Referee comment on "Two decades of flask observations of atmospheric δ(O₂/N₂), CO₂, and APO at stations Lutjewad (the Netherlands) and Mace Head (Ireland), and 3 years from Halley station (Antarctica)" by Linh N. T. Nguyen et al., Earth Syst. Sci. Data Discuss., https://doi.org/10.5194/essd-2021-213-RC2, 2021

Review of “Two decades of flask observations of atmospheric δ(O₂/N₂), CO₂, and APO at stations Lutjewad (the Netherlands) and Mace Head (Ireland), and 3 years from Halley station (Antarctica)” by Nguyen et al.

In this paper, the authors present 20 years of observational δ(O₂/N₂) and CO₂ data obtained at three ground-based stations. They also present a detailed description of the calibration procedures of their δ(O₂/N₂) scale over 15 years. The δ(O₂/N₂) scale was confirmed to be stable enough to estimate global ocean and land CO₂ sinks based on the long-term trends in the observed δ(O₂/N₂) and CO₂. It is important to validate the global CO₂ budget, reported by Global Carbon Project, using independent estimations such as those reported in this study. Therefore, the dataset is a valuable contribution to a better understanding of the global carbon cycle. However, I have found some issues that need to be addressed before publication. These are listed below. In particular, some of the interpretations of the observational results are unwarranted. I understand that the ESSD is a data journal, but I think a substantial discussion is also recommended in the paper, particularly considering the high impact of the journal.

1) Line 61: Tohoku University, Japan should be added as a research organization that continues to make long-term systematic observations of CO₂ and O₂. Goto et al (https://agupubs.onlinelibrary.wiley.com/doi/full/10.1002/2017JG003845) and/or Ishidoya et al. (https://www.tandfonline.com/doi/full/10.3402/tellusb.v64i0.18964) need to be listed as suitable references.

2) Line 126: “(Sturm et al., 2004))” should be corrected to read “(Sturm et al., 2004)”.
3) Lines 116–142: The descriptive detail of the flask sampling procedure at each of the sites need to be the same. Information about the models of the pump used, as well as about the flow rates, inner pressures of the flask, drying agents, and usage of an aspirated inlet need to be described for all the sites. If the size of the flask is different at each site, for example, then the size information needs to be given.

4) Lines 164-180: The measurement precision of $\delta(O_2/N_2)$ for flask measurements is not shown. Is it the same as the long-term standard deviation of 10.2 to 13.5 per meg for cylinder measurements? Please clarify.

5) Line 188 and references: “(Tohjima, 2005)” should be corrected to “(Tohjima et al., 2005)”.

6) Line 197: “(van der Laan-Luijkx et al., 2013)” should be corrected to “van der Laan-Luijkx et al. (2013)”.

7) Chapter 3: Examination of the long-term stability of the $\delta(O_2/N_2)$ scale presented in this chapter is highly detailed. It ensures reliability of the long-term trends in the observed $\delta(O_2/N_2)$. However, I was not able to follow how the authors evaluated the uncertainty in the observed long-term trends caused by the uncertainty of the $\delta(O_2/N_2)$ scale. The authors described “Bilbo and Frodo present a minor drift similarly to that observed by our SIO cylinder 7008 (while the other 2 SIO cylinders did not exhibit this behaviour as shown in Sect. 3.2); and our internal WTs all show no overall drifts, we consider our calibration procedure as sufficient” (lines 355–358). Does this mean that the observed $\delta(O_2/N_2)$ values are determined against “the other 2 SIO cylinders” and no uncertainty is considered for the long-term trends in the observed $\delta(O_2/N_2)$ associated with the scale’s uncertainty? In addition, quantitative information about the uncertainty in the $\delta(O_2/N_2)$ scale during the period prior to 2006 is not provided (line 387–394). Did the author consider the scale’s uncertainty before 2006 to determine the long-term trends of the observed $\delta(O_2/N_2)$?

8) Lines 379–381: If the larger fraction of discarded measurements at Lutjewad, compared to those at Mace Head, is related to the effects of local sources/sinks as the authors suggest, then not only $\delta(O_2/N_2)$ but also CO$_2$ would be observed to be more scattered at Lutjewad than Mace Head. Would the authors agree with this? If the scatter is seen only in $\delta(O_2/N_2)$, then it is highly likely that the scatter is due to an artificial fractionation of O$_2$ and N$_2$ rather than due to any of the local effects.

9) Lines 495–499: What is the protective cap made of? If the authors confirmed that a permeation effect was reduced significantly by using the cap, then it is valuable to provide a fuller description. Anyway, I agree with the authors that the permeation effect and incomplete drying are not the causes of the significant difference in the long-term trends
between Lutjewad and Mace Head.

10) Lines 516–524: I think the discussion surrounding the interpretation of the difference in the long-term trends between Lutjewad and Mace Head from the viewpoint of changes in the North Atlantic oxygen ventilation is too speculative. Hamme and Keeling (2008) discussed differences in the interannual variations between the northern and southern hemispheres in relation to the North Atlantic oxygen ventilation (the authors referred to Keeling & Manning (2014), but the original paper on this topic was published by Hamme and Keeling (2008)). However, since both Lutjewad and Mace Head are located on the European continent, the horizontal atmospheric transport is much faster than the meridional transport. Therefore, I expect the contribution of the North Atlantic oxygen ventilation to the interannual variations observed at the two sites would be similar. Do the authors have any supporting information to clarify this issue, such as the simulated results using an atmospheric transport model?

11) Line 552: The ER for globally averaged fossil fuel combustion should be calculated using the latest Global Carbon Budget data (Friedlingstein et al., 2020)

12) Lines 603–621: I think the argument to conclude that the CO$_2$ and $\delta$(O$_2$/N$_2$) anomalies were most likely caused by a small inwards leak is weak. The CO$_2$ values at Halley observed by CIO appear to be higher by about 2 ppm than those obtained by UEA and NOAA, so that the corresponding APO decrease is about 10 per meg by assuming biospheric signal. On the other hand, short-term variabilities of $\delta$(O$_2$/N$_2$) at Halley appear to be larger than 10 per meg, compared to the data from CIO and UEA, and I cannot distinguish systematic difference between them. Therefore, consistency between the APO from CIO and UEA does not provide enough evidence of the small inwards leak. I suspect the increase in CO$_2$ measured by CIO may be due to deterioration of CO$_2$ during the storing period, such as desorption of CO$_2$ from inner wall of the flask or some other effects. I would like to hear the authors’ thoughts on this.