

Responses to Referee 2

It was very good for the manuscript that the study of Luz and Barkan (2011) was included, eventually. It makes the analysis much more balanced and emphasizes that delta-18O of O₂ adds another interesting piece to the puzzle of constraining carbon gross fluxes but it is not the silver bullet solution as presented before.

Thank you very much for your significant and useful comments on the paper “Diurnal, seasonal, and interannual variations in $\delta(^{18}\text{O})$ of atmospheric O₂ 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.

My biggest concern with the paper now are the leaf water isotopes.

The current manuscript shows the equation for canopy intercepted water, i.e. Eq. (6) of Yoshimura et al. (2006). This is not leaf water. The latter is in their Eq. (18) and some text above that references to Eqs. (5) and (6). α_k should, for example, not be from Merlivat and Jouzel (1979) for leaves.

As mentioned earlier, the current leaf water isotopic composition looks more like precipitation and the authors arbitrarily shifted the calculated leaf water isotopes. Is it possible that the authors just used the wrong variable from the MATSIRO-iso output? Please check, perhaps together with Kei Yoshimura.

Lines 245-255: Thank you for your comments. We double-checked and are sure that the variable used in the manuscript is correct (isotopic ratio of leaf water). Equation (5) in our previous manuscript was not an equation either for canopy water or leaf water. It was the isotope ratio of transpired water and has a similar form as Eq. (6) of Yoshimura et al. (2006) as written in Sect. 2.5 in their paper; “Transpiration flux E_t estimates include the isoflux that considers equilibrium and kinetic fractionation from liquid to gas at stoma by the similar equations as (5), (6),...”. With the equation, we aimed to show that the isotope ratio of transpired water is not the same as that of source water. However, this could be the cause of the confusion. For clarity, we have changed Eq. (5) from that for the isotopic ratio of transpired water to that for the isotopic ratio of leaf water.

My second point is the discussion about the seasonal cycle of leaf water isotopes. It is clear that if I change the isotopic composition of leaf water, I change the isotopic cycle without the elemental cycle. So this obvious fact is overstated in the manuscript.

It was rather interesting to see that the seasonal cycle of delta-18O did not change by more than 3 months when the cycle of leaf water isotopes was shifted throughout the whole year. So my conclusion would be that delta-18O will probably not be very suitable to constrain leaf water isotopes.

The discussion would have been better if seasonal cycles from MATSIRO-iso would have been used. The cited papers are mostly in the northern hemisphere while most photosynthesis happens in the tropics. How are leaf water isotopes there? What's the timing of the cycle?

Lines 440-450, and Fig. 7d: We have rewritten the sentences as follow considering your suggestion. The simulated seasonal $\delta_{\text{atm}}(^{18}\text{O})$ cycles based on the $\delta_{\text{LW}}(^{18}\text{O})$ calculated by MIROC5-iso have also been included in Figure 7d.

“We also carried out additional box-model simulations that incorporated the average monthly $\delta_{\text{LW}}(^{18}\text{O})$ around TKB (36° N, 140° E) and at lower latitude (30°S – 30°N) calculated by MIROC5-iso for the period 2013–2022. The results are plotted in Fig. 7d, and both the monthly $\delta_{\text{LW}}(^{18}\text{O})$ and simulated seasonal $\delta_{\text{atm}}(^{18}\text{O})$ cycle fall within the range of those represented by blue solid, dashed, two-dot chain, and dotted lines in the figure discussed above. Another factor to change the simulated seasonal $\delta_{\text{atm}}(^{18}\text{O})$ cycle is the choice of the isotopic effects from B94 or L&B11 (Table 1). If we use the isotopic effects from L&B11 and ignore R_{Res} and R_{PS} (i.e. we consider marine respiration/production only), then the seasonal amplitude of the simulated $\delta_{\text{atm}}(^{18}\text{O})$ increase by 20% compared with that simulated by using the isotopic effects from B94. This is due to the difference in the isotopic effects of ocean respiration, which are 18.9 and 23.5 ‰ for B94 and L&B11, respectively. Such difference will become apparent in the southern hemisphere, where seasonal $\delta(\text{O}_2/\text{N}_2)$ cycle is driven mainly by air-sea O_2 flux (e.g. Keeling and Manning, 2014). Therefore, spatiotemporal variations in the seasonal $\delta_{\text{atm}}(^{18}\text{O})$ cycle will be useful to constrain not only spatiotemporal variations of $\delta_{\text{LW}}(^{18}\text{O})$ but also the isotopic effects of ocean respiration.”

More minor comments are:

- It is Cuntz and not Cunz in the references.

Lines 411, 412, and 419: The word “Cunz” has been corrected to “Cuntz”. Sorry for the typo.

- I found the notation R_{Res} , etc. not very intuitive. It is only defined by words: "annual fluxes of O_2 from terrestrial respiration [...] to the total amount of O_2 in the atmosphere". There is no unit given. Could there be simply fluxes (as in Table 1) and the amount goes to the left-hand-side?

Lines 169-173: The sentences have been rewritten as follows to make the meanings and units of the “ R_{xx} ” clearer.

“ R_{Res} , R_{PS} , R_{OR} , and R_{OP} (the unit is a^{-1}) represent the relative ratios of the annual fluxes of O_2 from terrestrial respiration, terrestrial production, marine respiration, and marine production, respectively, to the total amount of O_2 in the atmosphere ($=3.706 \times 10^4 \text{ Pmol}$). For example, if we assume that the terrestrial flux is 16.7 Pmol a^{-1} , R_{PS} will be $16.7/(3.706 \times 10^4) = 4.5 \times 10^{-4} \text{ a}^{-1}$, as shown in Table 1. R_{TS} and R_{ST} denote the relative ratios of the annual fluxes of O_2 between the troposphere and

stratosphere, respectively.” In addition, the definitions and units of all variables, including R_{xx} , are summarized in Table A1.

