by fossil fuel (high in CO2, depleted in O2 and ER around 1.4) you do not necessarily get an averaged ER of (1.1 + 1.4)/2 = 1.25 or necessarily between 1.1 and 1.4. With a large photosynthesis signal the ER could potentially even become lower than 1.1, whereas with a large fossil fuel signal, the ER would more likely be in between 1.1 and 1.4.
Lines 196-209, Fig. 3b, c: The sentences and figures have been added to discuss about combining OR signals of different processes. The sentences are as follows.
"We also plotted the ER values calculated by least-squares fitting of regression lines to the observed $\Delta y(O_2)$ and $\Delta y(CO_2)$ values during successive 24-h periods in Fig. 3b. As seen in the figure, both ER values higher and lower than 1.1 were observed throughout the observation periods. When terrestrial biosphere emits CO_2 to the atmosphere, i.e. respiration signal is larger than photosynthesis signal, the ER values ranging from 1.05 to 2.00 are expected from combination fluxes of terrestrial biospheric activities, gas, liquid, and solid fuels combustion. Similar ER values have been observed at other Japanese sites (e.g. Minejima et al., 2012; Goto et al., 2013; Ishidoya et al., 2020).
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. However, we consider the observed low ER values are attributed to substantial CO_2 flux from cement production, of which ER value is 0, rather than the photosynthesis signal because the low ER values and high $\Delta y(CO)$ appeared simultaneously. These characteristics can be seen from the typical ER and $\Delta y(CO)$ in August 2018 plotted in Fig. 3c. Therefore, it is considered that the ER lower than 1.05 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. Similar characteristic relationships have previously been observed only in artificial CO_2 release experiments of which ER value is 0, such as those described by van Leeuwen and Meijer (2015) and Pak et al. (2016)."

Another point in the text where this applies is equation 4, where alpha_B+F is indeed an ER of the atmosphere without cement production (line 186), but not as the term seems to indicate an average of the ER of the biosphere and fossil fuel.

Lines 161-163 and Lines 233-235: The α_{B+F} is not an average of the ER of the biosphere and fossil fuel, but monthly average ER values calculated from the simulated O_2 and CO_2 values without considering the contribution of cement production. Therefore, we have modified the sentences as follows. "For α_{B+F} values, we use monthly average ER values calculated from the simulated O_2 and CO_2 values without considering the contribution of cement production (black dotted line in Fig. 5, bottom, discussed below)" and "Both the observed ER values and those simulated are frequently lower than 1.1, while the ER values simulated without including cement production show lower values than 1.1 occasionally (Fig. 5 and Fig. A1a-f in Appendix A)".

In line 172 it is also not clear to me how the authors converted. From the text it seems that the atmospheric mole fractions of CO2 are converted to O2 with the ER. However, these relationship between CO2 and O2 are for the surface fluxes. Could you please specify how the ER based on the surface fluxes or process level could relate directly to the atmospheric mole fractions?

Lines 147-149: The sentences have been rewritten as follows to make the meaning clearer. "For this purpose, O_2 amount fractions are calculated by summing up the respective contributions of CO_2 amount fractions for fossil fuel combustion, terrestrial biospheric activities, and cement production multiplied by the –ER values of –1.4, –1.1, and 0. Here the 1.4 and 1.1 are typical ER for fossil fuel combustion and terrestrial biospheric activities, respectively".

Overall, I do not think something is necessarily wrong in the method, but the formulation could be more precise and a discussion about mixing different atmospheric ER signals could possibly be added. A validation of the atmospheric transport model and with that the input of the fluxes, together with a validation of the data itself is currently missing. For example, in line 234 it is stated that the complex topography can influence the model results in this area for February 2018. It is not clear why this is only the case in this month, and it would be good to see further details and validation.

