RC1: , Anonymous Referee #1, 05 Jan 2023 reply

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.

We thank the reviewer for the constructive comments, which will help to improve the manuscript.

 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 $\delta^{18}O$ and δ^2H values of the test waters they used were.

We will add more details to the description of our calibration procedure to make clearer how we assessed precision and accuracy of the obtained isotope values.

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."

We will add a detailed SOP/ best practice to the revised manuscript for potential users.

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.

Our sampling system is mobile in opposite to the immobile in situ setups, which we try to develop further. There, a field site is instrumented with probes and analyser, with the disadvantage that the sampling site has to be chosen according to the setup's restrictions and requirements (slopes, tubing lengths, distances to the instrument, access to power supply, etc.). Our method allows the position of sampling to be detached from the position of the analyzer which means the sampling is mobile relative the lab-based measurement.

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 â€¨the field for subsequent lab-based analyses"

We sampled 'discrete' in contrast to the 'continuous', on-site vapor measurements, the capabilities of which we want to expand with our approach. We will consider changing the title under consideration of the reviewer's suggestion.

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

The suggested additional literature will be included in the revised manuscript.

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.

To eliminate the confusion, we will rephrase this section to: "A sophisticated calculation procedure is necessary for both approaches (Havranek et al., 2020; Magh et al., 2022) to remove the effects of the initial pulse of water vapor during the start of the measurement phase. This initial pulse is mixed with pre-sample vapor which clearly biases the obtained isotope data."

P7, L8-20: I don't understand this section completely. Are you doing this in the lab or field?

> The effect of changing gas throughflow rates on the isotopic composition was investigated in a lab experiment. We will add this information to the revised manuscript.

> 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?

> No bags were filled in this part of the study. In this section we investigate the effect of changing gas throughflow rates on the isotopic composition. We increased the throughflow rates through the probe and thus produced more vapor than the analyser takes. Therefore, a spillover was needed.
> We tested the effect of increased flowrates in order to facilitate shorter bag filling times in the future application.

> If you are in the field, how do you power the mass flow controller and pump?

> In a field application mass flow meter and pumps can be powered by e.g. 12 V batteries.

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

As suggested, a figure with pictures of the bags will be added to the supplement.

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.

The spectral parameters are introduced in the method section on p. 7. There, we will add which parameter is indicative for what.

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.

We were surprised ourselves to find differently colored bags to perform differently, as we describe in the result section and discuss later on.

P10, L13: Bags from inside the storage cans?

We meant all the bags from inside the box. For clarification, we will add that we mean those from inside the storage cans as well as the uncanned ones.

L10, P18: Please define and describe DDS mode.

The working principle of the probe in the different modes (e.g. DDS) is described by Volkmann et al. (2014). We will describe the working principle in the revised manuscript but omit the abbreviation used in the cited literature to eliminate the confusion as other working principles were not used in this study.

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?

In this field experiment everything was carried out under identical conditions in the field. Also the bags were analysed with the analyser in the field two hours later.

P11, L5: I don't understand this calibration procedure. What was the d2H and d18O values of the water used for the wet-sand boxes? Why use the extreme d2H values? What about d18O? 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.

By writing 'the extreme d2H values' we describe which two of the four reservoirs we considered as calibration standards and which were thus used as validation standards in this field experiment. This selection was maintained for the calibration of the d18O values as well. We will rephrase the respective section for clarification.

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

We will elaborate on the d values of the isotopically different sources in the revised manuscript.

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.

The 'respective target value' is the in situ value we measured in the lab which we tried to reproduce with our calibration procedure.

P12, L15: This seems to me to be due to the concentration-dependence of the d2H and d18O 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.

We addressed this matter on P12 in L17 and also later in the discussion.

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

Thanks for pointing to this; we will add the information to the method section.

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.

We will add the name codes where they are missing.

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.

We will expand this introductory sentence with the requested bag type description.

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.

We found that the figure was better readable when using color gradients rather than different colors or symbols (as e.g. in the supplement Fig. S3 and Fig. S4). We will try to improve the figures by enlarging the symbols.

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

Thank you.

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

We were surprised ourselves to see that differently colored bags performed differently.

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

We will include a detailed SOP/ best practice for potential users.