Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
https://doi.org/10.5194/acp-2022-570-RC2, 2022
© Author(s) 2022. This work is distributed under
the Creative Commons Attribution 4.0 License.

Comment on acp-2022-570

Anonymous Referee #2

Referee comment on "Measurement report: Method for evaluating CO_2 emission from a cement plant by atmosphere O_2 / N_2 and CO_2 measurements and its applicability to the detection of CO_2 capture signals" by Shigeyuki Ishidoya et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-570-RC2, 2022

Review of “Measurement report: Method for evaluating CO_2 emission from a cement plant by atmosphere O_2/N_2 and CO_2 measurements and its applicability to the detection of CO_2 capture signals” by Ishidoya et al.

The objective of this paper is to examine if it is possible to detect a CO_2 signal at a measurement station that is coming from a cement plant 6 km away, and to extract this specific atmospheric signal using continuous $O_2$and CO_2 measurements. It is important to have the ability to distinguish between different contributors to the atmospheric signal of CO_2, which gives the opportunity to study different carbon sources and sinks separately and verify CO_2 emissions. This paper studies the short term relationship between O_2 and CO_2 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 CO_2 signal of the cement plant at this measurement location can be detected. By subtracting the CO_2 signals of fossil fuel combustion and the biosphere from the total atmospheric CO_2 signal, based on their combined OR signals, the variations in the CO_2 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 O_2 and CO_2 to validate CO_2 fluxes from a cement plant in a transport model and to use O_2 as an indicator of possible leakages of carbon capture and storage locations.

This paper shows interesting and innovative results on how O_2 can be used in this context and to validate models. This work is very relevant, as studies using atmospheric O_2 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 O_2 and CO_2could 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 O_2. 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.

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 O_2 is produced there. I would recommend using ER instead. Note that there are several terms in use in the O_2 community that all indicate the link between CO_2 and O_2 but on a different scale/process (e.g. ER, OR, alpha_B, ARQ). Furthermore, I would recommend to add further clarification about combining OR signals of different processes where the flux sign of O_2 and CO_2 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 CO_2, high in O_2 and ER of 1.1) mixes with air that is mainly influenced by fossil fuel (high in CO_2, depleted in O_2 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. 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. 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 CO_2 are converted to O_2 with the ER. However, these relationship between CO_2 and O_2 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? 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. In line 162-165 it is stated that the observed and modelled CO_2 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 CO_2 modelled and observed? In line 210-215, it is stated that $y(CO_2^*)$ could be used to validate this transport model. However, I miss here a discussion/validation how accurate $y(CO_2^*)$ is before it could be used to validate the model. Is there a way to validate how accurate the O_2 method is to extracting the cement signal from the CO_2 atmospheric signal? This would help strengthen the argument that this O_2 based methods works well to capture such a signal.
- Something that was not clear for me, was why a baseline was subtracted from $y(CO_2^*)$? 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 $y(CO_2^*)$) by using the â□□ values of CO_2 and O_2? If this was not the case, does this mean that the results of â□□$y(O_2)$ and â□□$y(CO_2)$ 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 $y(CO_2^*)$ and â□□$y(CO_2)$ a baseline is subtracted? And add further discussion on the influence of the ocean exchange on the results?

- The terms $Dy(O_2)$ and $Dy(CO_2)$ and $y(CO_2^*)$ 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 $y(CO_2)$, but these do not have the same units. Maybe the current abbreviations that indicate the different kind of CO_2 signals could be changed into abbreviations that are more distinguishable. For example, the $CO_{2,cement}$ is more clear.
- 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.

Last, I have some minor comments. They are again mainly focussed on clarification but are more specific.

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.
- Line 10: I would recommend using $\delta(O_2/N_2)$ instead of O_2/N_2 ratios (throughout the manuscript).
- Line 14: please change 'amount fraction' to mole fraction (throughout the text).
- Line 43: Friedlingstein et al. (2020) should be updated to Friedlingstein et al. (2022).
- Line 43-44: The value given for the contribution of cement to the global fossil fuel CO_2 emission (4%), is not correct, and is 2% for the recent decade. Also, this value is not based on atmospheric O_2/N_2 ratios as suggested in the text by the reference to Manning and Keeling, 2006.
- Line 52: 'Leeuwen and Meijer' should be '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 O_2 measurements done here, including e.g. the precision and accuracy of the measurements etc.
- 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.
- Line 96: How was the reproducibility of 5 per meg determined? Please specify.
- Line 101: Please include which WMO scale was used (X2019?)?
- Line 111: Can you include the domain in figure 1?
- Line 145: Why did you choose for 1-week to subtract from the measurements? How did you determine this specific time frame?

- 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?
- Line 163: Are these the monthly average correlations?
- Line 190-192: How valid is your assumption that ocean fluxes are not influencing the results?
- Line 208: Does this statement mean that you miss some of the CO_2 signal of the cement plant in Figure 5? Please specify.
- 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.
- 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.
- 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.
- Line 217: I wonder if there is a way to go from the CO_2 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?