- Eq. (4) is odd. There is a d missing, probably. And it shows the strangeness of the R_x notation because the right-hand-side suddenly has $y(O_2)$ (after multiplying with it) while most fluxes do not depend on it.

Line 182: We have revised eq. (4) since there was a “d” missing, as you pointed out. Other terms in Eq. (4) are correct. Derivation of eq. (4) is as follow.

$$\frac{dM_{O_2}}{dt} = (r_{MR} + r_{PR} + r_{DR})F_{Res} + F_{PS} + F_{OR} + F_{OP} + F_{TS} + F_{ST} + F_{FF}$$

Here, M_{O_2} is the total amounts of atmospheric O_2 ($=3.706 \times 10^4$ Pmol), and F_{xx} are O_2 fluxes (Pmol a^{-1}). The ratio F_{xx}/M_{O_2} is R_{xx} .

$$\frac{1}{M_{O_2}} \frac{dM_{O_2}}{dt} = (r_{MR} + r_{PR} + r_{DR})R_{Res} + R_{PS} + R_{OR} + R_{OP} + R_{TS} + R_{ST} + R_{FF}$$

In the one box model, the ratio of the total amounts of O_2 and atmospheric molecules is O_2 amount fraction, so we get:

$$y(O_2) = \frac{M_{O_2}}{M}$$

Here, M is the total amounts of atmospheric molecules (Pmol). Because M is a constant value, the time derivative is given by:

$$\frac{dy(O_2)}{dt} = \frac{1}{M} \frac{dM_{O_2}}{dt} ,$$

and

$$\frac{1}{M_{O_2}} \frac{dM_{O_2}}{dt} = \frac{1}{y(O_2)} \frac{dy(O_2)}{dt} .$$

As a result, we get (Eq. 4) as follows:

$$\frac{1}{y(O_2)} \frac{dy(O_2)}{dt} = (r_{MR} + r_{PR} + r_{DR})R_{Res} + R_{PS} + R_{OR} + R_{OP} + R_{TS} + R_{ST} + R_{FF} .$$

Responses to the Editor

Thank you very much for your significant and useful comments on the paper “Diurnal, seasonal, and interannual variations in $\delta(^{18}\text{O})$ 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.

One of the reviewers has raised some concerns about the leaf water isotopic composition. Could you please address them?

Lines 245-255, 440-450, and Fig. 7d: We have addressed the concerns. Please confirm our responses for Referee 2.

Regarding the reviewer's minor technical comments, I believe Eq. 4 is correct, but please double-check their query.

Line 182: We have revised Eq. (4) since there was a “d” missing. Other terms in Eq. (4) are correct. We have also showed derivation of Eq. (4) in our responses for Referee 2.

Regarding the symbols, there are indeed a lot of symbols used in your manuscript. Could you please include an appendix with a list of symbols used, with their meanings and definitions, and SI units?

Lines 146-147, 606-608, Table A1: Table A1 including the symbols used, with their definitions and units have been added, considering your suggestion.

I'd also like to ask for a few other technical corrections:

1) Symbols in equations should consist of a single Latin or Greek character. While the symbols OR and ER are fine as abbreviations, they should not be used in equations. Please find a suitable replacement, e.g., α_F and α_B instead of OR_{FF} and OR_B ; α_{obs} instead of ER_{obs} .

Lines 342-345: We have replaced OR_{FF} and OR_B by α_F and α_B , respectively.

2) The definition of ER and OR should include a physical quantity symbol for the amount fraction, i.e., $\alpha = -\Delta y(\text{O}_2) / \Delta y(\text{CO}_2)$. Chemical symbols such as O_2 and CO_2 should not be used to designate physical quantities.

Lines 299-301: The word “ $\Delta\text{O}_2\Delta\text{CO}_2^{-1}$ ” has been corrected to “ $\Delta y(\text{O}_2)\Delta y(\text{CO}_2)^{-1}$ ”.

3) For clarity and ease of reference, please be consistent in your choice of labels. For example, in Eq.

6) you use both "B" and "TB" for terrestrial biosphere, associated with different quantities. Please use the same index label.

Lines 341-347: The word "TB" has been changed to "B".

4) In Eq. 9, the symbols $p(O_2)$ and $p(CO_2)$ should be used instead of "O" and "C" as quantity symbols. "O" and "C" as index labels for the other quantities are fine.

Lines 485, 489-490: The sentences have been rewritten as " $y(O_2)$ and $y(CO_2)$ are amount fractions of O_2 and CO_2 , respectively, in equilibrium with their dissolved amount fractions in the chloroplast stroma. We used atmospheric $y(O_2)$, and atmospheric $y(CO_2)$ multiplied by 0.7 following B94.", and the symbols "O" and "C" in Eq. (9) have been changed to " $y(O_2)$ " and " $y(CO_2)$ ", respectively.

5) Please explain the extraneous factor 10^{-3} in Eq. 9.

Lines 492-493: The sentence " 10^{-3} is a coefficient to compare the calculated ϕ with those in Farquhar et al. (1980) directly since they used units of mbar and μbar for the $y(O_2)$ and $y(CO_2)$, respectively" has been added.

6) Please remember to make the data available in a public repository that does not require user registration.

We have confirmed the WDCGG will allow us to deposit the monthly mean $\delta^{18}O_{\text{atm}}$, $\delta(O_2/N_2)$, and CO_2 amount fractions in their public repository. I will let you know the once the data become available.