

Review of: Controversial 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
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Reviewer: Leonard Wassenaar

General Comments

This technical paper provides a very thorough review and assessment of various approaches and materials types aimed at standardizing the isotope analysis of porewaters using the vapor-equilibration and laser analysis approach. This is a much needed review, and the testing of materials makes this a worthwhile contribution for informing new practitioners about adopting rigorous approaches for porewater isotopic determinations. I will not repeat the comments of Review #1 – I add here only additional comments to those already made.

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).

Title – I think the word “controversial” is not a good one here, I suggest substituting it with “unresolved”. The former suggests conflict (at least how an English speaker would read it), whereas what you are really trying to address are “unresolved technical challenges”.

We will change the title to:

“Unresolved aspects of the direct vapor equilibration method for stable isotope analysis ($\delta^{18}\text{O}$, $\delta^2\text{H}$) of matrix-bound water: Standardizing protocols through empirical and mathematical scrutiny” to emphasize the importance of the scrutinized aspects as well as the fact that a consensus regarding these had not been reached yet within the community.

One clear operational conclusion for me from all the Figures is this: do not equilibrate longer than 1-2 days, if possible. This is obviously both a logistical and analytical consideration and dimension, which is a feature of many applied methods. But this is indeed possible for many types of permeable soils and geological media. Plan the sampling and analyses accordingly.

We agree that in an ideal setting, large numbers of samples can be processed within a few days. However, wouldn't it be nice to have the option to plan with a buffer that accounts for potential issues regarding cooling chain, transport time, remote field sites, unknown soil types etc.? The suggested Al-laminated bags would provide this option.

Para 1 – lines 32. What is missing here is relaying that DVE-LE is really a proxy approach over the physical extraction of water methods in the past. We know there are many problems with physical extraction, and so DVE-LS has some advantages, as noted. (you have this later in the MS – suggest moving it here)

We will rephrase the respective sentence to:

“Instead of physically extracting water, the method employs analysis of a corresponding vapor phase and thereby bypasses many of the previously necessary, laborious sample preparation steps.”

Figure 1 – I suggest replacing “work discipline” in panel 5 with, “time window” of data integration.

We will add “time window” to the list of critical aspects. “Work discipline” refers to the higher number of samples that can be processed if the measurements are conducted in a structured and disciplined manner.

Line 62 – I am aware of several student DVE-LS attempts (not published) on plant water and xylem extracts – they have serious issues with a lot of VOC interferences. Suggest removing this sentence for now rather than appearing to promise what is not yet proven.

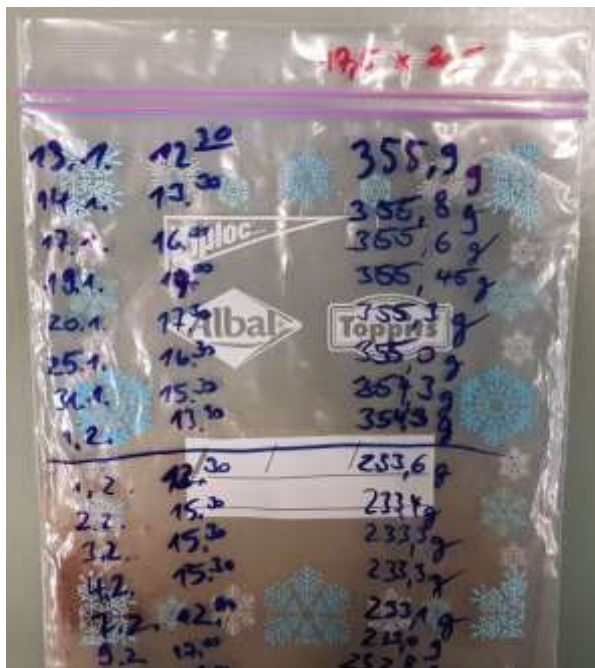
True, we ourselves have also tried DVE-LS analyses of plant and xylem samples and encountered related VOC issues. We will insert “published” before “field study”.

Line 135 - SOP – define this acronym in the first instance.

