

Hydrol. Earth Syst. Sci. Discuss., referee comment RC1
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Comment on hess-2022-393

Anonymous Referee #1

Referee comment on "Technical note: Discrete in situ vapor sampling for subsequent lab-based water stable isotope analysis" by Barbara Herbstritt et al., Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2022-393-RC1>, 2023

This manuscript presents a method to store water vapor sampled from matrix-bound waters in the field for later stable isotope analysis in the lab by laser spectrometer. I think it is a good contribution and such eventually be published, though I cannot give my endorsement without the following general and specific comments being addressed.

General comments:

The procedure and calculations used to calibrate the observed vapor measurements and assess their accuracy and precision are vague at best, and opaque at worst. This is troubling, and almost suspicious, because these metrics are the backbone of how to assess the effectiveness of the proposed methods. Why would the authors be so vague about such a fundamental component of assessment? I cannot endorse this manuscript without seeing a much more rigorous presentation of how they assessed accuracy and precision. Except for one instance, they don't even bother to state what the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the test waters they used were.

Also missing is a simple section that presents their recommendations of how to best employ the method. I suggest at the end of the discussion they present a brief and easily

digestible “Best Practices” section. Instead, what is now included is a litany of what worked better than others. This leaves the reader thinking, “OK, so what do I do? Just tell me and I will do it.”

Specific comments:

P1, L1: The use of “mobile” in the title is somewhat misleading. It implies that the analytical system is mobile, which is not the case. Of course, any sampling is inherently mobile, as you have to move to the location to do it. Also, why “discrete”? Isn’t any sample discrete? I suggest rephrasing the title to better describe what you are doing here: A method for sampling in situ water vapor to make stable isotope measurements. Or as you state later (P5, L12): “the aim of this study is to develop a technique to collect discrete vapor samples in the field for subsequent lab-based analyses”

P2, L15: Dawson and Ehleringer, 1991 is certainly a pioneering paper, but they didn’t actually identify the water source for their streamside trees, just that the trees were not using soil water. Suggest including Oerter et al, 2017 because they did actually find the water source (using water vapor isotopes): soil water.

Oerter, E, G Siebert, D Bowling, G Bowen, 2019, Soil water vapor isotopes identify missing water source for streamside trees, Ecohydrology, v. 12: e2083, <https://doi.org/10.1002/eco.2083>

P5, L11: Either provide direct evidence and citation for your claim of “clearly biases the isotope data”, or leave it out. Otherwise this is an unsubstantiated claim.

P7, L8-20: I don't understand this section completely. Are you doing this in the lab or field? Why is the analyzer running at the same time you are filling sampling bags? Why is there excess gas flow if you are sucking moist air out of a bag and into the analyzer? If you are in the field, how do you power the mass flow controller and pump?

P9, L1: Suggest including a figure with pictures of the bags, focused on the fittings. These are hard to visualize otherwise.

P9, L9: What measurement or spectral parameter would identify diffusion or outgassing?

OK, I see later that you address this. I suggest either briefly discussing or pointing the reader to where you address it later.

P9, L19: Seems like you could employ a better, more intuitive bag naming system, so that the reader could reasonably understand what bag/valve combination you are talking about, rather than having to look it up in Table 1. I see you have made efforts toward this, but it could still be improved. Why does it matter if they are silver or red or gold? Is the material itself different? To replicate your results and use your method does the reader have to get red bags?

OK, I see later that you address this. I suggest either briefly discussing or pointing the reader to where you address it later.

P10, L13: Bags from inside the storage cans?

L10, P18: Please define and describe DDS mode.

P11, L4: Were the bags analyzed under the same conditions as the wet-sand boxes were kept and the bags filled in? Or taken back to the lab and analyzed there?

P11, L5: I don't understand this calibration procedure. What was the d_2H and d_{18O} values of the water used for the wet-sand boxes? Why use the extreme d_2H values? What about d_{18O} ?

This point is extremely important! The assessment of your whole study hangs on how you calibrated, and how you assessed the accuracy and precision of measurements derived from your method.

P12, L7: What were the δ values of the "isotopically diverse" sources?

P12, L11: This explanation of the precision and accuracy is very vague. What were the "calibrated isotope reading" upon which the SD was calced and how many? What is the "respective target value"? This is fishy, because this is the metric by which your whole method must be evaluated by.

P12, L15: This seems to me to be due to the concentration-dependence of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values. This is well known for Picarro L-2130 generation instruments operating in continuous flow mode. The magnitude of the effect is larger than I have experienced though, so it could have multiple causes.

OK, I see later that you address this. I suggest either briefly discussing or pointing the reader to where you address it later.

P13, L8: Finally, you tell us what the d values of the water you used were. This information needs to be included throughout.

P14, L9: This approach where you briefly describe the bags, then mention their name code helps me understand which bags you are talking about. I suggest you do this throughout the entire manuscript.

P14, L15: Here again with no bag type description I don't know which bags you are talking about. Use the description approach in the previous paragraph to help your reader understand which bags you are talking about.

Figure 6: It is hard to tell the various symbols apart, especially since so many overlap. I suggest naming the symbols larger and more distinct colors. This applies to the other figures as well.

P22, L13: OK, now I see that you are considering vapor-concentration effects. This discussion section is nice and complete.

P 23, L 7: OK, now I see you are discussing the color issue.

P 26, L22: I suggest a short section here that summarizes "Best Practices" about how to employ your method.