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

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Abstract. High temporal and spatial resolution water sampling of stream water or precipitation for subsequent stable water isotope analysis (δ^2H and $\delta^{18}O$) is commonly conducted with self-made or commercial automated samplers. However, prolonged storage of water samples in open bottles inside autosamplers can lead to isotopic alterations caused by evaporative fractionation and vapor mixing.

In this study, we tested the effectiveness of different evaporation barriers—dip-in tubes, ball valves, and siphons—under controlled laboratory conditions. Experiments were conducted using glass bottles with varying filling levels (50 mL to 250 mL in 250 mL bottles) and exposure times of up to 52 days. Our results demonstrate that all tested barriers effectively reduce isotopic alterations. Among these, the dip-in tube emerged as the simplest and most efficient solution, reliably preserving isotopic data even over extended storage durations. We also observed isotopic differences between the water in the dip-in tube and the main bottle. This phenomenon becomes particularly relevant when sample volumes are very low, as water from the dip-in tube may influence the overall isotopic composition of the sample. This finding highlights the need for careful consideration of bottle design, funnel size and sample handling, especially with low water volumes.

These findings provide valuable insights for the design of cost-effective, automated water sampling systems for stable isotope applications, emphasizing the importance of evaporation barriers to ensure reliable and accurate isotopic analyses.

Keywords: stable water isotopes, evaporation barriers, automated water sampling

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1 Introduction

Isotopic analysis of water requires collecting and storing samples without long and large interference to the gas phase to ensure results are as close as possible to true values. While this may sound straightforward, it presents significant challenges, as sampling often introduces the largest errors in analytical outcomes (Romañach et al., 2021; Esbensen, 2020). Therefore, it is crucial to focus on refining sampling techniques. Numerous sampling systems for water collection are available, each suited to specific applications or climatic conditions.

Cavity Ring-Down Spectroscopy (CRDS), such as the Picarro L2130-i Isotopic Water Analyzer, exemplifies how the growing accessibility and efficiency of laser spectrometry have significantly reduced the cost of isotopic measurements while providing a user-friendly, and relatively precise method for analyzing stable isotope ratios in water molecules (Hachgenei et al., 2022). This advancement allows for an increased number of samples to be analyzed rapidly, facilitating better understanding of the water cycle and associated processes. A critical prerequisite for successful rainwater sampling is the strict prevention of evaporation during the collection and storage period, as even minimal losses can lead to isotopic fractionation and compromise data quality (Schürch et al., 2003).

Extreme events often catch researchers unprepared, forcing them to use improvised sampling containers like empty soda bottles or honey jars (Fischer et al., 2019). Financial constraints may also limit access to commercial bottles or automated sampling devices. To address these challenges, do-it-yourself (DIY) instructions for constructing rainwater samplers have become increasingly common in the field of isotopic hydrology (e.g. (Carton et al., 2024; Prechsl et al., 2014; Fischer et al., 2019; Von Freyberg et al., 2020)). They explored different low-tech, low-budget rainfall sampler for stable isotope analysis, assessing its effectiveness in maintaining sample quality. Such innovations highlight the continuous efforts to improve sampling systems, making them more efficient, reliable, and compatible with modern analytical requirements.

Among commercially available systems, the widely used cumulative rain water sampler (RS1) for water isotope analysis first published by (Gröning et al., 2012) and sell by Palmex Ltd. employs a 3-liter bottle with a long tube (15m polypropylene plastic hose with an inner diameter of 5mm) to prevent evaporation. This system forms the backbone of the International Atomic Energy Agencys' Global Network of Isotopes in Precipitation (GNIP) (Iaea, 2014), which continues to expand (Terzer-Wassmuth et al., 2021; Terzer-Wassmuth et al., 2022) (Link website: https://nucleus.iaea.org/wiser/ accessed 17 January 2025). The International Atomic Energy Agency (IAEA) has also developed detailed technical guidelines for sampling procedures, ensuring consistency across its global network of stations (Gat, 1981).

Early solutions to evaporation challenges included the use of paraffin oil, which forms a protective layer over collected rainwater. In such designs, a 5 mm-thick oil layer prevents evaporation during the collection period (Iaea, 1997; Sevruk, 1972). However, these systems present practical difficulties as it can be challenging to remove the oil from the water as it can form a gelatinous phase and leave behind residues that can contaminate laboratory equipment such as mass spectrometers (Gröning et al., 2012; Friedman et al., 1992). An alternative is described by (Weaver and Talma, 2007) who was creating a cumulative rainfall sampler using a tennis ball and oil for water and chloride isotope studies. Michelsen et al.

https://doi.org/10.5194/egusphere-2025-272
Preprint. Discussion started: 5 February 2025

(2018) compare precipitation collectors commonly used in isotope hydrology, providing an overview of various sampling systems and the challenges associated with their use.

High-resolution sampling is essential for many scientific investigations, as monthly intervals are often inadequate for addressing research questions that require detailed temporal data. Numerous studies have shown that the isotopic composition of precipitation can vary significantly during individual rainfall events (e.g. (Mcdonnell et al., 1990; Munksgaard et al., 2012; Aemisegger et al., 2015; Fischer et al., 2017; Graf et al., 2019)). Capturing these variations in stable isotope composition requires sequential sampling with high temporal resolution. Applications such as numerical models (e.g., transSAS from (Benettin and Bertuzzo, 2018) and used in (Radtke et al., 2024)) particularly benefit from high-resolution, volume-based sampling. Additionally, understanding water residence times demands monitoring multiple compartments, such as precipitation and surface water, across various locations within a catchment. However, surface water sampling presents additional challenges, such as high sediment loads and microbial activity, which can compromise sample integrity and must be considered when designing automatic sampling systems.

Automatic samplers, which are essential for collecting high-frequency data, often cannot be emptied immediately after extreme events due to the inaccessibility of study areas. This limitation can require extended storage times, as observed in arid regions (Michelsen et al., 2018; Michelsen et al., 2015). These challenges underscore the need for evaporation-proof sampling systems.

All these sampling systems aim to minimize or prevent isotopic fractionation due to evaporation or sample loss. For commercial applications, laboratory tests should be conducted prior to market release to validate device suitability and application range. Collaborating with ‘MAXX Mess- und Probenahmetechnik GmbH’, we are developing a low-cost, autonomous water sampler tailored for isotopic water analysis. This study presents laboratory tests evaluating potential evaporation barriers, examining factors like bottle filling and exposure time. Our goal is to create a robust and adaptable system for use in various climatic regions. The findings provide valuable insights into system design and highlight potential pitfalls to consider when maintaining sampling systems over extended periods.

