Comprehensive Response to Reviewer Comments (RC1–RC3) and Editorial Decision (11 April and 3 June 2025)

We have carefully addressed all comments provided by the reviewers. The reviews were consistently constructive and have significantly contributed to improving the quality and clarity of the manuscript. We would like to sincerely thank all reviewers for their valuable input.

We have also taken into account the editorial decision and responded to the points raised. The arguments presented are of great importance. While we are currently unable to conduct additional experiments, we respectfully ask for your understanding. In response, we have expanded our discussion of the relevant variables in the manuscript.

RC1: 'Comment on egusphere-2025-272', Anonymous Referee #1, 11 Mar 2025

The Technical note: Efficiency of various evaporation barriers for use in automated water samplers for subsequent water isotope analysis by Mueller, Pekarev, and Knoeller evaluate in two experiments evaporation minimizing closers.

The manuscript overall well-written and clear, requiring only minor clarifications (detailed below). It makes a valuable contribution to water sampling best practices by presenting novel findings on evaporation effects, particularly with different closure types. This builds upon existing research and helps to design optimal water samplers for stable isotope analysis.

Minor points:

- To better present the difference between different closers, the authors should include a Z-score to compare different closers.
- A more detailed comparison with varying tube-dip diameters and d-exe used and found by other studies, e.g., Prechsel et al. 2014, Carton et al. 2024, and **Natali et al. 2024**, should be performed to potentially see the effect of different diameters of tube-dips and evaporate/ D-exe.
- To make consistent with the literature, use tube-dip instead of dip in
- L38-> Keep general or include other manufacturers.
- L40-> "in" or ratios of water...?
- 55-> "Iaea" capital letters and make manuscript consistent
- L84 -> I'm not sure if this is a research gap. It should be based on the scientific gap, not on a company's collaboration and test. Although the study was in collaboration, it is better to remove the company name from the main text and refer to it only in the acknowledgements.

This will allow to see the technical note in a broader view and application, which is more beneficial for the community.

- L100-> The experiments were unclear from the text; only after seeing Figure 3, it became clear. Therefore, state here as text as in Figure 3 that Experiment 1 consisted of bottles with different caps, such as Ref closed ref open siphon, etc.

  What was the goal of the experiment? Experiment 1 tested the syphon as an evaporation barrier.

- L106-> specify what temperature and humidity. In our lab in the tropics this could affect the evaporation and isotopic composition compared to other climate zones.
- L110-> Mention already here what the purpose of the experiment 1 and 2 were?
- L111-> "15 m long hose" Provide diameter
- L144-> It seems in the open bottle, there was evaporation. Include.
- L145 ->This sentence is not clear. Which method and what was challenging? Rephrase.
- L147-> 151 and 153 "mean = 0.12 ...." units are missing.
- Figure 3 -> Consider using a log scale for the y-axis.
- L206-> move to method
- L223 ->max or min? Double-check
- Why in experiment 2 the evaporation in % was not shown?
- Figure 8 ->evaporation lines? Is it the same axis interval? S
- Figure 9 -> Craig-Gordon evaporation lines?

Author comment on behalf of all Co-Authors (AC)

We thank the anonymous reviewer for providing useful feedback on our technical note, *Efficiency of Various Evaporation Barriers for Use in Automated Water Samplers for Subsequent Water Isotope Analysis*, submitted to HESS on 20 January 2025.

In the following, we provide detailed responses to the reviewer's comments.

- To better present the difference between different closers, the authors should include a Z-score to compare different closers.

We carefully considered including a Z-score but ultimately decided against it for the following reasons:

A Z-score is useful when comparing values within a dataset by standardizing them relative to their own mean and standard deviation. However, our study compares separate closer-systems, each of which performed at different levels despite being tested under the same conditions. In this context, a Z-score could misrepresent the actual differences between setups by emphasizing each system's relative performance within its own dataset, rather than facilitating a direct comparison between systems.

While using the mean and standard deviation of a reference system (e.g., closed reference bottles) to calculate Z-scores for other closer-systems would allow for a relative performance comparison, we find that presenting the raw performance data in a visually clear and statistically relevant manner provides a more informative and transparent representation of closer-system effectiveness.

All closer-systems were tested under the same conditions. Furthermore, our objective is not only to compare different closer-systems but also to identify the most accurate and cost-effective solution. Given that the setups share identical conditions, direct comparisons of the raw performance metrics (evaporation and isotopic fractionation) provide meaningful insights without the need for standardization via a Z-score.

- A more detailed comparison with varying tube-dip diameters and d-exe used and found by other studies, e.g., Prechsl et al. 2014, Carton et al. 2024, and Natali et al. 2024, should be performed to potentially see the effect of different diameters of tube-dips and evaporate/ D-exe.

Yes, we agree. The diameter of the tubes affects the efficiency of the evaporation barrier. In this study, we kept the tube diameter constant and tested different approaches to prevent sample evaporation (Experiment 1). Additionally, we conducted long-term experiments (Experiment 2).