We have found a mistake in the analysis of the $y(CO_2^*)$ in February 2018. In the revised manuscript, discrepancy between the monthly means of $y(CO_2^*)$ anomalies and $y(CO_2\text{, cement})$ is not so serious, so that we have removed the sentence you pointed out.

In line 162-165 it is stated that the observed and modelled CO2 amount fractions showed weak correlation and that the general characteristics are observed but not the phase and the amplitude. This is not visible in Figure 4. Could you please elaborate more on this? Maybe by showing a graph that shows the relationship between CO2 modelled and observed?

Lines 212-221 and Fig. 4: Following sentences have been added to discuss validity of the atmospheric transport model. "Figure 4a shows monthly average of hourly CO_2 amount fraction is slightly overestimated at night and underestimated in the daytime except for February, however, absolute value of the difference is less than 2 μmol mol^{-1} in most case. Figure 4b is a scatter plot of the difference from 391.14 μmol mol^{-1} (the minimum concentration of observed CO_2 in the7-months) between calculated and observed concentration for all the hourly data in the seven months. FAC2 (fraction of calculations within a factor 2 of observations) is 0.976, where model acceptance criterion of FAC2 is greater than 0.5 (Hanna and Chang, 2012), and Pearson's correlation coefficient is 0.69. The discrepancies between observed and simulated values can be attributed to the limited resolution of the model in the complex terrain, or to problems in the parameterization of transport processes, or in the CO_2 sources/sinks incorporated into the AIST-MM".

In line 210-215, it is stated that y(CO2*) could be used to validate this transport model. However, I miss here a discussion/validation how accurate y(CO2*) is before it could be used to validate the model. Is there a way to validate how accurate the O2 method is to extracting the cement signal from the CO2 atmospheric signal? This would help strengthen the argument that this O2 based methods works well to capture such a signal.

Lines 270-281, 338-341 and Fig. A3: We consider it is difficult to validate the O_2 method itself directly. Instead, we have expanded the discussion about a comparison between the observed $y(CO_2^*)$ anomalies and simulated $y(CO_2$, cement) as follows. "We have also confirmed monthly mean $y(CO_2$, cement) values were related to the occurrence of northwesterly winds (i.e. wind blowing from the cement plant). However, the average wind direction simulated by the AIST-MM when high $y(CO_2$, cement) values appeared (around 300°) was slightly but systematically different from that for observed wind direction (around 270°) (Fig. A3a and A3b in Appendix A). This discrepancy is probably due to the underestimation of the altitude of Ryori ridge which locates between the cement plant and the RYO site. Such the underestimation makes it easy to transport the CO_2 emitted from the cement plant directly to RYO over the ridge since the cement plant is located around 300° from the RYO site. This is also consistent with the fact that the larger monthly mean $y(CO_2$, cement) than the monthly mean $y(CO_2^*)$ anomalies are found in January and February when prevailing wind direction is northwesterly. The complex terrain around RYO such as Ryori ridge would also contributes to the discrepancy between the monthly mean $y(CO_2^*)$ anomaly and $y(CO_2$, cement) in May and August at least partly. In May, it is considered that an effect of the oceanic O_2 flux on $y(CO_2^*)$ anomaly is also substantial, since we can distinguish short-term variations in $\delta(O_2/N_2)$ without simultaneous changes in CO_2 amount fraction (Fig. A1e)."

Something that was not clear for me, was why a baseline was subtracted from y(CO2*)? Was this done to exclude the effect of the ocean? If so, does this mean that the ocean signal was already excluded in equation 4 (to calculate y(CO2*)) by using the Δ values of CO2 and O2? If this was not the case, does this mean that the results of Δy(O2) and Δy(CO2) are still affected by the ocean and that for example

Figure 3 should be interpreted more carefully as in line 222 it is given that ocean exchange can significantly influence the observations? Could you please elaborate on this and indicate more precisely why for both y(CO2*) and Δy(CO2) a baseline is subtracted? And add further discussion on the influence of the ocean exchange on the results?

