Comment on hess-2022-37
Rachel Havranek (Referee)


General comments:

In this paper, the authors test a flexible, cost effective way to sample water vapor from trees for stable isotope geochemistry. This kind of system fills a strong need for the stable isotope community, and will be very useful for many different applications. To test that their system was reliable, the authors performed storage tests both in the lab and in the field. The authors found that there was systemic storage bias in oxygen isotopes over time, and that bias was only present for 'crazy heavy' waters for hydrogen isotopes over time. Below, I suggest the addition of one simple experiment to the manuscript to demonstrate that the vial cleaning protocol is sufficient, and that the vials are sufficiently resistant to atmospheric intrusion over the proposed storage timescale (3 days or less). Broadly, I think this is an excellent paper and the system will be widely used by the community. I strongly support the publication of this paper in HESS.

Rachel Havranek

Specific Comments:

Atmospheric intrusion & vial cleaning protocol: My largest comment on this paper is that the authors did not sufficiently address the issue of atmospheric intrusion, nor did they demonstrate that they sufficiently eliminated an atmospheric signal from their vials prior to sampling.
With regards to the cleaning protocol: I appreciated the discussion of vial cleaning protocol and I think that baking the glass vials at 65°C for 24H is likely sufficient. However, I have concerns that the PTFE caps were sufficiently dried (since PTFE is SO ‘sticky’), and suspect that might be the source of some of the observed drift. When I have played with PTFE fittings in the SWISS system, I’ve been disappointed by how much PTFE exchanges. I am also curious what gas the vials were purged with prior to sampling? If there is atmosphere in the vials when they are crimped, and then they cool post heating, I would expect atmosphere to stick to walls of the vial, which could ultimately exchange with sample vapor, even after so many vapor ‘turns’ during sampling.

I also think that the authors need to do a little more work to demonstrate to the readers that atmospheric intrusion is not a source of error for this system. The authors didn’t include data in this initial submission to allow readers to evaluate if that was a source of error. This would be a simple and convincing addition.

Encouragingly, for most natural waters the VSVS system was within error of direct measurement. What worries me is that 0-day did not overlap within uncertainty for either oxygen or hydrogen for the light standard – which is a pretty typical high altitude and/or high latitude value. It’s not clear to me that method precision is truly accounted for.

To hit two birds with one stone, I suggest a very simple, short timescale experiment where the authors fill a set of vials (perhaps 10 to sufficiently catch crimping variability?) with just dry air from the drierite system, and then do a storage test, just as they did with the rest of their lab tests. Given the authors’ recommendations in the discussion, I think a 3 – 5 day experiment should be sufficient. I would also recommend that the authors measure the dry air the day they fill the vials so that small changes in water concentration can be detected. With our drierite system, I know that there can be some variability and so it's nice to have that baseline value recorded.

**Other protocol questions**: Given that this paper is directed towards an audience of potential future users, I have a few small questions about lab protocols that could likely be answered either through some supplemental text or the addition of a few short sentences into the main body of the manuscript.

- Crimping: I am unfamiliar with how the crimping process worked, I think a very short (a few sentences at most) discussion of how to know that a cap has been sufficiently crimped or has been over-crimped (and therefore leaky) would be very helpful for the target audience. Alternatively, is there a way the authors imagine they could screen for that during sample measurement?
- Did the vials re-cool between heating and measurement or were they measured warm? (did they have the hot plate under them as you measured them?).
- Your total flushing time is somewhat based on flushing volume ‘turns’. I noticed on figure one you cite an inlet rate of 35 ml/min. On our 2130 we actually only pull ~25
ml/min. So, I wonder if you have double checked that rate? It might be nice to put a note on line 103 that says something like "time to one full volume can vary Picarro to Picarro".

- How do the authors identify spurious vials?