2 Methods and Materials

1.1 Design and Setup

The experiments aimed to identify an effective evaporation barrier for water samples intended for isotopic analysis. Generally, SCHOTT glass bottles were used to store the water samples during the experiment. For the tubing, polypropylene hoses were used with an inner diameter of 5mm. As evaporation barrier, three inlet-methods were tested (Figure 2): (1) inserting a tube before the sampling bottle to act as a siphon; (2) using a dip-in tube, which extends into the sampling bottle to minimize direct exposure to the atmosphere; and (3) employing a ball valve that opens when the bottle is filling and closes when the water flow stops, using a plastic ball to seal the opening. Due to the functionality of the ball valve, it can only be used in combination with a siphon because it needs to be filled from the bottom to allow the ball to float and open the valve.

https://doi.org/10.5194/egusphere-2025-272
Preprint. Discussion started: 5 February 2025

The experimental procedures were divided into two setups. In the first setup, all bottle inlets were equipped with siphons as evaporation barriers. In the second setup, no siphons were used. The designs and specific configurations of each method are explained in more detail below.

In the first experiment, the design of the test bottles (n = 44) varied at the inlet, with some equipped with a dip-in tube and/or a ball valve, while others had neither (Figure 1A). During filling, the siphon became water-filled. In bottles with a ball valve, the valve was positioned along the filling tube and after the siphon. This design allowed the ball to float as water entered the bottle and then sink back into place to seal the inlet after filling. To test only the effectiveness of the inlet system, the outlet vent of all bottles was sealed with a stopper, preventing any influence from evaporation through the outlet. Water volumes added to the bottles ranged between 50, 100, 150, 200, and 250 mL, and the exposure durations were 5, 7, 20, and 21 days at room temperature. After the experiment, water in bottle and in the siphon was sampled for subsequent water isotope analysis. Additionally, reference bottles—both sealed (n = 38) and open (n = 14)—were subjected to the same variation in filling volume and exposure time. The building of the bottle with these evaporation barriers for testing was design in cooperation with MAXX-Messtechnik GmbH.

The second experiment had a simpler design. All test bottles (n = 19) were fitted with a dip-in tube, but no siphons or ball valves were used (Figure 1B). Instead of sealing the outlet vent, each bottle was connected to a 15-meter-long hose. Water volumes again ranged from 50 to 250 mL. The exposure durations were 13, 26, 39, and 52 days, also at room temperature. Open and closed reference bottles (n = 10 for each) were handled with similar variations in filling volume and exposure time. Water was sampled after the exposure time from the bottled water (BW) and in the dip-in tube for water isotope analysis.

The experiments were conducted in the laboratory under nearly constant conditions. No variations in temperature or humidity were simulated, which would have further increased evaporation. Therefore, the setup represented an optimal scenario for sample conservation.

https://doi.org/10.5194/egusphere-2025-272
Preprint. Discussion started: 5 February 2025

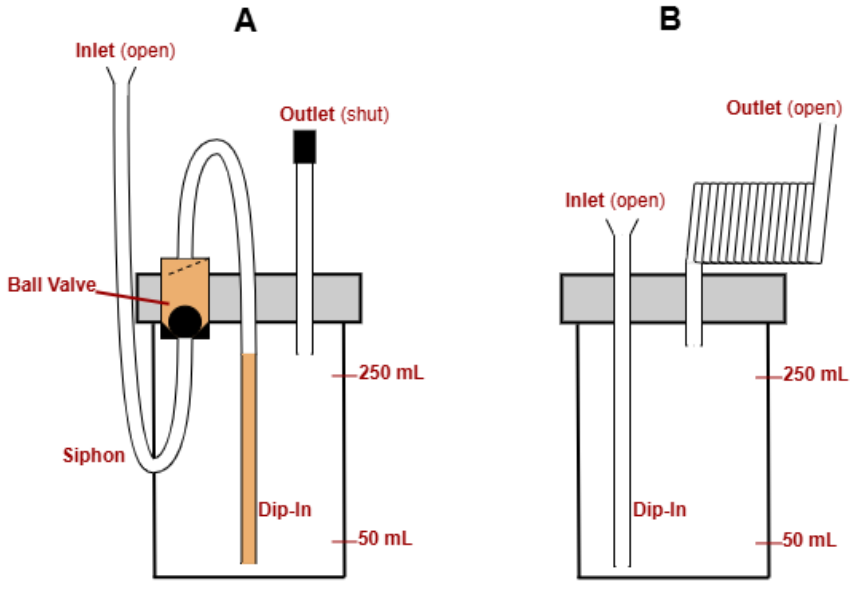

Figure 1: A shows the experimental set-up of the first experiment, which used evaporation barriers (siphon, ball-valve and dip-in tube). Light orange parts (ball-valve and dip-in) could be removed or added. B shows the experimental set-up of the second experiment, which used a dip-in tube as evaporation barrier. Here the outlet was a 15m long open tube. The type of bottle (SCHOTT glass bottle) used remained unchanged throughout the experiment.

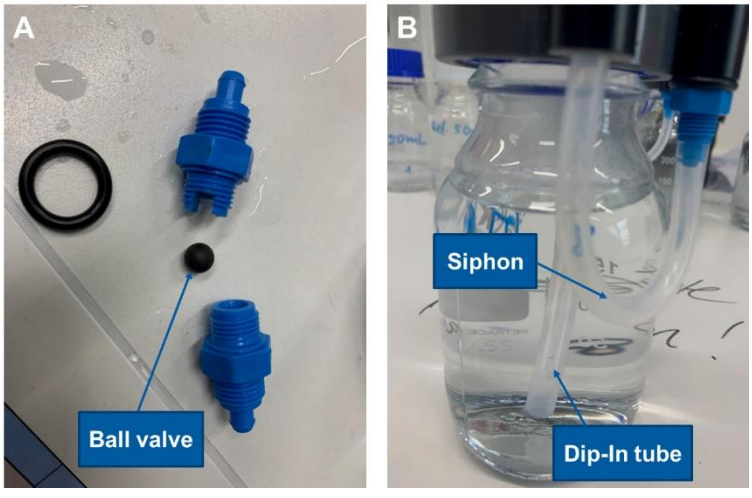

Figure 2: A: Tested evaporation barriers: Ball-valve which is consisting of a swimming plastic ball inside a cone sealed with an O-ring; B: Siphon outside the bottle and a dip-in tube, respectively, both are minimizing the atmospheric contact of the inflow.

https://doi.org/10.5194/egusphere-2025-272
Preprint. Discussion started: 5 February 2025

1.2 Laboratory methods

A liquid isotope analyzer (Picarro L2120-i) was utilized to conduct duplicate measurements of stable isotopic signatures in water. For this purpose, 20 replicates of internal standards, which had been calibrated to VSMOW and SLAP certified reference materials, were analyzed to normalize the samples to the VSMOW scale. The analytical uncertainties were determined to be ±0.15 ‰ for $\delta^{18}O$ and ±0.6 ‰ for $\delta^{2}H$. The isotopic ratios are reported in delta notation relative to Vienna Standard Mean Ocean Water (VSMOW) for both the oxygen and hydrogen isotope signatures of water.

