

The authors present measurements of the ^{18}O isotopic composition of atmospheric molecular oxygen from air taken at the roof of their building in the greater Tokyo region. They also measured O_2/N_2 ratios and CO_2 concentrations to assess the suitability of $\delta^{18}\text{O}$ in O_2 to probe the carbon cycle. They analyse the diurnal and seasonal variations as well as the interannual trend with a one-box model. The observations are pretty exciting. I am not aware of any group that measured the diurnal cycle of $\delta^{18}\text{O}$ in atmospheric O_2 before. Given the tremendous technical advances over the last years, it seems logical that they succeeded, eventually. They still have to average about 1000 individual measurements so that average diurnal cycles for each season are presented.

I am less convinced by the analysis with the one-box model. The method was not well explained, so that it is possible that I missed some things. I think that the manuscript needs some serious revisions before publication.

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.

Why are there only the values of Bender et al. (1994) but not the updated figures of Luz and Barkan (2011, doi: 10.1029/2010GB003883)?

Section 2.2 (lines 143-236) and Table 1: Considering your comment, we have carried out the simulations by using the isotope effects not only from Bender et al. (1994) but also from Luz and Barkan (2011) (referred to as “B94” and “L&B11”, respectively, in the manuscript), and compared them especially for the long-term variations of $\delta_{\text{atm}}(^{18}\text{O})$. Table 1 has also been added to summarize values of O_2 budgets and isotopic effects for both studies.

Where is fossil fuel in the box model? It looks like the model comes from Bender et al. (1994) who analysed the last 130,000 years and did not need fossil fuel.

Equations (3) and (4) and related sentences, lines 172-178, and lines 322-329: In the revised manuscript, contributions of fossil fuel combustion has been included in the equations for the box model. However, we assume that atmospheric oxygen is consumed without isotope effects in fossil fuel combustion considering high temperature during the industrial combustion processes. We have added some sentences to note future needs to examine the combustion processes as follows.

“(lines 172-178) We assumed that atmospheric oxygen is consumed without isotope effects in fossil fuel combustion ($\epsilon_{\text{FF}}=0$), taking into account that the industrial combustion processes usually occur at high temperature. Therefore, we consider no contribution to DME from fossil fuel combustion in this

study. In this regard, it is known that large oxygen isotope fractionation occurs in the combustion processes such as biomass burning due to complex combustion processes (Schumacher et al., 2011). In such cases, it will be necessary to consider isotopic fractionation in the consumption of atmospheric oxygen associated with combustion. However, at present, little is known about the impact of this on DME.”

“(lines 322-329) It would be generally reasonable since the combustion occurs at high temperature, which minimizes isotopic discriminations. However, Schumacher et al. (2011) reported isotopic discriminations on the order of up to 26 ‰ for stable oxygen isotopic ratio of atmospheric CO₂ ($\delta_{\text{CO}_2}(^{18}\text{O})$) derived from combustion of different kinds of material. They suggested that natural combustion processes on the long term might enrich $\delta_{\text{atm}}(^{18}\text{O})$ and contribute to the DME. Therefore, isotopic discriminations of $\delta_{\text{atm}}(^{18}\text{O})$ due to combustion processes should be examined carefully in future, based on precise observations of $\delta_{\text{atm}}(^{18}\text{O})$.”

The method of ignoring terrestrial or marine fluxes was not well explained. Only the terrestrial fluxes had a sinusoidal cycle in the methods. So how does the model calculate a diurnal cycle if terrestrial O₂ fluxes are ignored?

Lines 231-233: The sentence “We also carried out simulations of diurnal changes considering marine O₂ consumption and production approximated by the similar simple function, to examine sensitivities of $\delta_{\text{atm}}(^{18}\text{O}) / \delta(\text{O}_2/\text{N}_2)$ ratio to the terrestrial and marine signals” has been added to make the method clearer.

The rationale behind their calculations of the delta-¹⁸O_{atm}-method were not given. Why does the ratio give you delta-¹⁸O_{bio}? Is it because fossil fuel is missing in the box model?

As you expected, it is because we ignored the isotopic effect of fossil fuel combustion. Regarding this assumption, we have added some sentences to note future needs to examine the processes (please check our reply to your comments “Where is fossil fuel in the box model?...” above).

