

Report #1

We appreciate your review and comments on our manuscript, “Technical note: A fast and objective autosampler for direct vapor equilibration isotope measurements”. Your feedback is valuable to us and we will make the recommended minor revisions accordingly. However, we do not agree with the major revisions you ask for, as all the points raised are already addressed in the manuscript. We provide detailed responses to each of your comments below.

Writing Style

Regarding scientific writing style, there is widespread inconsistency in the manuscript in grammatical tense, causing confusion. The paper needs to be edited to correct this. It seems a minor thing, but it will improve how the paper reads. Here is the rule to follow: YOUR work and findings must be stated in the past tense (did, determined, tested, had, were), but all published citation findings and well-known knowledge are given in present tense (is, are). An example of this inconsistency referring to the same published work (present tense) is in Lines 19 “they are applied...” and Line 21 “they were ARE also used to estimate..”. Many other instances.

We partly disagree with this comment. While we agree that our work and findings must be presented in the past tense, we use the present tense when we directly refer to figure to explain them and for continuously relevant published work (like in line 19). However, when the publication is in the past, but still relevant, we use the present perfect tense (like line 21). We edit the paper again according these general guidelines.

Major Comments

Hardware – how are samples thermally controlled? You need to add a descriptive paragraph about this because it a critical aspect to back determine the porewater delta values. Are sample boxes held in an insulated box, T-controlled room? How is T controlled and to what precision. Etc. What is recommended for users?

This is stated in Line 125: “The prepared bags were then stored in a climate-controlled room maintained at $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 48 hours.” We added a sentence that the room in which they were stored is the same as where the are measured, so it is clearer

Sample bags – give a description (Part No., volume etc.) in the Methods and a clear summary of the procedure how samples are added and sealed – this is missing (but briefly referred to later). At least one detailed paragraph regarding this aspect of the operation is needed.

Again, this was already addressed in Line 123, and exactly in the format that you want us to revise it to: “These samples were then placed into aluminium-laminated plastic bags (WEBER Packing GmbH; CB400-420BRZ; 500 ml) and initially sealed with a ziplock. Afterwards, the bags were inflated with dry air, heat-sealed, and equipped with two silicone blots to ensure each measurement started with a "fresh" septum “

This must be linked to software timing (a small bag will deflate quicky etc.). Note too the gas sampling flow rate from a Picarro (CRDS) much slower than an LGR (ICOS) that is mentioned as compatible with the system.

We never mentioned that the system as it is is directly compatible to a LGR (OA-ICOS). Everything is made for Picarros and consistently stated so in the manuscript!

Minor Comments

Title: The word “objective” is not appropriate, and you are missing the main object of the assays (porewater). Suggest changing to “An autosampler for rapid and reproducible direct-vapor-equilibration stable isotope measurements ($\delta^{2}\text{H}$, $\delta^{18}\text{O}$) of porewater”

We like the suggested word “reproducible” and changed the wording in the manuscript and the title.

Line 3. “...bonded to substances like...”. Bonded is a poor work choice here (suggests a chemical structure). Suggest changing to “... water in or adsorbed to...”

We changed that.

Line 6. “... may undergo evaporative isotopic changes...”

We added this.

Line 7. “lack objectivity” – again poor work choice. Suggest “...manual measurements require many laborious procedural steps that can easily compromise reproducibility.”

As stated above, we changed it throughout the manuscript.

Line 7 – delete “currently”

We deleted it.

Line 10 - “...connect to a laser isotope analyzer... automated measurements.”

We added this.

Line 11 “... performance criteria can be specified... facilitating reproducible analyses”

We changed the wording.

Line 27 (and other locations) – I realize this can “theoretically” be used for plant water, however, its well known that plant water has a lot of VOCs that wreak havoc with laser analyses through spectral interference. In the experience of this reviewer, DVE does not work well on plant water and even on plant water extracts, unless there is cryogenic purification. Because plants are not the focus of this work, I strongly suggest leaving out any references to plant water unless you can prove with data that it works.