1.3 Statistics

The statistical analysis was conducted with Python 3.9.7. Data were grouped by experimental setups: experiment 1 (siphon) and experiment 2 (no siphon). The variables deuterium excess and weight loss were tested for variance homogeneity for each experiment using the Levene test, followed by a Shapiro-Wilks-Test to test for normal data distribution in the groups. Homogeneity of variance was not established, and normality was limited to only a few groups. Therefore, and due to the small sample size, the Kruskal-Wallis test was applied to assess differences between the groups, followed by Dunn's post hoc test with Bonferroni correction.

3 Results and Discussion

3.1 Weight loss due to evaporation

No weight loss was observed during the experiments, regardless of the filling volume or exposure time, in bottles that were simply closed (Figure 3). This method provides the best preservation of samples but is challenging to implement in an automatic sampling system (Mean = 0.03, n = 26, SD = 0.05).

The lowest volume loss was recorded using only a dip-in system as an evaporation barrier (Mean = 0.12, n = 4, SD = 0.09). However, the sample size in the first experimental setup was limited. Consequently, the experiment was intensified in the second setup, focusing exclusively on this method to further validate the results. Very low volume losses were observed when both the dip-in system and a ball valve were used in combination with a siphon (Mean = 0.61, n = 12, SD = 1.55). When the setup included a ball valve in combination with a siphon but without a dip-in tube, weight loss increased slightly (Mean = -1.14, n = 8, SD = 1.78). The siphon alone, without the ball valve or dip-in tube, showed the highest evaporation loss compared to all tested barriers (Mean = 1.38, n = 10, SD = 1.3). This method also posed a risk of sample contamination, as temperature or pressure differences (even under laboratory conditions) caused water movement within the siphon. Significant weight loss was observed when the siphon emptied completely, rendering the barrier inactive.

The duration of the experiment (comparing two groups: 5 & 7 days and 20 & 21 days) shows no significant impact on evaporation loss. However, the amount of sample in the bottle has a significant effect on percentage weight loss, as expected.

https://doi.org/10.5194/egusphere-2025-272
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Different significance levels (e.g., $p<0.05$, $p<0.01$, $p<0.001$) indicate the likelihood that an observed result is due to chance under the null hypothesis. Smaller p-values correspond to lower probabilities of random occurrence and provide stronger evidence against the null hypothesis. In Figure 3, the highest significance ($p<0.001$) is observed for the references (open vs. closed) as well as for the closed bottle compared to the siphon-only setup in the experiment. Statistical significance ($p<0.05$) for evaporation is still evident in the experimental setup where only a ball valve was used.

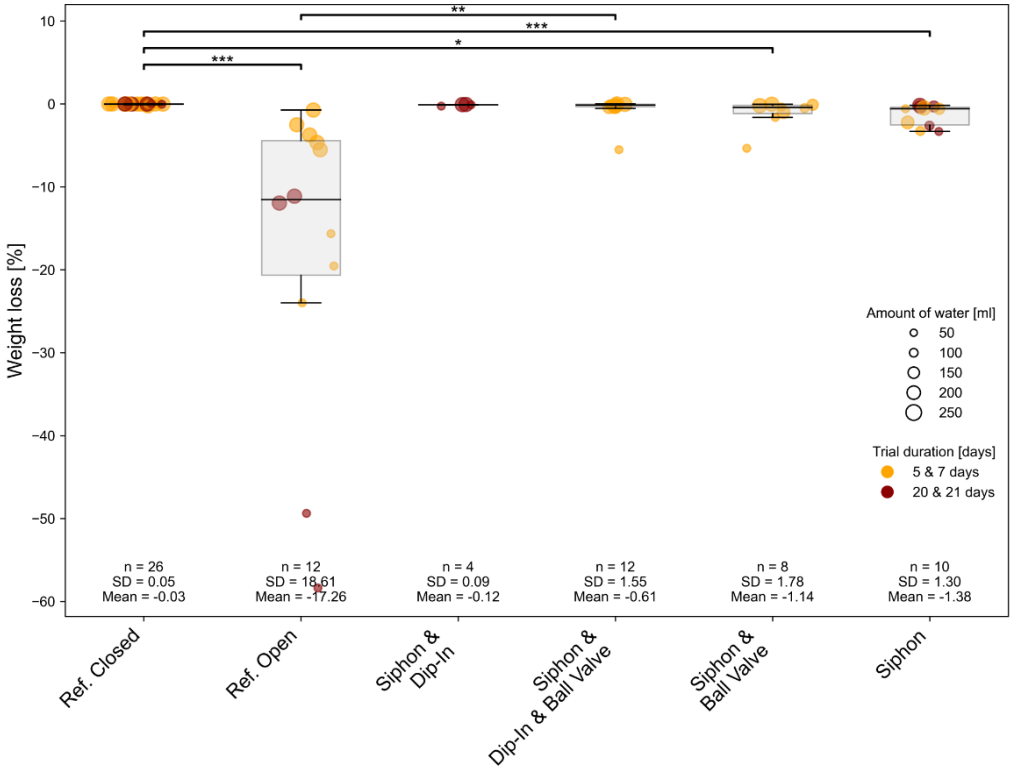

Figure 3: Weight difference between the start and end of experiment 1 in % was used as an indicator of evaporation. The exposure time ranged from short-term (5 to 7 days) to long-term (20 to 21 days). The initial water volumes in the 250 mL SCHOTT glass bottles varied between 50, 100, 150, 200, and 250 mL. Various evaporation barriers were tested, with a closed and open bottle serving as the references. Significant differences between groups, determined via Dunn's post-hoc test, are indicated by horizontal lines with corresponding significance levels p < 0.05 (*), p < 0.01 (**), p < 0.001 (***).