In general, we consider the tube diameter a trade-off. For real water sampling, it is important to avoid clogging due to dirt or sediments. Therefore, the tube must have a sufficient diameter. However, it should be thin enough to minimize evaporation. In our experiments, we used an inner diameter of 5 mm. During long-term field experiments (some results are published in [1]), we had positive experiences with these polypropylene tubing (5 mm inner diameter) in terms of handling and reliability.

- To make consistent with the literature, use tube-dip instead of dip in

We agree. For clarity, we changed ‘dip-in (tube)’ to ‘tube-dip-in’. Now, we are consistent with other publications (e.g. [2] or [3]).

- L38-> Keep general or include other manufacturers.

We agree and have excluded example to keep it more general.

- L40-> "in" or ratios of water…?

Thank you for this remark. We corrected the language error.

- 55-> "Iaea" capital letters and make manuscript consistent

We have updated the references and made the changes.

- L84 -> I'm not sure if this is a research gap. It should be based on the scientific gap, not on a company's collaboration and test. Although the study was in collaboration, it is better to remove the company name from the main text and refer to it only in the acknowledgements.

We applied minor revisions to the research gaps in this section and removed the company’s name to keep the text more general.

- This will allow to see the technical note in a broader view and application, which is more beneficial for the community.

Yes, we agree. Thank you for this comment. We have made changes to the manuscript.

- L100-> The experiments were unclear from the text; only after seeing Figure 3, it became clear. Therefore, state here as text as in Figure 3 that Experiment 1 consisted of bottles with different caps, such as Ref closed ref open siphon, etc.

  What was the goal of the experiment? Experiment 1 tested the syphon as an evaporation barrier.

That was good advice, thank you. We rewrote this section to make it clearer and more consistent.

- L106-> specify what temperature and humidity. In our lab in the tropics this could affect the evaporation and isotopic composition compared to other climate zones.

The temperature and humidity are regulated in the laboratory. The set temperature is approximately 23°C, and the mean relative humidity is around 50%. We have added these important details to the manuscript.

- L110-> Mention already here what the purpose of the experiment 1 and 2 were?

We have made it clearer for readers and added a sentence to explain: 'Based on the results of Experiment 1, we selected the evaporation barrier that was easiest to handle and demonstrated the best performance compared to the other tested evaporation barriers.' (L132)

- L111-> "15 m long hose" Provide diameter

We clarified and gave information on the inner diameter of the used long hose.

- L144-> It seems in the open bottle, there was evaporation. Include.

Thank you. We included this information.

- L145 ->This sentence is not clear. Which method and what was challenging? Rephrase.

We agree and have rephrased this section. We removed the statement about the challenges of implementing a storage system in a sampler where bottles close automatically after sampling, as this information is confusing at this point.

- L147-> 151 and 153 "mean = 0.12 ...." units are missing.

Very true. We have corrected that and added the units.

- Figure 3 -> Consider using a log scale for the y-axis.

We changed it to a log-scale y-axis

- L206-> move to method

We agree and have moved this section to the Methods part. We rewrote it to ensure consistency.

- L223 ->max or min? Double-check

We double-checked and corrected it. We were describing the minimum value of the d-excess at this point. Thank you for your remark.

- Why in experiment 2 the evaporation in % was not shown?

We also performed weight measurements for experiment 2, but these are not reported in the manuscript. However, the results are interesting and consistent with the results of the isotopic analysis. For consistency, we have decided to include them as a new Figure 6. Detailed descriptions of the results have been added to the manuscript.

- Figure 8 ->evaporation lines? Is it the same axis interval?

The revised Figure 9A and B displaying the same results on different scales as mentioned in the labeling.

- Figure 9 -> Craig-Gordon evaporation lines?

We mentioned in the text that water sampled in the siphon (labeled with a star) plots along an evaporation line with a lower slope than the GMWL. To make this clearer, we have added the evaporation line to the figure.

References:

1. Radtke, C.F., et al., *Nitrate and Water Isotopes as Tools to Resolve Nitrate Transit Times in a Mixed Land Use Catchment*. Hydrol. Earth Syst. Sci. Discuss., 2024. **2024**: p. 1-32.
2. Michelsen, N., et al., *Comparison of precipitation collectors used in isotope hydrology.* Chemical Geology, 2018. **488**: p. 171-179.
3. Natali, S., et al., *On the reliability of tube-dip-in-water precipitation collectors in isotope hydrology: A field experiment for low rainfall amounts*. Journal of Hydrology, 2024. **644**: p. 132096.

RC2: 'Comment on egusphere-2025-272', Anonymous Referee #2, 19 Mar 2025 reply

The authors tested several different inlet designs of bottles designed for automated natural rainfall water sampling with the aim of preserving the samples' isotopic composition for up to several weeks prior to lab-based analysis. This is an attempt to optimize the design first described by Gröning et al. (2012). Ultimately, the authors found the original design to be superior compared to the tested alternatives. Nonetheless, the findings are of interest for readers of HESS and I recommend publication after minor revision.

