

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
Author(s): Benjamin Gralher et al.
MS No.: hess-2021-255
MS type: Technical note

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.

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”.

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.

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)

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

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.

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

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. Would be good to add the thickness (in mil). Its not clear to me what strength means in this context.

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.

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?

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.

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.

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.

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?

Line 458 – remove the word “pitiful”

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.

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.

Line 565 – replace controversial with unresolved.

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.

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.