The decision to apply DVE-LS ultimately rests with the researcher, who must determine whether it is a suitable method for their study. In this context, VapAuSa is just an automation for DVE-LS.

The cited studies in Line 27 by Bertrand et al. (2014)

(<https://onlinelibrary.wiley.com/doi/abs/10.1002/eco.1347>), Smith et al. (2020)

(<https://onlinelibrary.wiley.com/doi/abs/10.1002/hyp.13838>), and Kuhlemann et al. (2020)

(<https://doi.org/10.5194/hess-2020-425>), all employed DVE-LS successfully for plant samples.

While we acknowledged the co-extraction of VOCs as a potential issue, this influence can be corrected, as demonstrated by Hendry et al. (2011) (<https://doi.org/10.1021/ac201341p>) and recently also by Hebstritt et al. (2024) (<https://doi.org/10.1002/rcm.9907>). Moreover, Millar et al. (2018) (<https://onlinelibrary.wiley.com/doi/abs/10.1002/rcm.8136>) found that for plant samples, “direct

vapor equilibration outperformed all other methods" due to reduced co-extraction of volatile organic compounds. For these reasons, we have decided to retain this method in the manuscript.

Lines 39-42 – Somewhere in this section you need to emphasize that thermal stability is absolutely critical (and tolerance) because you are using the highly temperature dependent isotope fractionation between measured vapor and the liquid to back calculate the porewater isotopic composition. Also give the equilibrium equation used, e.g. Majoube and others ...

We added a sentence to the relevance of temperature stability.

Line 55 alters through? evaporation and diffusion...

We added “ evaporation and diffusion” for clarification.

Global: never use the term isotopic “signature” – use “values” instead.

We changed it to “composition” or “value” throughout the manuscript.

Line 56 replace “objectivity” with “automation” (everywhere in the paper).

We replaced it with “reproducibility”.

Line 57 – stray ? in Ceperley reference

We fixed the citation.

Line 59 delete “autonomous” use “automated”

We changed that.

Software – are there any failure monitoring features – leak, pumped the bag too long etc.?

No, there are currently not.

Line 123 – how much soil place in the 500 mL bags? Is this ratio important?

We added the amount (2-4 Tablespoons). The ratio is less important as long as there is enough water in the soil.

Line 125 – samples were stored at $20\text{ C} \pm 1\text{ C}$ – were samples measured in the same room, and was this potential error in T factored into the reported analytical uncertainty?

The samples were measured in the same room. The potential error of T was not factored in, as T was not recorded. However, all samples were ppm (H₂O) corrected, which resolves temperature changes. We added this to the manuscript.

Line 163 - should be superscript on delta values

We updated the formatting.

Line 169 – “pinched” – do you mean “punctured” ? - unclear.

We changed the wording.

Line 175-176 - ??? means differences were -XX e-15???

The bias means were that low, not the differences. So there is no bias.

Line 221 – you need to explain the reasons for drift (only evaporation?) and how it can be combated.

We added evaporation and diffusion as drift reasons. Also we added that they should be cooled

4.3 Objectivity (not a good word) -> Improving Replication?

We changed it to “reproducibility”.

Line 248 - replace personal with manual

We changed this.

Line 251 – avoid speculating about plant water as noted.

As stated above, we will keep it in.

Report #2

We appreciate your review and comments on our manuscript, “Technical note: A fast and objective autosampler for direct vapor equilibration isotope measurements”. Your feedback is valuable to us, and we will make the recommended revisions accordingly. We provide detailed responses to each of your comments below.

The manuscript: "Technical note: A fast and objective autosampler for direct vapor equilibration isotope measurements" (egosphere-2024-528) Submitted on 22 Feb 2024 by Jonas Pyschik, Stefan Seeger, Barbara Herbstritt, and Markus Weiler has been drastically improved after (1st round) reviewing. There are still some important pitfalls mostly regarding the presentation of results. Here by I "paste" a list of detailed suggestions: "

Ln 1: stable water isotopes to stable isotopes (2H and 18O) ratios of water

We changed this.