General comments:

The authors refer to various climatic conditions for which users of automated sampling systems should carefully choose between the available options. However, the only "climatic" scenario tested in this study was 'stable (room-)temperature in the lab'. There was no other scenario tested in which the ball valve and/or the siphon could/would have been advantageous. In addition, the proposed solution for dealing with enrichment of heavy isotopes inside the dip-in tube is not applicable in (to be expected) cases of sequential rainfall. The authors only tested a scenario where they filled the bottles to their final filling level at the beginning of the respective observation periods. This does not reflect natural conditions, under which sequential rainfall during the selected observation period would flush out the dip-in water. I ask the authors to expand on this in the discussion.

The authors appreciate and understand the general comment from RC2. The evaporation experiments conducted for automatic samplers were performed under controlled laboratory conditions to minimize external influencing factors such as temperature and humidity fluctuations. These factors would further accelerate isotopic fractionation.

The findings from the Dip-In experiment, which demonstrated intense separation within the Tube-Dip-In system, are indeed interesting. However, they are not relevant when the sampler is operated as a single-bottle system, where water is continuously collected (e.g., rainwater as a monthly composite sample). That being said, there are also automatic samplers with multiple collection positions, where bottles or containers are stored for extended periods (e.g., HiRAS Sampler from UGT). For this reason, we have specifically focused on optimizing storage conditions within a sampling system. The goal should be to minimize exposure of the bottles to environmental fluctuations and to implement an appropriate evaporation barrier system, especially when subsequent water isotope analyses are planned

Specific comments:

L16 (and throughout the manuscript): "water stable isotope", not "stable water isotope"
Thank you for your comment. We agree and made the corrections accordingly.

L19: instead of vapor mixing, I think the physical process is rather unidirectional diffusion caused by vapor pressure gradients
Thank you for your insightful comment. We agree that the process is better described as unidirectional diffusion driven by vapor pressure gradients rather than vapor mixing. We have revised the manuscript accordingly to reflect this more precise terminology.

L27: You mention funnel size in the abstract but you do not investigate/discuss this aspect in the manuscript
We have removed this aspect from the abstract to ensure consistency with the manuscript.

L33: "long and large" = "long-term and large-scale"?
Thank you for your comment. We have adjusted the sentence to use "long-term and large-scale" instead of "long and large" for better clarity and precision.

L37: Please provide references for this statement
See [1], they tested different sampling systems, and provided an overview of rain collectors used in stable isotope studies (Table 1). We prove references for this statement like the modified ISCO sampler from [2].

L48: "isotope", not "isotopic"
We agree and have made the changes.

L53: "sold", not "sell"
We agree and have made the changes, using "sold" instead of "sell."

L55 and elsewhere: "IAEA" (all caps), not "Iaea"
Changed, see RC1.

L64: "created", not "was creating"
We agree and have made the changes.

L75: 'high sediment loads and microbial activity' is not a problem addressed in this study. Why do you unnecessarily lead the readers in this direction?
We agree that sediment loads and microbial activity were not directly addressed in this study. Although the statement is accurate, we acknowledge that it could be misleading for readers. Therefore, we have decided to remove it from the final manuscript.

L80: was aridity the problem or rather limited access to the sampling site?
The study by Michelsen, van Geldern [1] was a laboratory experiment simulating arid conditions with high temperature fluctuations (26-45°C) and low relative humidity (5%), aimed at assessing sampler designs suitable for arid regions. The focus of this study was on harsh conditions and comparing different sampler designs. In contrast, Michelsen et al. (2015) focused on immediate sample collection after rainfall events. Although the study took place in arid regions, storage-related challenges were not addressed.
We have revised this section to remove the specific mention of arid regions and instead focused on the challenges associated with extended storage times. Additionally, we have included another recent reference by Nigro, Žagar [3].

L81: what do you mean by "sample loss" other than evaporation?
We have revised this sentence and deleted the 'sample loss' to avoid any confusion.

L86: if "use in various climatic regions" was the goal, then why did you not specifically test various conditions?
We have revised this sentence to avoid any confusion regarding testing different climatic conditions in our experiments. The revised version emphasizes the "easy application for a large number of users.

L105: instead of "ranged between" + the list of settings, I'd recommend "was xx, yy or zz mL"; also: "5, 7, 20, or 21 days"
We revised this sentence which was already suggested from RC1.

L108: "designed", not "design"
We removed this information which was suggested by RC1.

L112: "or", not "and" (13, 26, 39 or 52 days)
We agree and revised.

L117: why was that an 'optimal scenario'? Wouldn't low temperatures like in refrigerators – the standard place for sample storage in all labs I know – be much better to reduce evaporation? Or high relative humidity to prevent/reduce vapor pressure gradients?
We have revised this section as suggested by RC1 and removed the term "optimal scenario" for laboratory conditions. While low temperatures, such as those in refrigerators, could reduce evaporation, water isotope samples are typically not stored there due to the risk of condensation, freezing, and water loss, which can compromise sample integrity.