**Storage time correction:** I think more explanation of your choice to use a generalized storage correction is needed here. From what I can tell from your data, the offset between ambient air and the measured isotopes should dictate how much it moves. For example, the storage correction for d18O from the ‘light’ isotopes is very different than the one predicted by the ‘crazy’ heavy. It’s relatively easy to imagine a scenario where the ambient air isotopes are very similar to those sampled for an experiment and so just using a light or medium correction would be more appropriate. If the scale of correction is indeed not very different across isotopes, it would be helpful to demonstrate that some way in the supplement.

These papers are really hard to do, and I applaud the authors for the effort. But given that they are going to apply a linear regression to correct data in the future, I question whether or not they have gotten enough data to truly say that they are representing real variability. Some further discussion of sample size, as it relates to creating a correction factor would be helpful. Further, do you think each lab should create their own correction line or do you think that this is more universally applicable?

I appreciated that the authors included a preceding works section – it demonstrated the motivation for their work and helped show context. I also appreciated the discussion of how current system constraints have introduced location and social biasing into the scientific literature.

**Technical Corrections:** In this section, I have labeled my correction by line

32-33: I think it would be appropriate to significantly expand this citation list to showcase the variety of kinds of in situ work that is being done. For example, it would also be appropriate to cite Maria Quade’s, or T.H.M Volkmann’s work here. Beyer et al., 2020 (HESS) would also be a nice addition here.

43: I think it’s also fair to cite Orlowski et al., 2016 here

48: Beyer et al., (2020) *HESS* would also be good to cite here

49: The word choice interferences doesn’t sit well with me, I wonder if this sentence could be reworded to make your meaning clearer. Perhaps “… Direct equilibration between
liquid and vapor water in the soil …”

91: Were you able to dry the PTFE tubing that goes between the sample vials and the CRDS to eliminate any memory effect from that part of the system? I imagine that could be done quite simply by just having a ‘dry’ vial that you flush through between samples.

Figure 1: These kinds of figures are very challenging to make well. I appreciate that the photo demonstrates practical complexity in the lab setting. I think this figure could be improved with the addition of a small, simplified cartoon to the side showing all the components. This would help readers hone in on the important components without getting too distracted by all of the real-world lab complexity. Or, another way to make the figure more readable to be to add a small white box behind the text boxes, I had a hard time with the red text in particular.

103: You cite a 35 ml /min pull rate from the Picarro, with a 50 ml container & 10 minutes of flushing that should only be 7 turns (35*10/50 = 7). I’m not sure that nit-pickiness really matters for the scope of this experiment given that the authors observed signal stabilization. But, I think given that this is a methods development paper its most helpful to the community to be hyper-specific about some of these details.

156: A huge advantage of this system over the SWISS is the size and therefore ease of transport (e.g. 50 ml vials vs. 650 ml flasks), so I think one selling point that could be an estimate of total size & weight (just as the authors did with the battery). The SWISS also requires quite a bit of time consuming construction and plumbing and so some sentence to that effect, and an advantage of this system is that it is easy to set up.

180: Is your data reduction code widely available (e.g. github)? This development paper would be even more helpful to the community if we can also see the data handling process.

Figure 3:

- I’m not sure if it’s the file the authors provided, or a formatting issue from HESS, but it would be great if figure 3 was the full width of the page. If it is an author-side issue, using ggsave you can set the figure width to 6.5 inches - ggsave(plot, “plot.pdf”, width = 6.5, units = c(“in”)).
- Where does ambient air sit in isotopic space relative to the standards measured? I think for the “crazy heavy” water it’s easy to see that its trending towards room values, but it’d be nice to have a sense for how far it got towards that value.
190: Please expand on why a Wilcoxon test is appropriate here, and what you hope to learn through it. Unfortunately, many people reading your paper might be unfamiliar with that statistical test – and a short 1-2 sentence explanation of its use and limitations would help your reader assess suitability.

220 – this paragraph as written is a little confusing. I think this could be solved with just a quick additional introduction sentence that says something along the lines of "We observe two different patterns between hydrogen and oxygen isotopes, we first address storage effect on hydrogen isotopes and then oxygen isotopes."

243: Ahh, very clever. I initially didn’t like that choice, but with the explanation, it makes sense.

336 – My feeling is that this contradicts what was stated in the results