Done

Table 1 / line 261 - I do not see any of the widely used Ziploc® thick-walled double seal freezer bags used here as is suggested in Line 151/Line 261. The Trademark for Toppits® is Zipper®, isn't it? Unless I am mistaken these are separate trademarked brands and products. These zippers may not be the same between these. And you do not want to confuse two company separate products! I am aware that Ziploc brand bags are not easily available in Europe. If this was the case for the omission of the Ziploc bags, perhaps note this.

Thank you for raising this point. Actually, ‘Ziploc’ brand was in fact used by Toppits for their freezer bags at the time when we conducted the weight loss experiments. As proof, we provide here a picture of an originally used Toppits freezer bag as well as the package in which they were sold.



Apparently, in the meantime Toppits changed the zip closure from ‘Ziploc’ to ‘Safeloc’ brand, which may have caused the confusion. However, ‘Ziploc’ and ‘Safeloc’ branded Toppits freezer bags are

identical in terms of material type and thickness. This should make our findings transferable to nowadays available 'Safeloc' bags.

To avoid confusion to the readers, we will remove the word 'Ziploc' in line 261. Except for line 261, the bags were called 'Toppits' throughout the manuscript.

Overall, we would like to emphasize that the distinction should not be made between 'Toppits' and 'Ziploc' but rather between 'Toppits' versus e.g. 'SC Johnson', regarding the manufacturer/distributor potentially using different material types and thicknesses, or 'Ziploc' versus e.g. 'Safeloc' brand which refers to the closure type.

Would be good to add the thickness (in mil). Its not clear to me what strength means in this context. Thickness data in micrometers (μm) are provided in Table 1. The header will be changed from "material strength" to "material thickness"

Lines 263-264 Costs – would be good to mention Al-bags cost ca. 5.5 times more than plastic so the reader can assess budget implications.

At this point, we meant to emphasize that both tested bags are available at low costs, ranging two orders of magnitude below e.g. specialty Tedlar bags or Linde plastigas® bags, which cost about € 25/unit and are thus prohibitive.

Figure 3 & 4 – one conclusion that seems obvious to me from Figure 3 & 4 is that if you "triple-bagged" Toppits, you would be very close to the performance of the Al bags - is that a reasonable interpretation of the reduction in water loss and isotope effects in these figures? If so, triple bagging would still be 50 % cheaper than Al, albeit a bit more awkward. Can this be tested?

We agree that, theoretically, triple bagging samples using freezer bags (€ 0.42/"unit" (a.k.a sample)) are ca. 36% cheaper than Al-laminated bags (€ 0.65/unit). Further, it can be assumed that water loss rates and isotope effects would be about one third of the effects observed for standalone Toppits bags due to the threefold material thickness. However, we hesitate to say that the effects would be "very close" to the case of Al-laminated bags. Instead, the latter – even without heat-sealing – would still perform 2.3, 2.7, and 4.4 times better regarding water loss rates, $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Apart from that, we would like to emphasize that in our lab routine we never use inflated Al bags without heat-sealing. We always work with heat-sealed bags, which outperform the theoretically triple bagged samples by factors of 10.7, 28.3, and 2135(!) for water loss rate, $\delta^{18}\text{O}$ and $\delta^2\text{H}$.

Further, from our experience, double-bagging bears the risk that the zip closure of the inner bag pops open during or after inflation when inserted into another bag of the same size. Clearly, this risk would increase when tripling the bags. Not to mention the additional time needed for handling of so many bags while dealing with evaporation-susceptible samples. Using freezer bags of different sizes might make smoother work but also increases the relevant areas of vapor-permeable materials, the effect of which would have to be quantified in a different study.

Page 15 – I think you need to add a section on implications for Los Gatos laser – the flow rate on ICOS vapor lasers is >700 mL/min. This can be reduced to around 120 ml/min (see original DVE-LS paper), but no lower. This means there are a different set of practical constraints for users of LGR vapor lasers. Sampling frequency is 1Hz for both suppliers.

This issue has already been addressed in the Discussion (l. 452) where we state that for users employing analyzers with higher gas flow demands larger sample bags or a different sampling design are necessary. We will add "(e.g. Los Gatos)" to the revised manuscript.