L121f: Please insert "part" or "panel" before "A" and "B", also: delete "evaporation barriers" and parenthesis and insert "as evaporation barriers" after "tube"
We agree and have made the changes.

L126: "floating", not "swimming"
We agree and have made the change.

L130: delete "liquid" or insert "water" after "liquid"
We agree and have made the change by inserting 'water'.

L131: please define abbreviations upon first appearance (you do so in L133f)
Thank you for your comment. We have ensured that all abbreviations are defined upon their first appearance in the manuscript.

L146ff: please add units to mean and SD
We made the changes suggested by RC1.

L147: please insert "relative" before "volume"
We agree and insert 'relative' before 'volume'.

L152: why was the mean weight loss negative (-1.14)?
Sorry, typo. We removed the minus.

L153: for me, "contamination" refers to the addition of unwanted substances. Maybe better "compromising" or "flawing"?
Thank you for this advise. We have made the change and replaced 'contamination' with 'compromising'.

L159: please define the null hypothesis
We define the null hypothesis. We will add the following: 'The null hypothesis assumed no significant differences in weight loss or isotopic composition changes among the tested closure systems.'

L162: please insert "a siphon and" after "only"
We agree and have made the changes.

L164 (Figure 3): Where do I find data for dip-in only (referred to in L147)?
We corrected this and added 'siphon' to the sentence, as already suggested by RC1.

L172: Deuterium excess is not the deviation from the GMWL, as a value of 0 does not mean 'no deviation' but a deviation of 10 (as you correctly explain in L175f). Also, not only the δ^2H-H_2O value is relevant but also the $\delta^{18}O$-H_2O. I'd suggest something like: "Deuterium excess refers to the vertical deviation of water isotope data in permill from the GMWL in dual isotope space. It provides..."
We agree and have made the changes according to the referee's suggestion.

L174: "variable", not "parameter"
A parameter is usually a derived quantity that describes a characteristic of a system. Since d-excess is calculated using the formula after [4]:
Deuterium-excess=$\delta^2H-8\cdot\delta^{18}O$
It is not directly measured but rather computed from measured variables (δ^2H and $\delta^{18}O$). Thus, d-excess is a parameter that characterizes isotope relationships in water and provides insights into evaporation, moisture sources, and atmospheric processes.
We keep 'parameter' in the manuscript.

L175: "Isotope data plotting" instead of "water"
We agree and have made the change.

L176: insert "value" after "excess"
We agree and have made the change.

L177: please insert "as reference for" and "values" after "GMWL" and "excess", respectively.
We agree and have made the change.

L178: please rephrase. Maybe: "Deuterium excess values from experiment 1 indicate the highest..."?
We rephrased this sentence based on the referee's suggestions.

L180: "highest" or rather "lowest"?
We totally agree and corrected this phrase.

L182: please insert ""of storage", "color and" and ", respectively" after "duration", "point" and "size", respectively (if that is what you mean).
We rephrased this sentence based on the referee's suggestions.

L191: please insert "measurements" after "isotope(s)"
We agree and have added this word.

L196ff: I'm afraid, sequential rainfall will make this effort pointless. Does this mean that siphons are only useful for sampling single rainfall events (if at all)?
Thank you for this comment. Our approach, as mentioned in the general comments, is to develop an automatic water sampler capable of collecting multiple samples. However, each sample is a composite and must be stored evaporation-free until it is emptied. Given the various applications and sampler designs, we believe it is important to retain this aspect in the manuscript.

L205 (and elsewhere): be consistent: dip-in, not Dip-in
We already made the changes due to the recommendation from RC1.

L211: delete "however" as the statements before and after do not contradict
We moved this section to the Methods (as suggested by RC1) and made the corresponding linguistic correction.

L214f: Please move this sentence to the method section and explain how dip-in water was sampled. What was the volume of dip-in water? What was the height of the water column inside the dip-in tube?
We agree with this suggestion, which was also made by RC1. We have moved this section to the Methods and added the following explanation on how the dip-in water was sampled: 'The sampling of the tube-dip-in water was performed using a straw-like principle, where the water inside the tube was held by blocking one end of the tube and releasing the water by removing the finger from the other end.'

L216: 54 days? Elsewhere in the MS you state 52 days as maximum storage duration. Typo?; also: consider inserting "2" after "with"
The total duration of the long-term experiment was 52 days. We corrected and harmonized the numbers. And we added 'two' after 'with'.

L218: please delete "the results of the" and insert "data" or "values" after "excess"
We agree and have made the change.

L219: please insert "data" or "values" after "excess"
We agree and have made the change.

L221: not largest, but lowest d-excess values were observed, right?
We totally agree and already made the changes due to the recommendation from RC1.

L222: min, not max
We already made the changes due to the recommendation from RC1.

L224: please insert "d-excess values of" after "only" and "GMWL by more than the" before "measurement"
We agree and have made the change.