3.2 Deuterium excess as indicator for evaporation efficiency

Deuterium Excess (d-excess), defined as the deviation in permill of the δ^2H-H_2O value from the Global Meteorological Waterline (GMWL: $\delta^2H = 8\delta^{18}O+10$), provides valuable insights into the processes affecting water's isotopic composition. This parameter is particularly useful for identifying the effects of evaporation and water fractionation. Deviations from the GMWL typically indicate isotopic fractionation caused by physical processes, such as evaporation. Water on the GMWL has

https://doi.org/10.5194/egusphere-2025-272
Preprint. Discussion started: 5 February 2025

a deuterium excess of 10‰, suggesting no significant fractionation or evaporation, which reflects natural isotopic ratios typical of rainwater (Craig, 1961; Dansgaard, 1964). The GMWL for deuterium excess is shown in Figure 4, along with the measurement accuracy (±1.34‰) in grey. The results from experiment 1, showing the deuterium excess, indicate the highest significance ($p < 0.001$) for the reference water compared to the siphon water. In general, the siphon water exhibits the highest deuterium excess, indicating the greatest extent of evaporation (1s-7 = 3.62‰, see Table S1 in Supporting information). All other evaporation barriers (dip-in, ball-valve in combination or alone) show variations within the measurement accuracy. The duration and amount of sample, indicated by the point size, do not have a significant impact in the experiment (Figure 4).

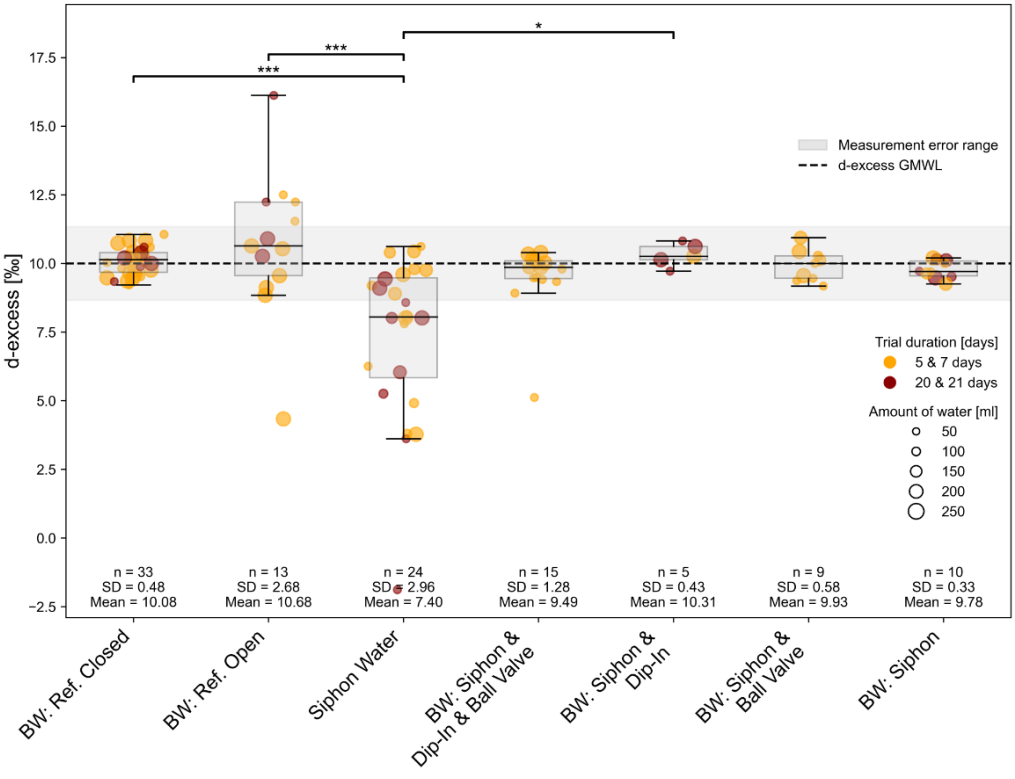

Figure 4: Deuterium excess from Experiment 1 as an indicator of isotope fractionation on H_2O through different time steps within the evaporation experiment. Significant differences between groups, determined via Dunn's post-hoc test, are indicated by horizontal lines with corresponding significance levels $p < 0.05$ (*), $p < 0.01$ (**), $p < 0.001$ (***).

3.3 Water isotopic signatures in evaporation experiments using various barriers

Results of water isotopes from the first evaporation experiment using different evaporation barriers are shown in Figure 5. The closed reference bottle provides the water isotope signature used as the target reference (δ^2H = -57.6 ± 0.7‰ and $\delta^{18}O$ =

https://doi.org/10.5194/egusphere-2025-272
Preprint. Discussion started: 5 February 2025

-8.5 ± 0.1‰) and serves as a control throughout the experiment. The open reference bottle is clearly unsuitable and exhibits the highest water isotope shifts (mean δ^2H = -44.5 ± 16.7‰, mean $\delta^{18}O$ = -6.9 ± 1.8‰), which are significant.

195 Throughout the duration of the experiment, all evaporation barriers yielded reliable results. The dip-in system, ball valve, and siphon showed no significant differences among their results of water isotopes (Figure 5). However, when a siphon is used as a barrier, it must be ensured that the water standing in the siphon does not mix with the sample, as its isotopic signature shows significant enrichment. Notably, if the sample volume is large, the impact of potential contamination from siphon water becomes less pronounced.

https://doi.org/10.5194/egusphere-2025-272
Preprint. Discussion started: 5 February 2025

