Reviewer two comments

Manuscript Number: essd-2023-129

Title: 12 years of continuous atmospheric O_2, CO_2 and APO data from Weybourne Atmospheric Observatory in the United Kingdom

Authors: K. E. Adcock, P. A. Pickers, A. C. Manning, G. L. Forster, L. S. Fleming, T. Barningham, P. A. Wilson, E. A. Kozlova, M. Hewitt, A. J. Etchells, and A. J. Macdonald

General comments:

The authors of this study present high-quality record of the atmospheric CO_2, O_2, and APO data observed at Weybourne Atmospheric Observatory (WAO) in UK for decadal period between May 2010 and December 2021. They carefully assess the stability of CO_2 and O_2 scales and the repeatability and compatibility based on the measurements of variety of cylinders including intercomparison round robin cylinders, Target Tanks, Zero Tanks, Working Secondary Standards and so on. These results reveal that the data at WAO have high quality and significantly reliable. They also investigate the characteristic features of the trend, seasonal cycles, and diurnal variations of CO_2, O_2, and APO. The data at WAO would contribute to various studies including the global carbon cycle, air-sea gas exchanges and so on. I found that the paper is well written and contains material that should be published in Earth System Science Data. I highly recommend the manuscript to be published with the minor corrections as suggested below.

We thank the reviewer for their positive review and assessment of our manuscript which has helped us to improve the text and figures. We will address the points raised below.

Specific comments:

1. Page 2, line 51: The authors described that a standard with a known O_2/N_2 ratio is used to report the change in atmospheric O_2/N_2 ratio. Is it possible to show the exact number of the O_2/N_2 ratio of the standard scale of this study?

We realise that the way this is written is misleading, so we have changed this sentence from:

> As such, atmospheric O_2 mole fractions are typically reported as changes in the ratio of O_2 to N_2, relative to a standard with a known O_2/N_2 ratio.

To:

> As such, atmospheric O_2 mole fractions are typically reported as changes in the ratio of O_2 to N_2, relative to a reference O_2/N_2 ratio. This study uses a O_2/N_2 reference derived from a suite of compressed air reference gases stored in high-pressure tanks and maintained but the Scripps Institution of Oceanography, U.S.A. (SIO; Sect. 2.2; Keeling et al., 2007).

2. Page 2, line 52: I think the sentence "O_2 and N_2 mole fractions are affected by changes in trace gases" is a little misleading. The major atmospheric components like O_2 and N_2 are affected by the change in the total amount of the air caused by changes in any atmospheric components, which is called as a dilution effect. Therefore, O_2 mole fraction is affected not only by trace gases, such as CO_2, but also O_2 itself. The dilution effect is, however, negligible for the trace gases. Therefore, the direct comparison between O_2 and CO_2 concentrations is rather confusing when they are expressed as mole fractions.

We agree with the reviewer and have changed this sentence from:

> O_2 and N_2 mole fractions are affected by changes in trace gases, such as CO_2, since mole fractions are relative to the total amount and therefore changing the total number of molecules in the air will make it appear as if the amount of O_2 and N_2 are changing even when they are not. Reporting O_2 as the O_2/N_2 ratio circumvents this issue.

To:

> Since mole fractions are relative to the total amount of air, changing the total number of molecules, for example by changing the number of CO_2 molecules, will make it appear as if the amount of O_2 and N_2 are changing even when they are not. This dilution effect is problematic for O_2 and N_2 because they are not trace gases, however, reporting O_2 as the O_2/N_2 ratio circumvents this issue. The dilution effect also exists for trace gases but has a negligible effect.

3. Page 2, line 56-57: As far as I know, a mass spectrometric method, which is adopted by many laboratories, directly measure the O_2/N_2 ratio.

CO_2 still needs to be measured to do a correction even when using a mass spec. So, this sentence needs to be changed as the point about measuring CO_2 is not really dependent on whether the O_2/N_2 ratio is measured directly or not.

We have changed this sentence from:

> In practice most analytical techniques in use do not measure the O_2/N_2 ratio directly and therefore when measuring O_2, CO_2 must also be measured concurrently, and a correction applied to account for changes in CO_2.

To:

> When measuring O_2, CO_2 must also be measured concurrently, and a correction applied to account for changes in CO_2.

4. Page 2, line 58-59: The authors describe that O_2 variations are refer to as O_2 mole fraction changes rather than $\delta(O_2/N_2)$ ratio changes in this manuscript. But $\delta(O_2/N_2)$ ratios are used in the most of this manuscript.

It's common in the literature to refer to atmospheric $\delta(O_2/N_2)$ measurements as O_2 mole fractions to simplify the text and because some methods do not measure the $\delta(O_2/N_2)$ ratio directly.

A couple of examples of articles that refer to O_2 mole fractions are:

- Keeling, R. F.: Measuring correlations between atmospheric oxygen and carbon dioxide mole fractions: A preliminary study in urban air, 7, 153–176, https://doi.org/10.1007/BF00048044, 1988.
- Tohjima, Y., Machida, T., Watai, T., Akama, I., Amari, T., and Moriwaki, Y.: Preparation of gravimetric standards for measurements of atmospheric oxygen and reevaluation of atmospheric oxygen concentration, J. Geophys. Res. D Atmos., 110, 1–11, https://doi.org/10.1029/2004JD005595, 2005.