L225f: the slope of an evaporation line is a function of relative humidity (Gonfiantini, R., 1986, Environmental Isotopes in Lake Studies. In P. Fritz, & J.-Ch. Fontes (Eds.), Handbook of Environmental Isotope Geochemistry (pp. 113-168)) with greater slopes occurring under more humid conditions. Potentially, the layer of quasi-saturated air above the water surface inside the open bottle was thick enough to mimic saturation and cause the slope of the evaporation line to be very close to eight – although this contradicts the case of dip-in tube and siphon(?)
Yes, we cannot explain this phenomenon with certainty. However, we consider our possible explanation to be quite plausible ('A possible explanation could be fluctuations in relative humidity and temperature during the experiment, which may have induced interactions between evaporation and condensation processes.'). That the experimental setup with the tube-dip-in and siphon shows 'normal' evaporation behavior is interesting. All types of bottle closures and reference bottles were always placed side by side under identical conditions in terms of temperature and humidity. In the case of the open bottles, the closure was placed on the bottle opening, which is why we formulated our possible explanation in this way.

L228 and L232: please insert "values" or "signatures" or equivalent after "isotope(s)"
We agree and have made the changes.

L258: How would you determine the appropriate bottle size? I assume, it is a function of expected rainfall depth and collector funnel area(?) Please share your thoughts on this and ideally make a suggestion
The choice of an appropriate bottle size is crucial for maintaining the stability of the water isotope signature in water samples stored with a gas phase. The bottle size should correspond to the expected amount of water based on the anticipated rainfall and the collector funnel size. Additionally, the type of further analysis planned for the samples is important to ensure that an adequate volume of water is collected. Key factors to consider are the size of the funnel, the bottle size, and the sampling period. The sample volume should ideally fill the bottle as completely as possible. Overflow should be avoided, as it would lead to water loss, which could be problematic for many hydrological questions, such as transit time distribution studies.
We extended the manuscript and added the following suggestion: 'The bottle size should align with the expected volume of collected water (e.g., rainfall), considering the funnel area and desired sample volume. Overflow should be avoided to prevent water loss, which could compromise subsequent analyses and hydrological interpretations.'

L260: I think this sentence should appear before the statement in L256 where you already refer to a part of Figure 9.
We agree and have adjusted the order of the sentences to improve clarity.

L264: I seem to be unable to find the arrows in Fig. 9B
We removed the word 'arrow' and kept only 'within the measurement accuracy' to avoid making the figure too crowded.

L283 and L286: see comment to L19
We rephrased and explained 'vapor mixing' more precise according to the suggestion from the referee.

L287: please insert "combined" or equivalent after "dip-in tube" to clarify that the pressure compensation tube (and not the dip-in tube) was long. Generally, this sentence seems to suggest that you tested alternatives to the long tube, which you have not. Please consider rephrasing
We rephrased to avoid any confusion: 'The simplest and most effective setup tested was a combined tube-dip-in system and a long tubing to release air during filling.'

L291: why are these conditions more likely to cause differences that are more evident? I think that low (stable) temperatures and high (stable) humidity would rather reduce this effect, as low vapor pressure gradients would induce only little evaporation.
Thank you for your comment. We corrected our sentence ('These differences are likely to be more evident under variable temperature and humidity conditions.') and agree to the reviewer's point of view.

L295: under what circumstances would you recommend complicating a setup by adding ball valves and siphons? Imho, your data (and the conditions under which you collected them) do not give a hint in this regard.
Thank you for the comment. We agree that the data from our study do not suggest a need for complicating the setup with additional components such as ball valves or siphons. However, we included these options in the manuscript to provide a broader range of potential solutions that can also yield reliable results.

L300: please elaborate on this and be more specific about "specific" (here or in the discussion). What barriers are recommended under what conditions and why? Don't your data suggest that 'dip-in tube only' is the simplest (construction-wise) and best (isotope-wise) solution?
Thank you for your comment. We agree that additional clarification is needed to specify the conditions under which different evaporation barriers would be recommended. Based on our data, the "tube-dip-in only" setup appears to be the simplest and most effective solution for maintaining isotopic integrity, especially under stable environmental conditions. However, we tested and combined with other options like ball valves and siphons. We will revise the manuscript to more clearly outline the circumstances under which each barrier is most suitable.

References:

1. Michelsen, N., et al., *Comparison of precipitation collectors used in isotope hydrology.* Chemical Geology, 2018. **488**: p. 171-179.
2. von Freyberg, J., et al., *Technical note: Evaluation of a low-cost evaporation protection method for portable water samplers.* Hydrol. Earth Syst. Sci., 2020. **24**(12): p. 5821-5834.
3. Nigro, M., K. Žagar, and P. Vreča, *A Simple Water Sample Storage Test for Water Isotope Analysis.* Sustainability, 2024. **16**(11): p. 4740.
4. Dansgaard, W., *Stable isotopes in precipitation.* Tellus, 1964. **16**(4): p. 436-468.