Line 361 (and discussion). You need to very clearly state that Toppits could be completely different from Ziploc. This section seems to muddy that discussion, leaving a rather unfounded impression that Toppit performance = Ziploc performance. This could be wrong (or correct) until you have data to prove it.

As elaborated above, we used 'Toppits' bags in our study, where the closure type was 'Ziploc'. Certainly, this should not be mixed up with 'Ziploc'-closed bags from a different manufacturer (e.g. SC Johnson?), apparently supplying other continents and called "Ziploc bags" in other studies.

To make it clearer, we will change the sentence

"However, it is unclear whether those bags and the ones tested here exactly match in terms of material type and strength."

to

"However, it is unclear to what extent those bags and the ones tested here match in terms of material type and strength as we only tested standard freezer bags available in supermarkets and drugstores in Germany"

Discussion on lines 380+ – you will recall that the Hendry et al paper suggested cold storage at 100 % RH to avoid the high flux potential of a low RH environment for storage.

We are aware of the suggestions of the Hendry et al paper.

However, Ingraham and Criss (1991, 1998) demonstrated that 100% RH does not prevent shifts in isotopes of adjacent liquid water reservoirs due to relative deviations from equilibrium regarding the heavier isotopologues (different vapor pressure deficits of the isotopologues).

Section 4.2 about containers. One foolproof albeit qualitative observational way for detecting leakage is if the bags deflate in <24h after being pressurized with dry air. There is no mention of this, despite its well known that any bag can leak – was this effect observed and used?

We are fully aware of this qualitative test. However, having worked with Al-laminated bags for several years, we literally never saw a leaking bag when properly heat-sealed - and handled, of course.

Line 458 – remove the word "pitiful"

Will be removed as suggested.

Line 486 – regarding porewater salinity this reference is also useful since it was done by DEV-LS. Koehler G, Wassenaar LI, Hendry J. Measurement of stable isotope activities in saline aqueous solutions using optical spectroscopy methods. *Isotopes in environmental and health studies*. 2013;49(3):378-386.

Thank you for alerting us to this reference, which will be inserted into the updated manuscript.

Line 541 – you really mean Toppits brand storage bags are not suitable... isn't that correct? You did not test Ziploc. Do not draw conclusions for products what you did not actually test.

As elaborated above, we used 'Toppits' bags in our study, where the closure type was 'Ziploc'. Certainly, this should not be mixed up with 'Ziploc'-closed bags from a different manufacturer (e.g. SC Johnson?), apparently supplying other continents and called "Ziploc bags" in other studies.

Line 565 – replace controversial with unresolved.

Will be changed as suggested.

Line 568 - "... the limits of Toppit brand transparent freezer bags. (again, do not generalize outcomes towards what you did not test). Cautionary notes are of course always welcome, and this paper clearly shows these.

We will insert "Toppits" as suggested.

Finally, there seems to be some confirmation bias against using Ziploc brand plastic freezer bags, despite the brand was not tested in this paper, leading to conclusions that can only be verifiably applied specifically to the Toppits brand alone.

Be sure that conclusions are drawn only for products you actually tested and not generalized to those you did not. The findings of this paper, while highly credible, do not fully agree with what others experienced using Ziploc which gives me some hesitation about seeing very strong conclusions

towards not using any plastic bags of any kind, and requiring at least 2 days of equilibration. I think this is walking on thin ice without any supporting evidence.

As elaborated above, we used 'Toppits' bags in our study, where the closure type was 'Ziploc'. Certainly, this should not be mixed up with 'Ziploc'-closed bags from a different manufacturer (e.g. SC Johnson?), apparently supplying other continents and called 'Ziploc bags' in other studies.

Apart from that, we certainly never intended to defame the work of other research groups – especially not the work that was inspiration for this study.

References

Ingraham, N. L. and Criss, R. E.: Effects of surface area and volume on the rate of isotopic exchange between water and water vapor, *J. Geophys. Res.-Atmos.*, 98, 20547–20553, doi:10.1029/93jd01735, 1993.

Ingraham, N. L. and Criss, R. E.: The effect of vapor pressure on the rate of isotopic exchange between water and water vapor, *Chem. Geol.*, 150, 287–292, doi:10.1016/s0009-2541(98)00109-0, 1998.