Per meg is the unit we use for O_2, in the same way that ppm is the unit we use for CO_2, whereas "O_2 mole fraction" is the name of what we are actually measuring in "ppm equivalent" units,

before we convert O_2 into per meg units. To make this clearer, the sentence about this has been shortened, from:

> For simplicity, in this paper we refer to O_2 variations as O_2 mole fraction changes rather than $\delta(O_2/N_2)$ ratio changes.

To:

> For simplicity, in this paper we refer to O_2 variations as O_2 mole fraction changes.

5. Page 5, Figure 2: I think it would be better to add an aspirator and a differential pressure transducer in the legend.

We agree with the reviewer and have added these two things to the legend in Figure 2.

6. Page 6, line 147-150: I'm curious about how to balance the pressures and flow rates between the sample air and WT air streams. In the manuscript, the authors described that the balance is manually achieved by adjusting the two needle valves. Is it possible to keep the balance for long period? In the Figure 2, the differential pressure transducer and the solenoid vale are connected to the "MKS" differential pressure gauge via green lines. Does it mean that the solenoid valve is automatically controlled to achieve the balance of the pressures between the sample air and WT air streams?

The two needle valves allow for fine control of the restriction on each side to ensure that the matched pressures do result in matched flows, however, we agree that the way this was written before gave the impression that the pressure balance is achieved manually, which is not correct. We have therefore changed this sentence from:

> This balance is achieved with a differential pressure transducer (MKS Instruments, model Baratron 223B, ±10 mbar full scale range) and the two manual needles (Brooks Instrument, model 8504) valves immediately downstream of the Ultramat (Fig. 2).

To:

> This balance is achieved with a differential pressure transducer (MKS Instruments, model Baratron 223B) which measures the pressure difference between the sample and WT air streams, and then adjusts the sample side pressure to match the pressure of the WT air using a fast-response solenoid valve (MKS Instruments Inc., 248A; Fig. 2).

7. Page 6, line 149-150: Is "the two manual needles valves" a typo?

We have removed this phrase. Please see the reply above.

8. Page 6, line 152: Does "A solenoid valve" correspond to "4-way switching valve" in Figure 2? Are those same things?

The 4-way switching valve is a type of solenoid valve, we have changed "A solenoid valve" to "A 4-way switching solenoid valve".

9. Page 6: I think it would be better to clarify the flow rates of the sample air and WT air in this section of "Analytical set up". I know the flow rate (about 100 ml/min) is mentioned in in line 599, but it would be better to mention it here too.

We agree with the reviewer and have added a sentence about the flow rate to this section.

> The system flow rate is established on the WT side of the system, to 100 mL/min using a mass flow controller (MFC, Fig. 2).

10. Page 8, line 189-190: Don't the authors use the interpolated calibration coefficients from the bracketing calibrations?

As mentioned in line 189-190, we use the calibration coefficients from the most recent calibration:

> With the exception of the CO_2 c-term, the calibration coefficients are redetermined every 47 hours, and then these new values are used until the next calibration.

11. Page 13, Figure 3: The shade of ±10 per meg range is unclear.

We have made the shading into a darker grey to make it more visible.

12. Page 14, line 340 (Figure 4 caption): "Target Tank (TT) measurements of CO_2 (top panel) and O_2 (bottom panel) at …"

We thank the reviewer for spotting this. We put them the wrong way around. We have now changed the caption so that it matches the figure.

13. Page 15, line 351-352: "… with slopes (in ppm $year^{-1}$ and per meg per $year^{-1}$ for CO_2 and O_2, respectively) …" "…each TT, for CO_2 (top panel) and O_2 (bottom panel) …"

We thank the reviewer for spotting this. We put them the wrong way around. We have now changed the caption so that it matches the figure.

14. Page 27, line 618-619: "Manning, 2001" is not listed in References.

We have added this reference to the reference list:

> Manning, A. C.: Temporal variability of atmospheric oxygen from both continuous measurements and a flask sampling network: Tools for studying the global carbon cycle, Ph.D. thesis, University of California, https://cramlab.uea.ac.uk/Publications.php, 2001.

15. Page 33, line 725-726: It would be better to clarify what the ranges in the parentheses mean. Are they 95% confidence intervals?

Yes, this is correct. We have amended the sentence as follows:

> On average, atmospheric CO_2 at WAO increased by 2.40 ppm yr^{-1} (2.38 to 2.42; 95% confidence intervals), atmospheric O_2 decreased by 24.0 per meg yr^{-1} (24.3 to 23.8) and APO decreased by 11.4 per meg yr^{-1} (11.7 to 11.3).

16. Page 35, line 767-768: I think that the effect derived from seasonal and/or diurnal covariance between surface fluxes and atmospheric transport including PBL dynamics is termed as rectification effect. The seasonal cycle of PBL height itself isn't termed as the rectification effect.

We have removed the phrase “called the seasonal rectifier effect” from this sentence and have changed it from:

> There is also a seasonal cycle in the height of the atmospheric boundary layer, called the seasonal rectifier effect, that influences all three species (Stephens et al., 2000).

To:

> There is also a seasonal cycle in the height of the atmospheric boundary layer, that influences all three species (Stephens et al., 2000).

17. Page 46, line 1036-1037: “Stephens, B. B., …, 2000” has been already listed in line 1033-1035.

We thank the reviewer for noticing this error. We have removed the duplicate reference.