Equation 4 and Fig. 6: We have removed "Δ" from eq. 4 to avoid confusion, considering your comments. In this regard, we use Δ in Fig. 6, as the meaning shown in the caption: "Variations in $\Delta y(CO_2^*)$ calculated from the observed CO_2 amount fractions and $\delta(O_2/N_2)$ (black filled circles) in October 2017, and the baseline variation (blue solid line). Δ denotes deviations from their monthly mean values."

The terms Dy(O2) and Dy(CO2) and y(CO2*) are not clear, and especially the 'y' is not clearly explained and this can lead to confusion for the reader. I would recommend not using these terms and changing this throughout the manuscript, as it makes the paper more difficult to read very quickly or to interpreted the figures on their own. Also, the definition used now does not always seem consistent, as e.g. in Figure 4 the top and middle panels y-axis are both y(CO2), but these do not have the same units. Maybe the current abbreviations that indicate the different kind of CO2 signals could be changed into abbreviations that are more distinguishable. For example, the CO2,cement is more clear

We understand your suggestion, however, I have used the "*y*" following the Editor's comment. At lines 157-158, we describe the meaning of *y* as "Here, *y* stands for the dry amount fraction of gas, as recommended by the IUPAC Green Book (Cohen et al., 2007)". The middle panel y-axis in Fig. 5 (Fig. 4 in ACPD) has been changed to $\Delta y(CO_2)$, considering your comments.

There are quite some subplots in each figure and not every subplot is indicated with a letter or legend. This makes reading the figures confusing. Next to that, the amount of subfigures for each month makes it difficult to see all the details. For example, the statements in lines 157 and 193 are difficult to see in the figures. I also think the monthly figures do not contribute to the story. I would recommend moving part of Figure 4 and 5 in the appendix and only focus on one month to make your conclusions from them more clear.

We have chosen an example month and moved the others to the supplement and added needed legends to all the figures, following your suggestion.

Minor comments:

Title: the title of this paper could be improved. I do not think this paper is a measurement report, but rather a new method to detect cement signals. Also, the authors do not apply this method to detect carbon capture signals. It would be good to remove these points from the title and focus it in the core of the paper which is detecting cement signal.

We understand your suggestion, however, I wrote the phrase "measurement report" following the Editor's comment. Therefore, we have revised the title considering your suggestion as follows: "Measurement report: Method for evaluating CO_2 emissions from a cement plant using atmospheric $\delta(O_2/N_2)$ and CO_2 measurements and its implication for future detection of CO_2 capture signals".

Line 10: I would recommend using δ(O2/N2) instead of O2/N2 ratios (throughout the manuscript).
The words O_2/N_2 ratio have been changed to $\delta(O_2/N_2)$ throughout the paper, as suggested.

Line 14: please change 'amount fraction' to mole fraction (throughout the text).
We recognize "mole fraction" you suggested are more familiar with our research field, however, I have used the phrase following the Editor's comment.

Line 43: Friedlingstein et al. (2020) should be updated to Friedlingstein et al. (2022).
Line 44: "Friedlingstein et al. (2020)" has been updated to "Friedlingstein et al. (2022)", as suggested.

Line 43-44: The value given for the contribution of cement to the global fossil fuel CO2 emission (4%), is not correct, and is 2% for the recent decade. Also, this value is not based on atmospheric O2/N2 ratios as suggested in the text by the reference to Manning and Keeling, 2006.
Line 44: "about 4 % of… " has been changed to "about 2 % of… ", as you pointed out. The words "…and this value is included in global CO_2 budget analyses based on the atmospheric O_2/N_2 ratio (e.g. Manning and Keeling, 2006)" have been deleted to avoid confusion.

Line 52: 'Leeuwen and Meijer' should be 'van Leeuwen and Meijer'.
Line 53: "Leeuwen and Meijer" has been changed to "van Leeuwen and Meijer".

