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Comment on hess-2021-255

Anonymous Referee #1

Referee comment on "Technical note: Unresolved aspects of the direct vapor equilibration method for stable isotope analysis ($\delta^{18}\text{O}$, $\delta^2\text{H}$) of matrix-bound water: unifying protocols through empirical and mathematical scrutiny" by Benjamin Gralher et al., Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2021-255-RC1>, 2021

Summary

The authors present a laboratory and modelling study in which they compare different sample container materials and equilibration times for the direct vapor equilibration laser spectrometry (DVE-LS) method. This method was first introduced in 2008 and has since been used in numerous studies, however with inconsistent application of sample containers and equilibration times. Therefore, this manuscript provides a consistent standard operation protocol that will help to enhance data quality and comparability of isotope measurements across future studies that apply the DVE-LS method.

Given the widespread application of the DVE-LS method, the presented study is of great relevance for the research community. Novel data are presented and the conclusions reached are substantiated by the results of the laboratory experiments. The scientific methods are valid and clearly outlined

Major comments:

The laboratory experiments are reasonable and carried-out well. In my opinion, the simulation of Rayleigh-type fractionation is warranted for the less vapor-tight containers; for the very vapor-tight containers (Al3z, Al3z_hs), the simulations yield highly uncertain results because fractionation effects were minimal. I wonder whether the discussion of the simulation results for Al3z and Al3z_hs could be shortened in 3.2 and 4.1 because they don't contribute much to the core message of the paper. The figures are well-made and informative. Overall, the presentation of the study is well structured and clear, however, the language could partly be improved (some sentences are very long and difficult to understand and I refer to some specific examples below).

I have struggled the most with section 2.2. Although the theories outlined here seem reasonable, I found it difficult to understand the reasoning behind some analysis steps. I would suggest to better structure and explain why and how each analysis step was carried out. For instance:

- The authors write that eq. (1) was used to simulate the theoretical Rayleigh-curve, however, only in Sect. 3.2. it becomes clear that it was used to determine the fractionation factor α . Can this information be included in Sect. 2.2? Was this (fitted) fractionation factor then applied in eq. (5)?
- L 209: I'm not familiar with the term "isotope separation" for ϵ in the context of water stable isotopes studies (Coplen (2011) refers to ϵ as "isotope fractionation"). Could the authors provide a short mechanistic description of ϵ and why is a useful parameter for this analysis (especially with respect to the results reported in L 338)?
- What is eq. (9) used for? The explanation "Equation (9) is somewhat similar to equation (4)." Is not very informative.
- In eq. (9), how are $V_{H_2O,eq}$ and $V_{H_2O,sam}$ determined? Whereas $V_{H_2O,eq}$ could be measured based on weight differences of the filled containers over time, I don't understand how $V_{H_2O,sam}$ could be reliably measured.
- L237-240: How did the authors determine the "mean isotope enrichment rates"?
- L237: "Ratios of mean isotope enrichment rates were calculated as estimates of the slopes of so-called evaporation lines that water stable isotope data plot on in dual isotope space when affected by gradual evaporitic enrichment of heavy isotopes. We compared these to the ratio of deviations from unity of the model-derived isotope fractionation factors α (Eq. 1)." What will this comparison analysis tell us?
- L240: "Individually, these deviations yield the respective isotope separations (Eq. 5)." I think that this sentence is relevant for eq. (5) and should therefore be moved there.

Minor comments:

L42-44: It is not clear what "manifested" and "enabled" refer to. Can the authors rephrase the sentence to be more specific?

L75-78: I would suggest to use commas in this sentence or make two sentences out of it.

L81: What is meant by "measurement iterations"?

L105: I don't understand the example "groundwater vs. root uptake water". Do the authors mean that a study focusing on groundwater samples will need to adapt a different correction strategy than a study focusing on root uptake water? Why?

L128-131: I would suggest to use commas in this sentence or make two sentences out of

it.

L173: This sentence seems to be out of context. Can the authors explain why "each of these bag candidates were then equipped on one side with custom-made septa of silicone blots or adhesive tape"?

L185: Do the authors mean the Al3z_hs bags? Also, it is not clear to me how the PIT was implemented if the same bag type was used as reference for the other (different) bag types.

L175, L187: Were the sample water and the standard water isotopically identical? How many standards were used?

L338: If the authors used eq. (5) to calculate ϵ , what are the respective fractionation factors?

L446: How would it be possible to re-measure a punctured bag again or should punctured bags be discarded regardless? I could imagine that after the measurement is done, the needle puncture could be sealed again with silicone blots or adhesive tape.

L452: What is meant by "...trying to balance unwanted spatial variability."?

L468: Could the authors include a recommendation for the required minimum volume of liquid isotope standards used for calibration and drift control?

L475: "Then, Equation 9 can be applied and solved for $\delta\text{-}\delta_{\text{CS}}$ in order to calculate the impact of a

too-small sample liquid water reservoir on isotope data accuracy." Can the authors be more specific? How would ϵ , $V_{\text{H}_2\text{O,eq}}$ and $V_{\text{H}_2\text{O,sam}}$ or f be determined?

L504: Does "this effect" refer to "the small-sample effect"?

L555: "The case of zip-closed-only Al3z bags can be seen as a representation of sample

transport and storage..." In introductory sentence will make it easier to grasp the motivation of this paragraph. A suggestion:

The comparison of zip-closed-only Al3z bags and heat-sealed zip-closed Al3z_hs bags allow us to assess the negative impacts of sample transport and storage on vapor loss.

L560: Could the authors provide some more detailed recommendations on how to store filled sample containers if isotope analysis is possible only after more than 2 days? Should the containers be stored in a fridge/freezer until analysis?

L569: "...over unprecedentedly long periods ...". Can the authors be more specific here?

L580: What is meant by "extreme conditions"?

References

Coplen, T. B.: Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results, *Rapid Commun Mass Sp*, 25, 2538–2560, <https://doi.org/10.1002/rcm.5129>, 2011.