The box model has a shifted diurnal cycle by about two hours. You would get a strange signal when dividing two sinusoidal signals shifted by some delta. This does not seem the case here and I was wondering why? Is it possible that you get a false diurnal cycle of the biospheric fluxes because of the wrong timing of the box model?

In the simulations, diurnal cycles of respiration and photosynthesis fluxes were approximated by simple sinusoidal signals. We could not know true phases and amplitudes of the diurnal cycles, so that we adjusted the amplitude of the respiration and photosynthesis fluxes arbitrarily under the constraint that both fluxes became the largest around noon. Therefore, if we shift the peaks of the fluxes by two hours earlier, then we can reduce the phase shifts of the simulated $\delta_{\text{atm}}(^{18}\text{O})$ and $\delta(\text{O}_2/\text{N}_2)$ found in Fig.

4a. However, we consider it would be reasonable that the largest respiration and photosynthesis fluxes are found around noon, so that we leave the simulated diurnal cycles in Fig. 4a as they are.

The ER method is not explained. Where are the numbers 1.1, 1.4-1.7 coming from? I guess nowadays 1.05 is more accepted for photosynthesis.

Lines 335-338: The sentence has been modified considering your comments as "...we assumed the OR for activities in the terrestrial biosphere (OR_B) to be 1.1 (Severinghaus, 1995), which has been widely used in past studies (e.g. Manning and Keeling, 2006; Tohjima et al.), and the OR_{FF} to be 1.4, 1.5, 1.6, or 1.7 considering mixed combustion of solid fuel, liquid fuel, and natural gas. It is noted some recent studies have used the OR_B of 1.05 rather than 1.1 (e.g. Morgan et al., 2021)".

How is it possible that in O_2 leaf water isotopes are increasing by 9 per meg (Figure 8) when leaf water isotopes of H_2O are increasing by nothing until 2000 and then only about 0.2 permil?

Lines 512-516: Following sentences have been added to show the reason clearer.

"It is noted that the contributions of the changes of $\delta_{LW}(^{18}O)$ to the simulated $\delta_{atm}(^{18}O)$ increased with time monotonously while clear increase of $\delta_{LW}(^{18}O)$ was found after the 1980s (Figs. 8b-c). This is due to the choice of the initial $\delta_{LW}(^{18}O)$ in 1871; we set it to be 4.4 or 6.5 ‰ (the values for steady state by B94 or L&B11). As seen from Fig. 8c, the average $\delta_{LW}(^{18}O)$ during 1872-1980 was higher than the initial values, which made the monotonous increase of the $\delta_{atm}(^{18}O)$ driven by the $\delta_{LW}(^{18}O)$ changes..

What are the leaf water scenarios in Figure 7? I could not find any explanations. I would be curious how you get a time shift of up to two months from different formulations of leaf water.

Lines 421-435: The sentences have been rewritten to explain the scenarios. The scenario for the thick dashed blue line in Fig. 7 was determined based on some past studies reported seasonal variations of $\delta_{LW}(^{18}O)$, and other two scenarios represented by two-dot chain and dotted lines were carried out as sensitivity tests to the phase difference in seasonal $\delta_{LW}(^{18}O)$ cycle.

You get an increasing or decreasing secular trend if the right-hand side of Eq. (3) is non-zero. This can have many reasons and you do not have to have increasing GPP or anything. The authors have tweaked so many fluxes in their model that I do not think that we can say anything about the secular trend.

Section 3.3 (lines 441-558) and Fig. 8: We have revised the analysis and discussion for the secular trend including the simulations by the box model incorporated not only B94 but also L&B11. As you expected, the secular trends of the simulated $\delta_{atm}(^{18}O)$ are highly sensitive to the isotopic effects associated with the DME. Therefore, further studies are needed to determine the isotopic effects precisely, in order to evaluate long-term changes in GPP and photorespiration based on $\delta_{atm}(^{18}O)$.

This reminds me of the literature of delta-¹⁸O in atmospheric CO₂. There were the same issues: a secular trend due to unbalanced fluxes, a one- to two-month time shift in the seasonal cycle, etc. The authors could learn a lot from that literature but not a single paper is referenced in the manuscript.

Lines 408-413 and 498-502: Following sentences have been added to note the characteristics of seasonal and interannual variations in stable oxygen isotopic ratio of atmospheric CO₂ ($\delta_{\text{CO}_2}(^{18}\text{O})$) for a comparison with those of $\delta_{\text{atm}}(^{18}\text{O})$.