Line 70: Please specify at what height the measurements were taken and what the surface below the measurement tower consists of, and include references to previous work of the O2 measurements done here, including e.g. the precision and accuracy of the measurements etc.
Line 73 and 95, lines 92-111: The altitude of the RYO is 260 m a.s.l. (line 73). Sample air was taken at the tower heights of 20 m using a diaphragm pump (line 95). The sentences to describe the details of the O_2 measurements have been added (lines92-111).

Methods section: Some details were missing in the methods, but were eventually discussed in the results. For example: the methods to determine if a cement signal was seen in the data and how the cement signal was extracted from the model/data (lines 179-199 and equations 4 and 5). Please move this to the methods.

Lines 152-174: The sentences and equations you pointed out have been modified and moved to methods section.

Line 96: How was the reproducibility of 5 per meg determined? Please specify.

Lines 106-108: The sentence has been modified to describe how we determined the reproducibility as "The analytical reproducibility of the $\delta(O_2/N_2)$ and CO_2 amount fraction measurements by the system was determined by repeated measurements of standard gas and found to be about 5 per meg and 0.06 $\mu mol\ mol^{-1}$, respectively, for 2-minute-average values".

Please include which WMO scale was used (X2019?)?.

Line 114: The words "WMO scale" have been changed to "the WMO scale (X2007)".

Line 111: Can you include the domain in figure 1?.

Figure 1: The inner and outer domains have been included in the figure.

Line 145: Why did you choose for 1-week to subtract from the measurements? How did you determine this specific time frame?

Lines 192-194: The period is not necessarily to be 1-week, but it should be longer than short-term variations due to local effects of cement production. We have modified the sentences as follows to make the meaning clearer. "In this study, we focused on the short-term variations in $\delta(O_2/N_2)$ and the CO_2 and CO amount fractions (Fig. 2) to extract local effects of cement production. Therefore, we subtracted 1-week rolling average values of $\delta(O_2/N_2)$ and the CO_2 and CO amount fractions from the observed values to exclude their baseline variations…".

Line 145-149: It is not clear to me how the authors reached this conclusion. How many points were used to determine the OR signals that could be seen in Figure 3? Are these lines based on only 2 values? Could you please specify this?

Lines 193-201, Fig. 3a, b: The sentences have been rewritten as follows to make the meaning clearer. "Therefore, we subtracted 1-week rolling average values of $\delta(O_2/N_2)$ and the CO_2 and CO amount fractions from the observed values to exclude their baseline variations, and examined the relationships among the residuals ($\Delta y(O_2)$, $\Delta y(CO_2)$, and $\Delta y(CO)$; Fig. 3a). Here, $\Delta y(O_2)$ is the equivalent value in $\mu mol\ mol^{-1}$ converted from $\delta(O_2/N_2)$. We also plotted the ER values calculated by least-squares fitting of regression lines to the observed $\Delta y(O_2)$ and $\Delta y(CO_2)$ values during successive 24-h periods in Fig. 3b. As seen in the figure, both ER values higher and lower than 1.1 were observed throughout the observation periods. When terrestrial biosphere emits CO_2 to the atmosphere, i.e. respiration signal is larger than photosynthesis signal, the ER values ranging from 1.05 to 2.00 are expected from combination fluxes of terrestrial biospheric activities, gas, liquid, and solid fuels combustion. Similar ER values have been observed at other Japanese sites (e.g. Minejima et al., 2012; Goto et al., 2013; Ishidoya et al., 2020)."

Line 163: Are these the monthly average correlations?

We have removed the related sentence. Instead, the sentences have been added to discuss validity of the atmospheric transport model (Lines 212-221 and Fig. 4).

Line 190-192: How valid is your assumption that ocean fluxes are not influencing the results?

We cannot validate it completely. However, as we described in lines 164-174, $y(CO_2^*)$ anomaly obtained by subtracting the baseline variation is considered to indicate CO_2 changes due mainly to the contribution of the cement production since temporal variations in $\delta(O_2/N_2)$ due to the contribution of oceanic signal are generally slower than that of the cement production.