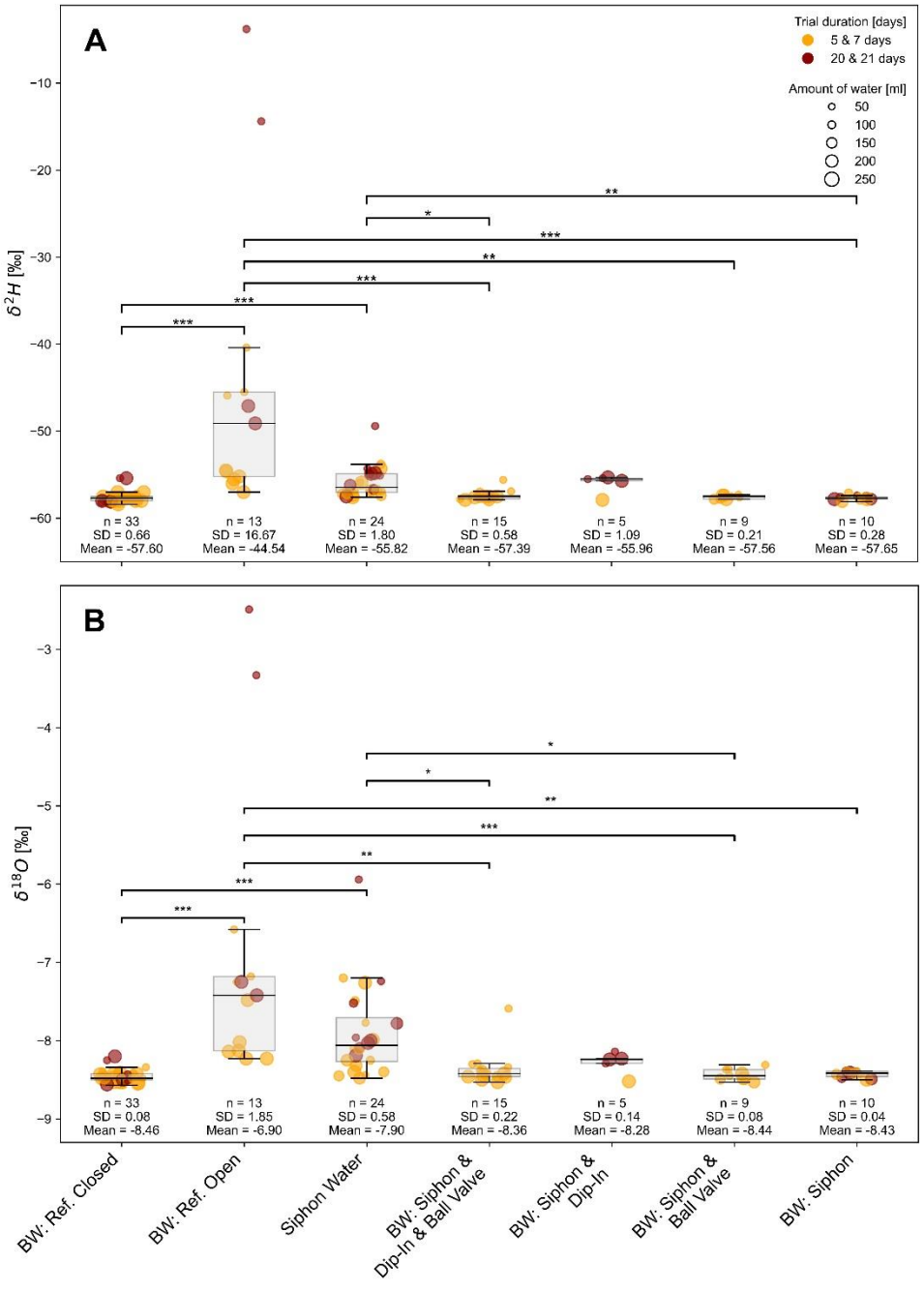

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Figure 5: δ^2H (A) and $\delta^{18}O$ (B) isotopic signature [‰] from experiment 1, indicating isotope fractionation of H_2O over different time steps in the evaporation experiment. Significant differences between groups, determined via Dunn's post-hoc test, are indicated by horizontal lines with corresponding significance levels, $p < 0.05$ (*), $p < 0.01$ (**), $p < 0.001$ (***).

https://doi.org/10.5194/egusphere-2025-272
Preprint. Discussion started: 5 February 2025

3.4 Long-Term experiments with Dip-in tubing as evaporation barrier

The second experiment focused on a long-term assessment of an evaporation barrier. Here we decided to use the Dip-in system combined with an extended tubing setup (15 m long PP tube with an inner diameter of 5mm). This setup, first mentioned by Gröning et al. (2012) allows for the release of air during the filling process but also serves as an effective evaporation barrier during storage. In Carton et al. (2024) calculations of the tubing length were performed based on temperature and pressure variations, applying the ideal gas law. The study concluded that a tubing length of 4 meters is sufficient for 125mL bottles in a monthly sampling. However, the Dip-in system is characterized by its simplicity, ease of application, and reliable performance that we could prove in the first experiment. It demonstrates low susceptibility to failure and eliminates the risk of siphon water contaminating the sample. These features make it particularly suitable for long-term evaporation experiments. All tests were conducted under controlled laboratory conditions. Sampling was performed on both Dip-in water and bottled water (BW), followed by water isotope analysis. The exposure times in this experiment were 12, 26, 39, and 54 days, and tests were conducted with different sample volumes (50 mL and 250 mL). All data are summarised in Table S2 (Supporting Information).

The results of the deuterium excess are summarized in Figure 6. For the long-term experiment, we measured the isotopic signature of a standard water before, during, and after the experiment. The d-excess remained within the measurement accuracy (mean 10.4 ± 0.5‰). The closed reference bottle exhibited a similar variation (10.1 ± 0.5‰), confirming the proper storage conditions of the standard water and the seal integrity of the bottles used. The largest d-excess was observed in water from the dip-in tube (max -11.8‰), with its isotopic signature significantly different from the closed system ($p < 0.001$). Throughout the experiment, the bottled water displayed d-excess values within the measurement error range (mean 9.43 ± 0.53‰). Only samples with a standing time of 52 days deviated from the measurement uncertainty, showing evaporation effects (minimum d-excess of 8.4‰). The reason why the sample water in an open reference bottle plots along the GMWL remains unclear. A possible explanation could be fluctuations in relative humidity and temperature during the experiment, which may have induced interactions between evaporation and condensation processes. However, the highest variation in water isotopes (δ^2H / $\delta^{18}O$ – H_2O) was observed for the open reference bottle (Figure 7), with mean values of -25.4 ± 27.5‰ for δ^2H and -4.4 ± 3.4‰ for $\delta^{18}O$ in the water. The fluctuations in water isotopes in the dip-in tube were much smaller (mean δ^2H = -51.6 ± 2.9‰, mean $\delta^{18}O$ = -6.6 ± 1.1‰), yet still significantly different ($p = 0.001$) from the water sample stored in a closed bottle. The sample water in the bottle (BW) showed no evaporation effects throughout the experiment duration (max. 52 days). No significant differences in water isotopes were observed between BW and the closed reference bottle. Additionally, the sample volume appears to play a minor role. However, for the water in the dip-in tube, differences between sample volumes were noticeable. The smaller the sample volume in the bottle, the greater the fractionations observed in the dip-in tube.

