Review of "Diurnal, seasonal, and interannual variations in δ(18O) of atmospheric O2 and its application to evaluate changes in oxygen, carbon, and water cycles" by Ishidoya et al., 2024

General:

The manuscript presents a study of highest relevance for the linkages among the carbon, oxygen and water cycles. For the first time, a research group has analysed long-term measurements of the atmospheric oxygen isotope ratio ($^{18}O/^{16}O$) intending to see the impact of natural (biospheric fluxes) and anthropogenic (fossil fuel combustion). It is a fascinating manuscript to read and I would like to congratulate them for their long-term measurement effort as well as their in-depth analyses.

The manuscript is nicely written and organized and can be considered for publication with minor changes outlined below.

Thank you very much for your significant and useful comments on the paper "Diurnal, seasonal, and interannual variations in $\delta(^{18}O)$ of atmospheric O_2 and its application to evaluate natural/anthropogenic changes in oxygen, carbon, and water cycles" 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 points:

(1) As already estimated in former studies, the expected signal in the atmospheric $\delta(^{18}O)$ by the above mentioned isotope fluxes is minimal. This requires high precision measurements over an extended period in order to see such a small signal as the single uncertainty is about 10 times larger. The required precision and accuracy, especially important for trend analysis, can only be achieved by averaging over many measurements as shown in the manuscript.

I am not sure whether the mass spectrometer was dedicated only to these measurements and whether it was run day and night autonomously. Controlling the long-term stability only every month is quite rare because the mass spectrometers behavior can change suddenly due to maintenance (filament change, ion source tuning etc). Can you please comment on these points and maybe add an additional short section about it.

Lines 99-109: Following sentences have been added considering your comments.

"In general, mass spectrometers behavior can change suddenly due to maintenance, such as filament change, ion source tuning etc.. To minimize the uncertainties associated with the changes in the conditions of the mass spectrometer, we used the specific filaments for the measurements of air samples with the atmospheric level amount fraction of O_2 supplied by the Thermo Scientific co.. This enabled us to carry out the continuous measurements in the present study for 11 months without exchanging the filament (when we used the original filament supplied for the mass spectrometer, then we needed to exchange it every 3 months). After the exchange of the filament, several weeks are needed to stabilize the condition of the ion source of the mass spectrometer by flowing the sample and reference air, especially for the elemental ratios as O_2/N_2, Ar/N_2, and CO_2/N_2. Once the condition is stabilized, we did not tune the ion source throughout the period using the same filament. Furthermore, the mass spectrometer was dedicated only to the measurements of $\delta_{atm}(^{18}O)$ and related components including those for flask samples (e.g. Ishidoya et al., 2021, 2022) and it was run day and night autonomously to keep the condition of the ion source."

(2) Regarding the long-term estimated change in $\delta^{18}O(O_2)$, the authors assume a constant increase rate of the GPP per year. For me, this does not make sense as there are many studies out there discussing the CO_2 fertilization effect. Therefore, I would rather assume a scaling based on the excess CO_2 level (CO_2actual – CO_2 preindustrial). Even though this will most probably not affect their results significantly (Fig. 8), but it still better than use a constant increase rate. In particular as the authors have used a CO_2-dependent photorespiration rate (eq. 5).
Lines 461-469 and Fig. 8: We have assumed a scaling of GPP based on the CO_2 amount fractions from Scripps CO_2 Program, considering your suggestion. Specifically, following sentences have been added and the simulated $\delta_{atm}(^{18}O)$ plotted in Fig. 8 has been revised.
"We first assumed that the global terrestrial GPP increases in proportion to the global average CO_2 amount fraction. As the global average CO_2 amount fraction, we used the data from Scripps CO_2 Program (https://scrippsco2.ucsd.edu/data/atmospheric_co2/icecore_merged_products.html) based on ice-core data and direct observations before and after 1959, respectively (Keeling et al., 2001; Rubino et al., 2019). We assume the initial terrestrial production of O_2 in 1871 as 16.7 Pmol a^{-1} (Table 1), which corresponds to 107 Pg a^{-1} (C equivalents) of global terrestrial GPP considering the r_{DR} of 0.59 and the OR_B of 1.1. Then, the GPP increased secularly with increasing CO_2 amount fraction, and it takes 141 Pg a^{-1} (C equivalents) in 2006. Although this is somewhat larger than the average GPP of 125 Pg a^{-1} (C equivalents) for the period 1992–2020 reported by Bi et al. (2022), it falls within a range of the global GPP estimates from various models summarized in Fig. 10 of Zheng et al. (2020)."