Line 208: Does this statement mean that you miss some of the CO2 signal of the cement plant in Figure 5? Please specify.

Lines 248-249: The sentence has been rewritten as follows to make the meaning of "overall ER" clearer. "This means CO_2 is presumably released as well, so that the overall ER for the CO_2 emitted from cement plant (cement production + fossil fuel combustion) would not be 0."

Line 222: Here, it is mentioned that the ocean fluxes can significantly influence the observed signals. See the major point above, and my comment at line 190-192, and please address this point in the discussion of the paper.

As we mentioned above, we cannot validate it completely whether the oceanic flux effect is excluded enough or not. This is a limitation of our method, so that we have add sentences "Therefore, as a next step, we should use higher-resolution atmospheric transport model to improve an agreement between the observed and simulated CO_2 amount fractions. It is also needed to develop more accurate method to extract $y(CO_2^*)$ due only to cement production especially for the period air-sea O_2 flux is substantial" (lines 321-324). We consider the oceanic flux effect is substantial in May, 2018 since we can distinguish short-term variations in $\delta(O_2/N_2)$ without simultaneous changes in CO_2 amount fraction (Fig. A1e) (lines 279-281).

Line 234: Why is the complicated topography only a problem in February 2018 and not in other months? And can this fully explain the difference between simulated and observed signals, also for other months? This issue needs more explanation.

As we replied to your major comments, we have found a mistake in the analysis of the $y(CO_2^*)$ in

February 2018. In the revised manuscript, discrepancy between the monthly means of $y(CO_2^*)$ anomalies and $y(CO_2$, cement) is not so serious, so that we have removed the sentence you pointed out.

Lines 241-247: The link between the method presented here to detect the cement plant emissions and detection of leakages from carbon capture sites is made several times throughout the paper. During this study it is made clear that with the help of CO we could see if the air came from fossil fuel sources or the cement plant. However, there would be no source of CO when the method is applied to detect carbon capture leakages. The method would work for carbon capture from a flue gas (line 60). I think it is good to make a distinction of when CO needs to be used, as it is quite an important component of this research.

Lines 288-290: The sentences "It should be also noted that we did not use CO amount fraction for the calculation of $y(CO_2^*)$. This is an important advantage to apply $y(CO_2^*)$ to detect CO_2 capture and/or CO_2 leak which do not emit CO." have been added to indicate the method works without help of CO.

Line 217: I wonder if there is a way to go from the CO2 anomalies caused by the cement plant (figure 5) to the emissions of the cement plant. As this could be a crucial step to use this approach for emission verification. Could you discuss this?

Could you please separate the results and discussion sections, including several subsections, and rewrite the summary section to a conclusion section?

Lines 319-325: Following sentences have been added to discuss future tasks needed to estimate the emission of the cement plant from the observed and simulated CO_2 anomalies.

"As a remaining topic, we point out the fact that detail variations in the CO_2 amount fraction were not reproduced by the AIST-MM enough. This is due to insufficiency of spatial resolution of the AIST-MM at least partly, to reproduce air transport from a point source such as the cement plant in the present study. Therefore, as a next step, we should use higher-resolution atmospheric transport model to improve an agreement between the observed and simulated CO_2 amount fractions. It is also needed to develop more accurate method to extract $y(CO_2^*)$ due only to cement production especially for the period air-sea O_2 flux is substantial. Such improvement will make it possible to estimate amounts of CO_2 capture and/or CO_2 leak around the observation site from an inversion analysis using the higher-resolution atmospheric transport model."

We have changed the "summary" section to a "conclusions" section, as suggested. We leave the "results and discussion" section as it is, since we think the reader can follow it without separating into subsections. Instead, we have moved some sentences to the method section from the results and discussion section, as you suggested above, and separated the method section into subsections.