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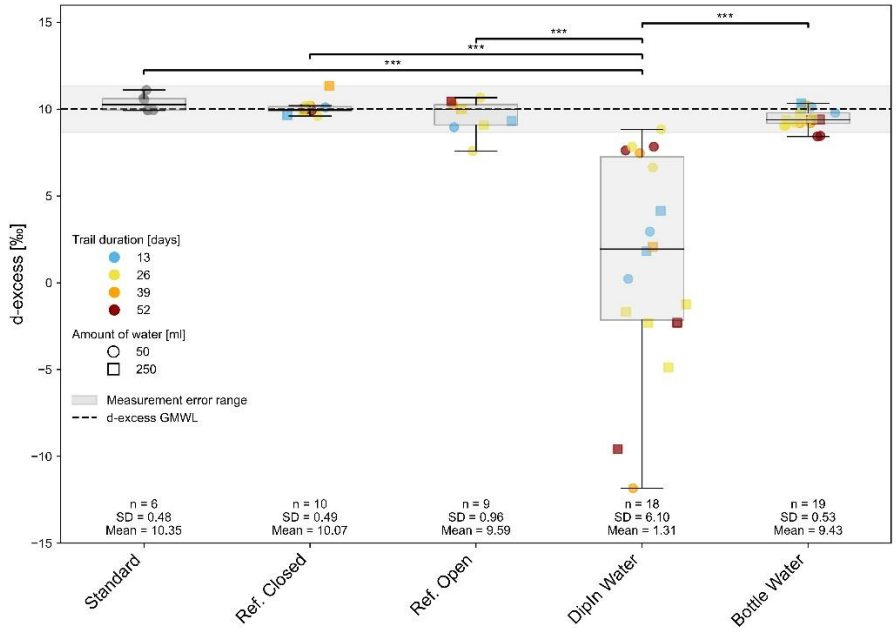

Figure 6: Deuterium excess from experiment 2 as an indicator of isotope fractionation on H_2O through different time steps within the evaporation experiment. Significant differences between groups, determined via Dunn's post-hoc test, are indicated by horizontal lines with corresponding significance levels p < 0.05 (*), p < 0.01 (**), p < 0.001 (***).

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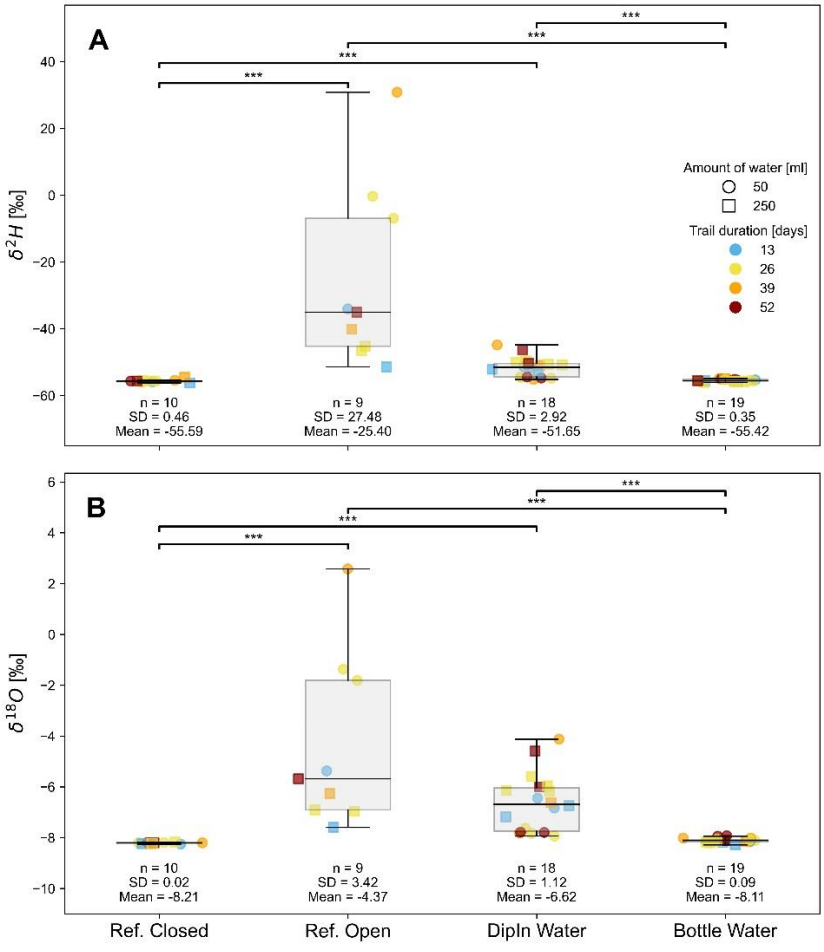

Figure 7: δ²H (A) and δ¹⁸O (B) isotopic signature [‰] from experiment 2 as an indicator of isotope fractionation on H2O through different time steps within the evaporation experiment. Significant differences between groups, determined via Dunn's post-hoc test, are indicated by horizontal lines with corresponding significance levels p < 0.05 (*), p < 0.01 (**), p < 0.001 (***)

3.5 Dual water isotope plots for different experimental investigations

The following section evaluates the dual water isotope plots for both experiments. Figure 8 illustrates the results of the first experiment, which used multiple evaporation barriers. Both diagrams (A and B) display the same data, but Figure 8A provides an overview, while Figure 8B focuses on the details. The isotopic values of the closed reference bottle plot along the Global Meteoric Water Line (GMWL) with minimal variability. In contrast, the isotopic values of the water sample stored in the open reference bottle exhibit greater variability. The isotopic values of water sampled using the siphon (labeled with a star) plot along an evaporation line with a lower slope than the GMWL. Here, exposure times appear to play a minor

https://doi.org/10.5194/egusphere-2025-272
Preprint. Discussion started: 5 February 2025

255 role. Similarly, for water samples in bottles with different evaporation barriers, exposure time also seems to be of lesser importance. Much more significant is the filling volume of the sample bottles, which is represented by label size (Fig. 9B). The smaller the filling volume, the larger the deviation from the GMWL, indicating greater fractionation in the water phase. Similar findings were reported by Carton et al. (2024). This underscores that the choice of an appropriate bottle size is of high importance for maintaining the stability of a water isotope signature of water samples stored with a gas phase.

