Comment on bg-2021-324
Anonymous Referee #2

Referee comment on "Determination of respiration and photosynthesis fractionation factors for atmospheric dioxygen inferred from a vegetation-soil-atmosphere analog of the terrestrial biosphere in closed chambers" by Clémence Paul et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2021-324-RC2, 2022

Paul et al. describe a novel environmental chamber apparatus, as well as its first results, focused on obtaining isotopic fractionation factors associated with respiration and photosynthesis in terrestrial analogue systems. In this case, the authors report results from a study of a commercial potting soil and a grass (tall fescue). It is a difficult system to control and to study, and the authors have done perhaps the best job of controlling the environment compared to all the terrarium studies done over the past two decades in this vein (i.e., those led by Luz, Angert, and Yeung), namely by maintaining carbon dioxide concentrations and a closed water cycle with constant relative humidity below saturation. In this sense the study is quite welcome and I look forward to seeing more studies come of this apparatus. However, I have technical concerns about a couple elements of the manuscript, which are listed below:

- When describing the mass balance equations for the experiment, the sign of $dn$ sometimes does not make sense relative to the direction of the oxygen flux. For example, in 2.4.3, equation 13 describes $dn_{\text{photosynthesis}}$ as “the number of molecules of O$_2$ produced by photosynthesis,” yet to have the correct sign I believe it needs to have a negative value in the equation (i.e., it is of opposite sign to $dn_{\text{total_respir}}$, which is a consumption term and has a positive value like in equation 8). I am not sure whether this confusion is an error in words only or if it propagates into the mass balance equations, but the authors should check.

- Accurate isotopic scaling between VSMOW and air is taken as a matter of fact when there is a known discrepancy of order 0.1 per mil in both $\delta^{18}O$ and $\delta^{17}O$ differences between labs that measure the O$_2$ analyte together with Ar (e.g., Hebrew U., Princeton, the present study) and those who measure it as pure O$_2$ (U. New Mexico, Gottingen, Open University, UCLA, Rice U.). It may seem like a minor point, but Yeung et al. RCMS (2018) showed that inconsistent/assumed scaling can lead to spurious disagreements in discrimination factors and triple-isotope slopes in the range of 0.1 per mil and 0.005, respectively. It poses a problem for the soil-respiration γ value because this type of
uncertainty is systematic and thus would not be included implicitly in the random errors; the reported uncertainty range is too small. Indeed, Stolper et al. GCA (2018) and Ash et al. ACS Earth Space Sci. (2020) report evidence -- from two independent labs -- that dark respiration might not be characterized by the “canonical” 0.516 value. Many of the other reported uncertainty ranges are significantly larger than the level of these disagreements, but the photosynthetic endmember does depend strongly on the assumed value of VSMOW, which Wostbrock and others have shown are far from in agreement. I suggest the authors (1) acknowledge that this disagreement in the field exists, citing the relevant literature, and (2) make note of the possibility that the fractionation factors may need to be revised in the future once everyone gets on the same reference frame. I don’t necessarily believe that the reported values need revision per se, but the field would do well to acknowledge outstanding issues in papers rather than continue to ignore them.

Minor comments

- There is some nonstandard notation: the use of $R^{18}_1$ instead of the more common $^{18}R$ when describing $^{18}O/^{16}O$ ratios; the use of $\gamma$ without mention of its equivalence to the symbol $\Theta$ used elsewhere in the triple-isotope literature; the use of “fractionation coefficient” rather than the more common term “fractionation factor” for $\alpha$.
- “Since” refers to a time in the past (e.g., since 1980) and “because” refers to a cause (“because Ar is an inert gas”). In most instances of “since” in the manuscript I think the authors should be using “because” instead.
- In the abstract, Table 1, L531, and 546: “respiration of leave” --> “leaf respiration”
- L451, 453, 458, and 460: “leave” --> “leaf”