RC3: **'Comment on egusphere-2025-272', Anonymous Referee #3, March 2025**

In the manuscript by Mueller et al. the authors present the effectiveness of three different evaporation barriers under controlled laboratory conditions, whereby the dip-in tube is a well-established method (Groening et al., 2012) for sampling of precipitation water for stable isotope analysis.

The two experiments they carried out were conducted with glass bottles of different sizes (50-250 mL) and exposure times from five to 52 days.

Overall, the manuscript is nicely written and well structured. The topic will be of interest for the readers of HESS and can be recommended for publication after minor revisions. However, the authors state that their goal is to create a system for use in various climatic regions (L. 86). This stated goal is a bit misleading, as all experiments were conducted explicitly under constant conditions, only (L. 116). I suggest rephrasing the statement in the introduction.

First of all, the authors would like to thank the anonymous third reviewer for their work, comments, and suggestions. We agree with the general comment provided and have rewritten this section accordingly, as already recommended by RC1 and RC2.

Apart from that I have the following specific and technical comments.

Specific Comments:

L. 30: and throughout the manuscript 'water stable isotopes' not 'stable water isotopes'

Thank you for your comment. We agree and have made the changes, which was already mentioned from RC2 (L16ff).

L. 33: '…long and large interference to the gas phase…' be a bit more precise and specific. I guess you mean exposition, diffusive exchange with ambient atmosphere, etc.

We agree and have made the changes, comment equal to RC2.

L. 37: REFs missing

We agree and have made the changes, comment equal to RC2.

L. 48 and throughout: check the order of your references (oldest – newest)

Thank you for this comment. We checked the manuscript and corrected.

L. 53 and throughout: check references that are included in the text e.g., '…published by Gröning et al. (2012)…' instead of '…published by (Gröning et al., 2012)'.

We have used this type of citation on purpose when references have been used directly, as is the case in this example. We think it is better in terms of clarity for the readers and keep it that way.

L. 55: introduce 'IAEA' here, not in L. 57. Throughout: 'IAEA' in capitals.

Changed, see RC1 and RC2.

L. 76: Please add REFs here and add a sentence to the discussion or delete this statement, as it's not your main topic.

RC2 already suggested rewriting this section. We have deleted L74-76 because it is confusing for readers as 'microbiological loads' are not part of this study.

L. 81: what do you mean with 'sample loss'?
Changed, see RC2.

L. 97-100: The first setup was used for the first experiment only. Please rephrase, to make clearer that 'setup' and 'experiment' is used synonymously here.
Thank you for this comment. We have rephrased this section to make it clearer for readers.

L. 146 ff.: Most of the 'Mean' values you are describing here are negative in the Figure. Please check.
We agree and revised all mean values in the manuscript and graphs.

L. 147: the numbers given here ('Mean' and 'SD') are from the 'Siphon&Dip-In' in Fig 3. Please check and change in either the text or the figure.
We agree and revised the figure.

L. 159: Where is the null hypothesis mentioned/ defined?
We added the null hypothesis which was already mentioned by RC2.

L. 172: Deuterium-Excess is not defined as the deviation from the GMWL. Please rephrase to be more precise.
We agree and made already the changes according to the RC2 suggestion.

L. 174: D-Ex can be used to identify 'isotope fractionation', not 'water fractionation'.
We agree and have made already the changes according to the RC2 suggestion.

L. 177: 'The GMWL for deuterium excess…' there is no GMWL for deuterium excess, please rephrase.
We agree and rephrased. It was also commented from RC2.

L. 180 and L. 221: It is the 'lowest', not 'highest' deuterium excess, when greatest extent of evaporation is indicated.
We totally agree and corrected this phrase. It was also commented from RC2.

L. 182: this sentence seems to be incomplete, please insert 'of storage' after 'The duration…' and then it's '…symbol color and point size, respectively…'
We have already reworded after RC2's comment.
L. 214-215: This detail of the sampling procedure is missing in the Methods and Materials-section.
We have already reworded after RC2's comment.

L. 264: which arrows, can't see any in Fig 9B?
We have already reworded after RC2's comment.

L. 292-293: This detail of the sampling procedure is missing in the Methods and Materials-section.
Already mentioned above (L. 214-215). We added details in 'Design and Setup'.

L. 296: '...can also be used' Do you mean equally recommended as the dip-in?
We have added details in the final section. Suggestions have already been made by RC2.

Fig 9: I suggest using a color scheme different from the one in Fig 8. It would be clearer for the reader that the topic is different.
Thank you for your suggestion. We tested different color schemes but decided to maintain a consistent style for both experiments. While we acknowledge that using the same color coding might make it slightly more challenging to differentiate between figures at first glance, we believe that the manuscript clearly explains the context. Additionally, we intentionally assigned the same colors and marker styles to samples that appeared in both experiments to ensure consistency. This approach allows readers to learn the legend once and then focus on the specific details of each experimental setup.