Minor points:

Title:

Diurnal, seasonal, and interannual variations in $\delta(^{18}O)$ of atmospheric O_2 and its application to evaluate changes in oxygen, carbon, and water cycles.

What kind of changes do you mean here? Changes in trend, seasonality, fossil fuel influence, natural changes?

Title: The title has been changed to "Diurnal, seasonal, and interannual variations in $\delta(^{18}O)$ of atmospheric O_2 and its application to evaluate natural/anthropogenic changes in oxygen, carbon, and water cycles".

L15-16

the amplitude is very small, how about its uncertainty? Because it is a mean of about 11 seasons, the seasonality could be smoothed.

Lines 387-390: The uncertainties for the seasonal amplitudes of $\delta_{atm}(^{18}O)$ and $\delta(O_2/N_2)$ have been added as "The minimum of the seasonal $\delta_{atm}(^{18}O)$ cycle appeared in late summer to early autumn, and the peak-to-peak amplitude was 2.1±0.6 per meg. The maximum of the seasonal $\delta(O_2/N_2)$ cycle occurred in summer, and its peak-to-peak amplitude was 113±10 per meg. The uncertainties for the amplitudes of $\delta_{atm}(^{18}O)$ ($\delta(O_2/N_2)$) was evaluated as a standard deviation of the 10-year average monthly mean values from the best-fit curve shown in Fig. 7b.". In the abstract, we did not state the uncertainty since we use the phrase "about 2 per meg".

L18

The secular increase is even more delicate to determine, which requires an extreme stability of the instrument and the standard gas measurements. What about the influence of filament changes, power interruptions, ion source tunings, inlet system, gas flow regime. I am amazed about the stability that is required. Isotope ratio may be less prone to changes but elemental ratios as O_2/N_2 or Ar/N_2 are generally more dependent on such changes. Can you comment on these. Thank you.

As our reply to your "major points (1)", we have added related sentences to lines 99-109. We note that the gas introduction methods (Lines 80-86) are primarily important to obtain the stability (details of the system can be found in Ishidoya and Murayama (2014)).

L26-28

consider rewording to:

The $^{18}O/^{16}O$ ratio of atmospheric O_2, $\delta_{atm}(^{18}O)$, is about 24 ‰ higher than that of ocean water (per definition 0 ‰ on the Vienna-Standard Mean Ocean Water (V-SMOW)) due to various processes in the global oxygen and water cycle (e.g. Craig, 1961; Barkan and Luz, 2005)

Lines 28-30: The sentence has been rewritten, as suggested.

L35-36

Please give corresponding references. There are many more than given here.

Lines 39-40: Some corresponding references have been added, as suggested.

L37

..of present air, ...

Line 41: The words "of air at present" have been changed to "of present air".

L37

….and that variations of the DME from the average are ±0.2 ‰. This addition is not clear, please be more specific here.

Lines 41-44: The sentences have been rewritten as follows, considering your comments.

"B94 have reported that the DME is on average lower by 0.05 ‰ than that of present air during the past 130,000 years, and the standard deviation of the DME from the average was ±0.2 ‰. They suggested that the DME was nearly unchanged between glacial maxima and interglacial periods, and the variability is small and may be due to variations of the relative rates of primary production on the land and in the ocean."

L45

Which value is now used? You may write...and have obtained a range of 22.4 to 23.3 for DME.

Lines 50-51: The words "…and have reproduced the average DME of 22.4 or 23.3 ‰" have been changed to "…and have obtained the average DME of 22.4 to 23.3 ‰d", as suggested.

L63-65

This is a very interesting statement.

Thank you very much for your evaluation.

L82-83

Switch sentence structure, 2nd part first and vice versa.

For the continuous measurements of stable isotopic ratios of O_2, N_2, and Ar ($\delta_{atm}(^{18}O)$, $\delta_{atm}(^{15}N)$, and $\delta_{atm}(^{40}Ar)$) as well as the O_2/N_2 ratio and amount fraction of CO_2, we repeatedly conducted alternate analyses of the sample and reference air.

