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

We thank the referee for the favorable evaluation and thoughtful comments. In the following, the referee comments (in black) are each followed by our response (in blue).

Mayor 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.

Our intention was a full-scale scrutiny of the DVE-LS method. Therefore we included the mathematical simulation of the observed isotope data. As discussed, the outcome of this effort is not supposed to be used for correction purposes. Rather, we wanted to show that in the case of Toppits bags unfavorable open system conditions exist and cannot be prevented. In the case of Al-laminated bags, however, this issue does not impact feasible storage and equilibration times.

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)?

Thanks for alerting us, we will include this information in the updated section 2.2.

Eq. 5 refers to equilibrium conditions (= closed system), whereas Eq. 1 describes the isotope evolution of an open system. Thus, the fitted fractionation factor was not 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?

Throughout the manuscript, we replaced "separation" by "enrichment" as we follow the definition of Clark and Fritz (1997) which will be referenced in the revised manuscript.

- What is eq. (9) used for? The explanation "Equation (9) is somewhat similar to equation (4)." Is not very informative.

What we meant to say was that Eq. 9 describes the same physical relationship as Eq. 4.

We will rephrase the respective sentence to: "Equation (9) describes the same physical relationship as equation (4)."

- In eq. (9), how are V_H2O,eq and V_H2O,sam determined? Whereas V_H2O,eq could be measured based on weight differences of the filled containers over time, I don't understand how V_H2O,sam could be reliably measured.

V_H2O,eq was calculated (not measured!) using Eq. 6 or Eq. 7.

V_H2O,sam is the liquid water content of an arbitrary sample. It is also not measured. However, we recommend that a certain threshold volume should be exceeded in order to avoid the 'small sample' effect which is discussed in section 4.3. This threshold volume (now called V_H2O,min) is calculated using Eq. 4.

We will add this explanation to section 2.2 of the revised manuscript.

- L237-240: How did the authors determine the "mean isotope enrichment rates"?

Mean isotope enrichment rates were determined by adding a trend line to the observed data (s. Fig. 4) and calculating the slope thereof.

We will add this explanation to the respective figure captions in the revised manuscript.

- 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?

The 'ratio of mean enrichment rates' as well as the 'ratio of deviations from unity' are two ways to calculate the slope of an evaporation line in dual isotope space (the numbers can be found in Tab. 2). Comparison of the two numbers is a way to check their plausibility. We rephrased the respective paragraph in the discussion section to:

"The wider ranges of underlying isotope and weight loss data of toppits bags are the reason for the higher respective parameter sensitivity. Especially in this case, we consider the good agreement between the ratio of mean isotope enrichment and the ratio of deviations from unity of model-derived fractionation factors (Tab. 2) to be proof for their plausibility."

- 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.

This sentence really is about the aforementioned deviations, not the separations (or rather enrichments). The reference to Eq. 5 was provided for additional guidance of the reader.

Minor comments:

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

We regret the confusion. We will reformat the respective sentence to:

"The growing distribution of laser-based water stable isotope analyzers in recent years and the DVE-LS method's relative simplicity, resulting from fairly little sample preparation workload, low-cost consumables and omission of sophisticated water extraction lines and analyzer peripherals, enabled its rapid, wide-spread adoption."

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

Commas will be added as suggested.

L81: What is meant by "measurement iterations"?

Details of this post-correction concept can be found in the provided reference. For better readability, we will rearrange the respective sentence to:

"They also presented a post-correction scheme of potentially affected DVE-LS samples based on an analyzer-recorded spectral variable and measurement iterations (Gralher et al., 2018)."

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?

This example was given in the aforementioned study of Wang et al. 2019. We will rephrase the respective sentence to make this clearer.

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

Comma will be added as suggested.

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"?

We will rephrase the sentence to:

"In total, 21 replicates of each of these bag candidates were then equipped on one side with silicone blots or adhesive tape which served as custom-made septa during direct headspace analyses."

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.

Yes, we mean the Al3z_hs bags.

For clarification we will replace "otherwise" by "apart from that".

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

Sample water and standard water were not isotopically identical. On each day of analysis two standards were co-measured.

We will add this information to the manuscript.

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

Temperature-dependent isotope fractionation factors α were calculated using the pertinent equation provided by Majoube (1971).

We will include the respective numbers in the manuscript.

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.

Pre-applied silicone blots provide sufficiently closed septa allowing for re-measurements. This has been done before (see e.g. Gralher et al., 2018). However, for this study we intended to perform only singular measurements on individual bags in order to ensure their structural integrity during the entire storage time prior to isotope analyses. In doing so, we wanted to ensure identical conditions for all investigated bags.

From our experience, the best way to allow re-measurements is to apply to each bag the respective number of silicone blots well in advance (~ 2 days). Freshly applied silicone outgases VOCs which likely flaws isotope readings.

We added the following sentence to the method section:

"In order to account for outgassing of VOCs from freshly applied silicone and thus compromising isotope readings, this step was conducted well in advance (≥2 days) of the isotope analyses."

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

This is a hypothetic scenario, where researchers might want to collect larger than usual samples. Theoretically this could be applied in cases of presumably high soil heterogeneity by mixing adjacent samples from identical soil depths into one sampling bag.

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

For clarification we will add the following sentence to section 4.3:

"For liquid water standards, prepared for calibration and drift control purposes of DVE-LS samples, the same holds true. This means that they also need to consist of at least this water volume."

L475: "Then, Equation 9 can be applied and solved for delta-delta_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, $V_{H2O,eq}$ and $V_{H2O,sam}$ or f be determined?

The definitions of the listed parameters are provided in section 2.2.

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

Yes, it does.

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.

We will rephrase the beginning of the respective paragraph to:

"The case of zip-closed-only Al3z bags can be seen as a representation of sample transport and storage. Comparison of zip-closed-only Al3z bags and heat-sealed zip-closed Al3z_hs bags allows assessing the negative impacts of sample transport and storage on vapor loss, as heat-sealing is generally not applied before inflation."

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?

We will add the following recommendation to the manuscript's conclusion section.

"In order to prevent evaporation, Al-laminated bags do not require extra measures. Nonetheless, cooling samples prior to inflation is advisable in order to reduce microbial activity as well as the associated build-up of CO_2 and changes of the gas matrix. Ultimately, this prevents reducing environments and the production of spectrally interfering gases. Freezing samples for this purpose, however, cannot be recommended as this might destroy soil aggregates and microstructures. The resulting effect on isotope readings has not yet been investigated systematically."

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

In this conclusional sentence we refer to the fact that samples stored in the proposed Al-laminated bags did not lose significant amounts of water over a time period of four weeks, which exceeds any routine storage time we are aware of.

L580: What is meant by "extreme conditions"?

We refer to "extreme conditions" such as cases of high salinity or strong aridity.

We will insert "regarding e.g. salinity or aridity" after "extreme conditions".

References

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