Technical corrections:
L. 33: 'isotope' instead of 'isotopic' analysis
Thank you. We corrected that.

L. 43: 'isotope' instead of 'isotopic' fractionation
We corrected that.

L. 48: 'isotope' instead of 'isotopic' hydrology
Already corrected after RC2.

L. 53: 'sold' not 'sell'
Already corrected after RC2.

L. 64: 'were creating' or 'created' instead of 'was creating'
Already corrected after RC2.

L. 89: '2.1'
We agree and have corrected the numbering.

L. 129: '2.2'
We agree and have corrected the numbering.

L. 135: '2.3'
We agree and have corrected the numbering.

L. 191: please insert 'measurements' after 'water isotope'
Already changed after RC2.

L. 206, 211, 215: 'dip-in' instead of 'Dip-in', in order to be consistent

We corrected that.

L. 218 and 219: please insert 'data' or 'values' after 'd-excess'
Already corrected after RC2.

L. 252-253: 'isotope' instead of 'isotopic' values
Thank you, we corrected that.

Citation: https://doi.org/10.5194/egusphere-2025-272-RC3

Answer to the editor from the 11 April 2024, HESS

EGUSPHERE-2025-272 | Technical note

Received: 20 Jan 2025 – Discussion started: 05 Feb 2025

Technical note: Efficiency of various evaporation barriers for use in automated water samplers for subsequent water isotope analysis

Christin Mueller, Tim Giorgio Pekarev, and Kay Knoeller

Dear Natalie Orlowski,

Thank you very much for your thoughtful assessment. We appreciate your reasoning and fully understand your perspective. The variation of tubing diameter as well as temperature fluctuations during the experiment are indeed important influencing factors and certainly worthwhile topics for further tests. We also considered both aspects during our experimental work, and we would like to provide you with a brief overview:

1) *Consider performing an additional experiment with different tube-dip-in diameters, as this was a point raised by R1*

We also find this approach very interesting. However, in our experiment, the tubing diameter was not varied. The primary reason is that the connectors used were specifically designed for the selected tubing size (visible in Figure 1B) and changing them would not have been straightforward.

We chose a tubing diameter that proved to be the most practical for real-world samples and one with which we have had good experiences over the past years when sampling river water, rainfall, and groundwater. While we acknowledge that a smaller tubing diameter could act as a more effective barrier to evaporation, in practice we often deal with sample contamination—such as sediments present in the water or organic matter that may fall into the rain collector funnel due to wind. These could lead to clogging issues. The selected tubing (LDPE 6x4 mm) still allows the passage of small particles and has proven to be a good compromise between functionality and robustness in the field.

2) *Additional experiments with different temperatures*

At the beginning of our experiment, we aimed to simulate high temperature changes to enlarge the evaporation pressure. We used a laboratory oven as Michelson et al. 2019 (HESS) used and set the temperature to 50°C. The final temperature shown by the device reached 66°C (Figure 1A).

However, after some time, we observed significant degradation of the O-rings, which are essential for maintaining the seal of the bottles. They became brittle and showed substantial damage (Figure 1B). We were concerned that this could lead to leaks, compromising the integrity of the results. For this reason, we decided to discontinue the use of the oven in subsequent experiments. All plastic components were replaced, and the experiment was restarted under ambient laboratory conditions.

Further testing under fluctuating temperature conditions would be valuable to evaluate the performance of the closure systems—not only with regard to their influence on isotope composition, but also concerning the long-term durability of the materials used. It should be emphasized that the main objective of this study was to assess the fundamental concept and effectiveness of various evaporation barriers.

Another key factor, which likely exerts an even stronger influence on isotope fractionation, is air humidity. Simulating humidity effects is more technically demanding and should receive increased attention in future research. In response to your comments, we have revised the manuscript to include a more detailed discussion of this aspect.

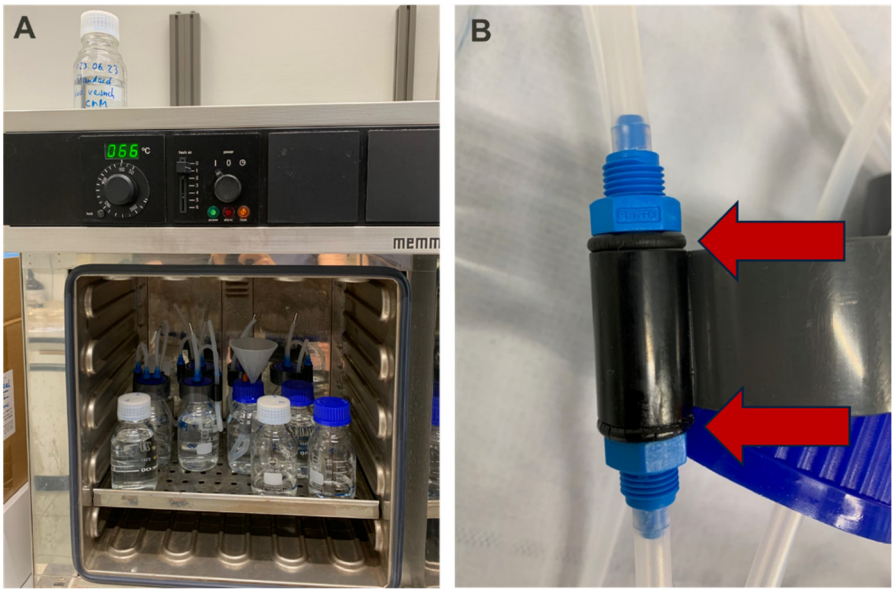

Figure 1: A First experimental setup using an oven for temperature changes; B: O-rings show brittle spots due to the high temperature fluctuations