Ln 14: $0.1e-12 = 1e-13$ ‰ (means $1e-16$ on absolute scale?)

We changed the value.

Ln 15: Have you performed a F test? Please report values of significance

We did not perform an F-Test but calculated measurement repeatability by applying standard deviation for the identical samples and calculated the measurement bias as the average difference of measurement to true value for the whole system. So there are no p-Values to report.

Ln 19: add abundances after isotopes

We like the wording of how it is currently written and will leave it this way.

Ln 20: why not hydrogeological?

We added that.

Ln 23: if you need biblio please evaluate to cite: “Nasta, P., Todini-Zicavo, D., Zuecco, G., Marchina, C., Penna, D., McDonnell, J. J., ... Romano, N. (2023). Quantifying irrigation uptake in olive trees: a proof-of-concept approach combining isotope tracing and Hydrus-1D. Hydrological Sciences Journal, 68(10), 1479–1486. <https://doi.org/10.1080/02626667.2023.2218552>”

In the intro, we only cite papers applying DVE-LS. Since the suggested paper applies CVD we will exclude it.

Ln50: Instead of “referenced” I would use “normalized”.

We changed the wording.

Ln 130: Performed instead of conducted

We changed that.

Table 1. add [units] after sd, sd has the same dimensions and measurement units of physical quantities.

We changed it to your suggestion.

Ln 159-60-61: It is not correct presenting errors with such a number of digits! Only 1 or 2 significant digits are allowed and reported values has to be cut appropriately. E.g. ln 159: 0.7 (+/-) 0.035 wrong! You must write 0.7x (+/-) 0.04 or 0.7xx (+/-) 0.035. Once again I regret that in a scientific paper this rule falls to be applied.

Thank you for pointing this out, we corrected it to a x.xx digit format.

Ln 184: sd with only 1 or maximum 2 digits

We also changed this to two digits.

Ln 181: “Although the standard deviation was relatively high, it is similar across the measurements and suggests that the variance is likely due to the bags being measured twice, a theme that will later be discussed.” Does this sentence refers to the secondly measured bags only? Why do no show box plot also for these sets?

It refers to the fact that we measured each bag once manually and then by autosampler or vice versa. This is what is displayed in Fig. 5, where we show all data.

Figure 5 GENERAL IDEA: Why do not you comment that both datasets plotted intercept zero in the text?

We added this to the text.

Ln185: If you refer to r^2 which should be written in capital letter R^2 this is the squared correlation coefficient. It is used to evaluate linear relationship between two variables. Moreover you should explicitly state what are the two variable that you want to correlate linearly.

We changed this and added upon your suggestion.

GENERAL IDEA

Once you applied such linear model to produce figure 6 why do not evaluate and comment slope values and intercepts? Theoretically one should expect that such relationship with no biases should produce a 1:1 line with 0 intercept. In such a case it is better to add to the plot 1:1 line and also use the same scales for x and y.

The line shown in Figure 6 is the 1:1 relationship, which we believe shows the divergence. However, we added to the figure caption that the line is the 1:1 ratio, which indicates the optimal ratio.

Ln 197 e 198 reported values are much smaller than what reported in the abs.

The measurement repeatability is identical to that in the abstract. The low values are the measurement bias and the individual water samples.

Ln 198: sigma for dD can be cut to 4 per mil

We changed that.

FIGURE 7 please try to improve figure 5. My suggestion is to add data to figure 5 to produce something easily ascribable to FIGURE 7. Moreover why there are dD missing in figure 5?

We now also plot dD in Fig. 5 & 6.

Ln 230: accuracies also should be reported with the same number of digits.
i.e. 0.7-1.0 no 0.7-1.03.

We changed this.

Ln 240: source of uncertainty not uncertainty variable

We changed this.