Lines 88-89: The sentence has been modified following your suggestion as "We repeatedly conducted alternate analyses of the sample and reference air, for the continuous measurements of stable isotopic ratios of O_2, N_2, and Ar ($\delta_{atm}(^{18}O)$, $\delta_{atm}(^{15}N)$, and $\delta_{atm}(^{40}Ar)$) as well as the O_2/N_2 ratio and amount fraction of CO_2".

L84

how come to determine a trend of 0.22 per meg or a seasonality of 2 per meg with a standard deviation of 20 per meg. This requires an well-defined long-term stability.

As described in the text (Lines 119-123), we evaluated the long-term stability from $\delta_{atm}(^{18}O)$ of three secondary standards against the primary standard air. Variations of the annual average $\delta_{atm}(^{18}O)$ of our three secondary standards were ±0.9 per meg on average (Fig. 2), which corresponds to uncertainty of ±0.13 per meg a^{-1} for the 10-year-long secular trend. This enables us to detect the average trend of 0.22 per meg per meg a^{-1} for the period 2013-2022. On the other hand, variations of each value of $\delta_{atm}(^{18}O)$ of our three secondary standards were ±2.3 per meg on average (Fig. 2). Therefore, it is difficult to detect a seasonality of 2 per meg of $\delta_{atm}(^{18}O)$ from 1-year observation only, but we can evaluate it as 10-year average seasonal cycle (±2.3 /sqrt(10) = ±0.7 per meg, which is consistent with the 2.1±0.6 per meg evaluated as a standard deviation of the 10-year average monthly mean values from the best-fit curve shown in Fig. 7b).

L86

…calculated by ...Keeling…

Line 92: The words "$\delta_{atm}(^{18}O)$ by Keeling…" have been changed to "$\delta_{atm}(^{18}O)$ calculated by Keeling…", as suggested.

L88-89

For this purpose, the measured values of the $\delta_{atm}(^{18}O)$ for the same air sample needed to not show any temporal drift, at least during the averaging period.

not clear what you want to say here, maybe you combine it with the previous sentence to

This averaging results theoretically in a standard error of the observed $\delta_{atm}(^{18}O)$ of less than 0.6 per meg assuming no temporal drift during the averaging period.

Lines 93-94: The sentences have been combined and rewritten as you suggested.

L106

…an uncertainty of ±0.13 per meg a^{-1}….how was this calculated?

Line 122: The uncertainty was calculated by $\pm\sqrt{(0.9)^2+(0.9)^2}/10$ considering the long-term stability (1 standard deviation) of the annual average of $\delta_{atm}(^{18}O)$ of three secondary standards (blue circles shown in Fig. 2).

L113-114

As seen in Figure 3a, $\delta_{atm}(^{18}O)$ increased linearly with increasing amount fractions of CO_2.

Why, what are the reasons? There is no isobaric interference. Has it to do with isotope exchange between CO_2 and O_2? Have you done CO_2 additions with O_2 labelling?

Lines 132-135: Unfortunately, the mechanism has not been clarified yet, so that we have added following sentences.

"The mechanism of the positive correlation between the $\delta_{atm}(^{18}O)$ and CO_2 was not clarified yet since there is no isobaric interference. In this regard, I found no significant influences of CO_2 amount fraction on $\delta_{atm}(^{18}O)$ for a different mass spectrometer, Finnigan MAT-252 (Ishidoya, 2003). This suggest that the influences should be examined carefully for each mass spectrometer."

We agree with you that CO_2 additions with O_2 labelling will be a useful method to evaluate the possibility of isotope exchange between CO_2 and O_2. We would like to leave it as a future task.

L120-121

reword to ....in our earlier flask studies in 2013.

Line 141: The words "in our earlier experiments in 2013 that involved use of flasks" have been changed to "in our earlier flask studies in 2013", as suggested.

L135-136

R_{TS} and R_{ST} denote the ratios of the annual fluxes of O_2 between the troposphere and stratosphere, respectively.

to what? It is a ratio.

Lines 168-170: These are the ratios to the total amount of O_2 in the atmosphere. We have revised the sentence as "R_{Res}, R_{PS}, R_{OR}, and R_{OP} represent the relative ratios of the annual amounts of O_2 from terrestrial respiration, marine respiration, terrestrial production, and marine production, respectively, to the total amount of O_2 in the atmosphere (=3.706 x 10^4 Pmol)."