“(lines 408-413) In this context, seasonal cycles of $\delta_{\text{CO}_2}(^{18}\text{O})$ have been reported by some past studies (e.g. Peylin et al., 1999; Cunz et al., 2003; Murayama et al., 2010). Peylin et al. (1999) and Cunz et al. (2003) used 3-D atmospheric transport models to reproduce the observations, and they found the main contributors are respiration and production for the respective seasonal cycles of $\delta_{\text{CO}_2}(^{18}\text{O})$ and CO₂ amount fraction. These characteristics are different from the seasonal cycles of $\delta_{\text{atm}}(^{18}\text{O})$ and $\delta(\text{O}_2/\text{N}_2)$ observed in this study, both of which are driven mainly by production (Fig. 7c).”

“(lines 498-502) It should be noted that Welp et al. (2011) suggested that $\delta_{\text{CO}_2}(^{18}\text{O})$ increases with increasing $\delta_{\text{precip}}(^{18}\text{O})$ and $\delta_{\text{LW}}(^{18}\text{O})$ through the redistribution of moisture and rainfall in the tropics during an El Niño, which leads to substantial interannual variations in $\delta_{\text{CO}_2}(^{18}\text{O})$ during 1977–2009 obtained from the Scripps Institution of Oceanography global flask network. Therefore, it will be important in future studies to examine not only secular trend discussed in this study but also interannual variations in $\delta_{\text{LW}}(^{18}\text{O})$ and $\delta_{\text{atm}}(^{18}\text{O})$.”

Nobody thinks that GPP increase over the last century comes solely from a decrease of photorespiration. The discussion from page 14 line 397 up to page 15 line 417 is weird regarding the carbon cycle and anything we know about photosynthesis.

The discussion you pointed out in the previous manuscript has been removed from the revised manuscript.

The leaf water from MIROC5-iso looks like source water. Most global models of water isotopes do not calculate leaf water enrichment because they assume steady state so that the transpired water is the same as source water. If not, I would have loved to know how delta-¹⁸O of leaf water is calculated in MIROC5-iso.

Lines 247-254: MIROC5-iso does calculate the isotopic fractionation effect when transpiration occurs. We added the equation to make the point clearer.

More minor comments are:

Why is the ¹⁸O in parenthesis in $\delta(^{18}\text{O})$? This is a weird notation.

We understand your comment, however, I have used the phrase following the Editor's instruction.

Given the current notation. It is never clear which molecule is looked at. Sometimes $\delta_{LW}(^{18}\text{O})$ is O_2 and sometimes H_2O . Perhaps making it clearer, e.g. adding the molecule behind such as $\delta^{18}\text{O}-\text{O}_2$ or $\delta^{18}\text{O}(\text{O}_2)$?

In the revised manuscript, we have used $\delta_{LW}(^{18}\text{O})$ for H_2O only. The words "...and the respective contributions of GPP (solid green line), photorespiration (solid red line), and $\delta_{LW}(^{18}\text{O})$ (solid blue line) to the simulated $\delta_{\text{atm}}(^{18}\text{O})$..." in caption of Fig. 8 has been changed to "...and the respective contributions of the changes of GPP (green line), photorespiration (red line), and $\delta_{LW}(^{18}\text{O})$ (blue line) to the simulated $\delta_{\text{atm}}(^{18}\text{O})$." to make the meaning clearer.

Lots of references are missing like all the references for the emission ratio method. Or $\text{ER} = 1.67$ for propane?

References for the DME, emission ratio methods, and $\delta_{\text{CO}_2}(^{18}\text{O})$ have been added in the revised manuscript (e.g. lines 39-40, 154, 176, 336-338, 362-364). As for the OR_{FF} for propane, the words "...the OR_{FF} is 1.67 for complete combustion" have been changed to "...the OR_{FF} is 1.67 assuming complete combustion" (line 350). If propane completely burned, $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$, then the OR is $5/3 = 1.67$.

I was wondering if MIROC5-iso has no carbon cycle? Most models have nowadays. So why not using these fluxes, or at least its dirunal and seasonal variations, instead of simple sinusoidal fluxes?

Thank you for the valuable suggestion. Unfortunately, the carbon cycle is not included in MIROC5-iso, although it is included in another version of MIROC; MIROC-ESM (Watanabe et al., 2011). We would like to leave it as a future task.