260 The dual isotope plot of the long-term experiment using the dip-in tube is shown in Figure 9. Here, as well, Figure 9A and B are not different but present the same data on various scales. The isotopic signature of the water within the dip-in tube exhibits significant isotopic fractionation. The results plot along an evaporation line (indicated by star-shaped labels). In the long-term experiment, fractionation effects become evident with prolonged exposure times, as reflected by the label sizes.

For short exposure times (13, 26 days), the variation remains within the measurement accuracy (indicated by arrows in

265 Figure 9B). As exposure time increases, a trend of enrichment in the water sample becomes apparent. However, the variation of all samples with certain evaporation barriers (mean δ^2H = -53.5 ± 6.2‰, mean $\delta^{18}O$ = -8.1 ± 0.1‰) remains minimal. A significant enrichment is observed in the dip-in tube (variation up to -44.8‰ for δ^2H and -4.4‰ for $\delta^{18}O$). Some experimental bottles show less pronounced enrichment compared to others. Generally, the trend of higher enrichment with longer exposure times is evident.

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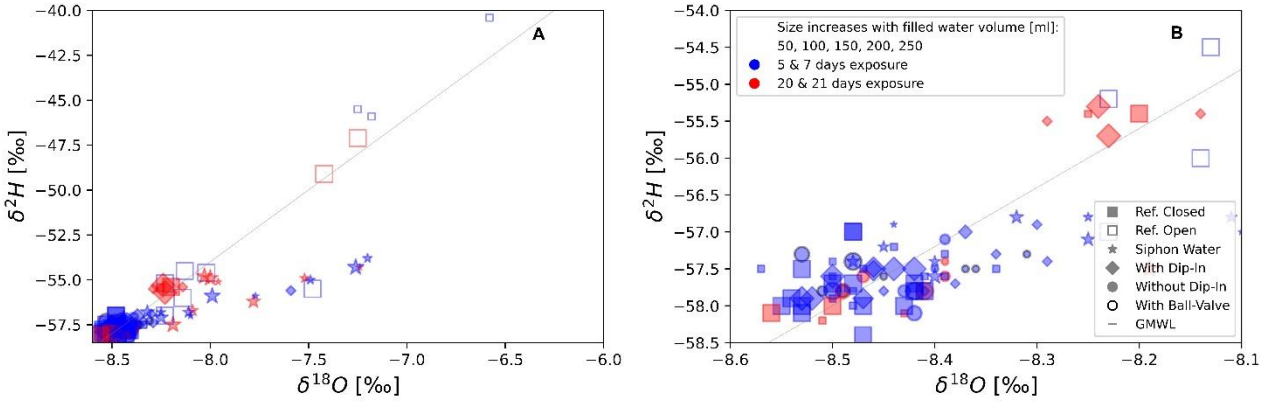

Figure 8: Dual water isotope plot showing isotope fractionation during experiment 1 using different evaporation barriers (siphon, ball valve, and dip-in tube). Both diagrams (A and B) display the same results on different scales. The label sizes correspond to the filled water volume, which varies between 50, 100, 150, 200, and 250 mL. Colors represent different exposure times, with blue

275 **indicating short exposure and red indicating long exposure.**

https://doi.org/10.5194/egusphere-2025-272
Preprint. Discussion started: 5 February 2025

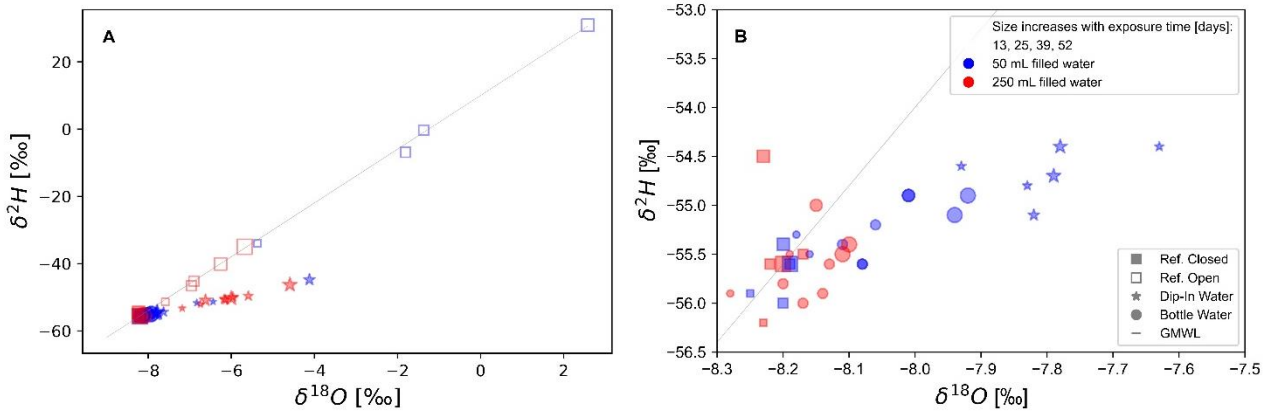

Figure 9: Dual water isotope plot showing isotope fractionation during experiment 2 using dip-in tubing as the evaporation barrier. Both diagrams (A and B) display the same results on different scales. Label sizes correspond to the exposure time, which varies between 13, 25, 39, and 52 days. Colors represent different water volumes (50 mL vs. 250 mL). The star labels indicate water samples from the dip-in tube.

4 Conclusion

In this study, we investigated various evaporation barriers to reduce evaporative fractionation and vapor mixing in water samples collected for subsequent stable water isotope analysis. Laboratory experiments were conducted using different barrier setups, fillings, and exposure times. Our findings demonstrate that water samples with certain evaporation barriers show significantly less isotopic alteration due to evaporative fractionation and vapor mixing compared to samples stored in open bottles. The simplest and most effective setup tested was a dip-in tube with a long tubing. This configuration allowed gases to escape during filling while compensating pressure and temperature-induced volume changes during the observation period. This method proved to be a practical and efficient evaporation barrier, achieving isotopic fractionation levels comparable to those observed in closed systems. However, significant isotopic differences were noted between the water in the dip-in tube and the water in the main bottle. These differences are likely to be more evident under conditions of relativity stable temperature and humidity. For small sample volumes, we recommend removing the dip-in water by maintaining the pressure in the tube while opening the bottle (similar to the “straw principle”) and then discarding the dip-in water. To ensure the effectiveness of this approach, it is essential to minimize evaporation and condensation within the bottle. This can be achieved by maintaining constant temperature and humidity in the automatic sampling system. Alternative evaporation barriers, such as ball-valves or siphons, can also be used. However, these methods come with higher maintenance requirements. Ball-valves may require regular cleaning or replacement and are prone to clogging, while siphons are susceptible to sample contamination if emptied due to large temperature or pressure fluctuations. Such incidents can create open conditions that accelerate fractionation.