L140

…the amount fraction of O_2 calculated by the box model was converted to $\delta(O_2/N_2)$.

how? Assuming a norm atmosphere or using the measurements to do it correctly. I ask this because of dilution effects.

Line 183: In the box model, the amount fraction of O_2 was calculated assuming a norm atmosphere.

L152-153

Here, ε_{ST} was set to –4 per meg so that the diminution of $\delta_{atm}(^{18}O)$ at equilibrium was –0.4 ‰.

How come?

Lines 195-198, Table 1: In this revision, we have slightly changed the value of the stratospheric diminution, taking L&B2011 results into account. We have added Table 1 to show budgets (fluxes) and isotopic effects of atmospheric O_2 used in the box model. As shown in the table, stratosphere – troposphere exchange (R_{ST} = 3.0 x 10^3 Pmol a^{-1}) is about 100 times larger than the total biospheric flux at the surface (16.7 + 9.8 Pmol a^{-1}). Therefore, ε_{ST} was set to 2.5 per meg to contribute to DME by about –0.3 per mil; $-0.3 = R_{ST} \times \varepsilon_{ST} / (R_{PS}+R_{OP})$.

L161-162

This uncertainty complicates the problem of inter-annual $\delta_{atm}(^{18}O)$ change and suggests that gravitational separation may be involved in small fluctuations in the DME.

One needs to look into O_3 and ^{14}C variations at high altitudes, ideally close to the tropopause.

We agree with you associated with the importance of S-T exchange through the tropopause for isotopically light O_2 in the stratosphere, but in this paragraph, we discuss gravitational separation which is not necessarily reflect STE alone, but is also influenced by the balance between molecular and eddy diffusion and/or strength of Brewer-Dobson circulation (e.g. Ishidoya et al., 2021). Therefore, we leave the sentence as it is.

L204-205

…and artificial inlet fractionation induced by radiative heating of an air intake (e.g., 205 Blaine et al., 2006).

You mentioned that thermal diffusion is not affecting the measurements due to the high flow rate.

Line 268: The words "…diurnal $\delta(Ar/N_2)$ cycle, which is driven by" have been changed to "…diurnal $\delta(Ar/N_2)$ cycle, which is potentially driven by", to clarify both the night-time vertical temperature gradient and artificial inlet fractionation are just the possible causes.

L234

1.46 ….in graph 1.45

Line 299: The number was corrected to 1.45. Thank you for pointing it out.

L239

why only to terrestrial and not to marine biosphere activities?

O_2 and CO_2 fluxes between the terrestrial biosphere and the atmosphere are tightly correlated with each other (with ER ~ 1.1), while those between the ocean and the atmosphere are not due to carbonate dissociation effect. Therefore, we consider the summertime diurnal $\delta(O_2/N_2)$ with the ER of 1.08 could be attributed mainly to terrestrial biosphere activities.

L243-244

(https://www.enecho.meti.go.jp/statistics/energy_consumption/ec002/results.html#headline2, last access: 28 March 2024, in Japanese) (Ishidoya et al., 2020).

paper in 2020, reference in 2024?

We found the past URL in Ishidoya et al. (2020) was not convenience of the readers to find specific data, so that we have shown the updated URL accessed recently on 28 March 2024.

L244-246

The implication is therefore that the isotopic discrimination of O_2 during activities of the terrestrial biosphere was the main cause of the observed summertime diurnal $\delta_{atm}(^{18}O)$ and $\delta(O_2/N_2)$ cycles, and the isotopic discrimination of O_2 during fossil fuel combustion was very small or negligible.

The same conclusion could be drawn by radiocarbon measurements. I guess ^{14}C measurements are being done at your station. Why not use and show it?

We agree with your suggestion, but unfortunately, our institute has not observed $\Delta^{14}C$ of CO_2. I guess National Institute for Environmental Studies (NIES) observed $\Delta^{14}C$ at TKB, so that the results shown in the present study will be a useful tool in future to validate $\delta_{atm}(^{18}O)$ and $\Delta^{14}C$ methods with each other.