General remarks:

The experiments presented in the paper were conducted as part of a knowledge transfer project financed from the Helmholtz-Centre for Environmental Research, UFZ. This allowed us to involve Mr. Tim Pekarev as a student assistant. Unfortunately, this project ended in November 2024. Tim is now pursuing his Master's degree in Norway, and I (Christin Müller) have taken on a new research position in Canada. The only remaining member of the original team still based in the UFZ laboratory is Prof. Kay Knöller. However, without our support, he unfortunately does not have the capacity to carry out or supervise additional experiments of this kind.

We have presented the results included in this manuscript at several scientific meetings and workshops in 2024, where they received considerable interest and stimulated constructive discussions. Although there is certainly potential for further refinement and follow-up experiments, we are confident that the findings presented here offer relevant and timely insights for the scientific community working on sampling systems.

We would be pleased to incorporate your suggestions into the conclusion section, as appropriate. It would be an honour if *Hydrology and Earth System Sciences* considered this work for publication as a Technical Note, even in the absence of additional experiments. The constructive and thoughtful feedback provided by the reviewers has been highly valuable and will substantially enhance the quality of the manuscript. We sincerely appreciate the review process and hope that it will lead to a positive decision regarding publication.

With best regards,

Christin Mueller and the co-authors Kay Knoeller and Tim Pekarev

Answer to the editor from the 3 June 2024, HESS

EGUSPHERE-2025-272 | Technical note

Received: 20 Jan 2025 – Discussion started: 05 Feb 2025

Technical note: Efficiency of various evaporation barriers for use in automated water samplers for subsequent water isotope analysis

Christin Mueller, Tim Giorgio Pekarev, and Kay Knoeller

Dear Natalie Orlowski,

Thank you once again for your thoughtful and constructive comments. We have carefully revised the manuscript and addressed the recommended points with further clarification and corrections as outlined below.

Major Comment:
We have now explicitly acknowledged in both the *Discussion* and *Conclusion* sections that the experiments were conducted under laboratory conditions, which come with certain limitations. In the clean version of the manuscript, we added the following statement in Lines 213–216:

"It should be noted that this experiment was conducted under laboratory conditions with minimal variation in temperature and humidity. Further testing under variable environmental conditions is recommended, particularly for evaporation barriers employed in long-term sampling systems and in regions subject to significant temperature and humidity fluctuations."

Additionally, we reiterated this point in the *Conclusion* (Lines 326–329):

"Minimizing temperature and humidity fluctuations within the sampler enclosure is essential during sample collection, as both factors significantly influence isotopic fractionation processes in water. In this study, temperature and relative humidity were kept relatively constant under laboratory conditions. However, future experiments should systematically vary and control these parameters to better understand their roles and interactions in driving isotopic changes."

We hope that these additions sufficiently highlight the limitations and the recommended directions for future research.

Minor Comments:
We have revised the figures as requested. Figures 6 and 7 (Trial) were corrected, and the symbols in Figures 9 and 10 were adjusted. Specifically, in Figures 9a, 9b, 10a, and 10b, we slightly increased the transparency of the data points and added edge lines to each marker to improve visibility. Additionally, a new marker style ("+") was introduced to help distinguish overlapping data points.

During this revision, we identified a minor discrepancy in the dataset: the number of samples for the tube-dip-in method is 19 not 18. This correction led to minimal changes (maximum 0.1‰). Figures 7 and 8 were updated accordingly, and the corresponding values in the text were corrected.

We have also adopted the journal's citation style with the EndNote output style to ensure correct formatting. Unfortunately, we encountered a problem with the capitalisation of citations in the manuscript. According to the Copernicus Publications style, all capital letters in citations were automatically converted to lower case. This is problematic for references such as (IAEA 2024), which incorrectly appear as (Iaea 2024).

We were unable to resolve this issue cleanly. As a workaround, we have removed the field codes from the two cases (IAEA 1997 and IAEA 2014) and inserted the reference manually. To ensure that the reference still appears correctly in the reference list, we have inserted it again at the end of the section and shaded it in white.

We look forward to receiving the reviewers' evaluation of the revised manuscript and thank you again for your guidance throughout the process.

With best regards,

Christin Mueller the team with Tim Pekarev and Kay Knoeller