L254-256

This method, hereafter referred to as the "$\delta_{atm}(^{18}O)$-method", enabled us to remove the impact on $\delta(O_2/N_2)$ of not only the activities of the terrestrial biosphere but also the contributions due to the air–sea O_2 flux, which is driven mainly by activities in the marine biosphere (e.g., Nevison et al., 2012; Eddebbar et al., 2017), from the estimated $\delta_{FF}(O_2/N_2)$.

Not clear as you first make the balance between observed and bio to obtain the FF. By doing this you cannot disentangle the air-sea O_2 flux from the terrestrial O_2 flux.

We did not separate (disentangle) the air-sea O_2 flux from the terrestrial O_2 flux in this case. Instead, we separate the contribution of "the air-sea O_2 flux + the terrestrial O_2 flux" from that of fossil fuel combustion. This is based on (1) the simulated diurnal cycle of $\delta_{atm}(^{18}O)$ and the $\delta_{atm}(^{18}O)$ / $\delta(O_2/N_2)$ ratio for the case considering terrestrial processes only were very similar to those for the case considering marine processes only, for both case the isotopic effects from B94 and L&B11 were incorporated into the box model (lines 312-315), (2) the contributions due to the air–sea O_2 flux is considered to be driven mainly by activities in the marine biosphere (e.g., Nevison et al., 2012; Eddebbar et al., 2017), and (3) the isotopic discrimination of O_2 during fossil fuel combustion was very small or negligible (Fig. 4). Then, we can estimate the variations of the observed $\delta(O_2/N_2)$ driven by the total activities of the terrestrial and marine biosphere ("$\delta_{BIO}(O_2/N_2)$") by dividing the observed variations in $\delta_{atm}(^{18}O)$ ($\delta_{atm}(^{18}O)$ is driven by the total activities of the terrestrial and marine biosphere) by the ratio of the simulated $\delta_{atm}(^{18}O)$ / $\delta(O_2/N_2)$.

L267-268

It is noteworthy that propane ($CH_3CH_2CH_3$), for which the OR_{FF} is 1.67 for complete combustion, should also be considered as the household gas consumed in the TKB area.

This is very interesting.

Thank you very much for your interest.

L278-281

y. Similar separation has been carried out for CO_2 based on the simultaneous analysis of the $\Delta(^{14}C)$ and amount fraction of CO_2 (e.g., Basu et al., 2020) or based on the simultaneous analysis of $\delta(O_2/N_2)$ and the amount fraction of CO_2 by assuming an average OR_{FF} based on a statistical assessment (Pickers et al., 2022).

There are more publications available that might be cited!

Lines 362-364: We have added some references to be cited.

L291-292

Figure 7a therefore shows 116 and 120 $\delta_{atm}(^{18}O)$ and $\delta(O_2/N_2)$ data, respectively.

rewrite

Lines 374-375: The sentence has been rewritten as "Therefore, Fig. 7a shows 116 and 120 data of $\delta_{atm}(^{18}O)$ and $\delta(O_2/N_2)$, respectively."

L306-309

Keeling (1995) expected $\delta_{atm}(^{18}O)$ to be lower in summer than in winter by 2 per meg based on the assumption that the 100 per meg seasonal increase of $\delta(O_2/N_2)$ was driven by the input of photosynthetic O_2, the $\delta(^{18}O)$ of which is about 20 ‰ lower than $\delta_{atm}(^{18}O)$.

Show how to calculate it!

Lines 393-398: The calculation method has been added, as suggested.

L316

We found that the box model could reproduce the observed seasonal $\delta_{atm}(^{18}O)$ cycles

You adjusted the corresponding values. Questions are remaining as to whether the used model values fall within known ranges.

Table 1: We have added Table 1 to clarify the specific values and references for the parameters incorporated into the box model, considering your comments.

L355-357

see major point 2

Fig. 2

The measurements are not equally distributed over time, this influences the uncertainty per year. Have you considered this?

We did not consider an effect of the non-uniform distribution you pointed out. I agree this could influence the uncertainty for secular trend, nevertheless the effect is not so serious since the measurements in 2012-2014 (the first period) and those after 2020 (the last period) is relatively denser than those in 2014-2020 as seen from Fig. 2. The uncertainty of the average secular trend throughout the period is determined mainly by the measurements in the first and last periods.