Overall, our results underscore the importance of selecting evaporation barriers tailored to the specific sampling conditions while considering maintenance demands and environmental stability to ensure reliable isotope measurements.

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Data availability statement

The stable water isotope measurements from the two experiments are provided as Supplement.

Author Contributions

CM: Conceptualization, experimental design, manuscript writing, funding acquisition, supervision, and project administration; TGP: Laboratory experiments, statistical analysis, Python scripting, review, and editing; KK: Conceptualization, resources, review, and editing.

Competing interests

The authors declare that they have no conflict of interest.

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References

Aemisegger, F., Spiegel, J. K., Pfahl, S., Sodemann, H., Eugster, W., and Wernli, H.: Isotope meteorology of cold front passages: A case study combining observations and modeling, Geophysical Research Letters, 42, 5652-5660, https://doi.org/10.1002/2015GL063988, 2015.

Benettin, P. and Bertuzzo, E.: tran-SAS v1.0: a numerical model to compute catchment-scale hydrologic transport using StorAge Selection functions, Geosci. Model Dev., 11, 1627-1639, 10.5194/gmd-11-1627-2018, 2018.

Carton, C., Barbecot, F., Hélie, J.-F., Horoi, V., Birks, J., Picard, A., and Mona, J.: Affordable event and monthly rain samplers: Improving isotopic datasets to understand meteorological processes, Rapid Communications in Mass Spectrometry, 38, e9710, https://doi.org/10.1002/rcm.9710, 2024.

Craig, H.: Isotopic Variations in Meteoric Waters, Science, 133, 1702-1703, doi:10.1126/science.133.3465.1702, 1961.

Dansgaard, W.: Stable isotopes in precipitation, Tellus, 16, 436-468, https://doi.org/10.1111/j.2153-3490.1964.tb00181.x, 1964.

https://doi.org/10.5194/egusphere-2025-272
Preprint. Discussion started: 5 February 2025

Esbensen, K.: Introduction to the Theory and Practice of Sampling, 10.1255/978-1-906715-29-8, 2020.

Fischer, B. M. C., van Meerveld, H. J., and Seibert, J.: Spatial variability in the isotopic composition of rainfall in a small headwater catchment and its effect on hydrograph separation, Journal of Hydrology, 547, 755-769, https://doi.org/10.1016/j.jhydrol.2017.01.045, 2017.

Fischer, B. M. C., Aemisegger, F., Graf, P., Sodemann, H., and Seibert, J.: Assessing the Sampling Quality of a Low-Tech Low-Budget Volume-Based Rainfall Sampler for Stable Isotope Analysis, Frontiers in Earth Science, 7, 10.3389/feart.2019.00244, 2019.

Friedman, I., Smith, G. I., Gleason, J. D., Warden, A., and Harris, J. M.: Stable isotope composition of waters in southeastern California 1. Modern precipitation, Journal of Geophysical Research: Atmospheres, 97, 5795-5812, https://doi.org/10.1029/92JD00184, 1992.

Gat, J. R.: Stable isotope hydrology Deuterium and oxygen-18 in the water cycle, IAEA, International Atomic Energy Agency (IAEA)1981.

Graf, P., Wernli, H., Pfahl, S., and Sodemann, H.: A new interpretative framework for below-cloud effects on stable water isotopes in vapour and rain, Atmos. Chem. Phys., 19, 747-765, 10.5194/acp-19-747-2019, 2019.

Gröning, M., Lutz, H. O., Roller-Lutz, Z., Kralik, M., Gourcy, L., and Pöltenstein, L.: A simple rain collector preventing water re-evaporation dedicated for δ18O and δ2H analysis of cumulative precipitation samples, Journal of Hydrology, s 448–449, 195–200, 10.1016/j.jhydrol.2012.04.041, 2012.

Hachgenei, N., Vaury, V., Nord, G., Spadini, L., and Duwig, C.: Faster and more precise isotopic water analysis of discrete samples by predicting the repetitions' asymptote instead of averaging last values, MethodsX, 9, 101656, https://doi.org/10.1016/j.mex.2022.101656, 2022.

IAEA, L.: GNIP precipitation sampling guide, IAEA Water Resources Program, 2, 4-15, 2014.

IAEA, N.: Technical Procedure for cumulative monthly sampling of precipitation for isotopic analyses, Technical report, IAEA, Vienna, 1997.

McDonnell, J. J., Bonell, M., Stewart, M. K., and Pearce, A. J.: Deuterium variations in storm rainfall: Implications for stream hydrograph separation, Water Resources Research, 26, 455-458, https://doi.org/10.1029/WR026i003p00455, 1990.

Michelsen, N., van Geldern, R., Roßmann, Y., Bauer, I., Schulz, S., Barth, J. A. C., and Schüth, C.: Comparison of precipitation collectors used in isotope hydrology, Chemical Geology, 488, 171-179, https://doi.org/10.1016/j.chemgeo.2018.04.032, 2018.

Michelsen, N., Reshid, M., Siebert, C., Schulz, S., Knöller, K., Weise, S. M., Rausch, R., Al-Saud, M., and Schüth, C.: Isotopic and chemical composition of precipitation in Riyadh, Saudi Arabia, Chemical Geology, 413, 51-62, https://doi.org/10.1016/j.chemgeo.2015.08.001, 2015.

Munksgaard, N. C., Wurster, C. M., Bass, A., and Bird, M. I.: Extreme short-term stable isotope variability revealed by continuous rainwater analysis, Hydrological Processes, 26, 3630-3634, https://doi.org/10.1002/hyp.9505, 2012.

https://doi.org/10.5194/egusphere-2025-272
Preprint. Discussion started: 5 February 2025

Prechsl, U., Gilgen, A., Kahmen, A., and Buchmann, N.: Reliability and quality of water isotope data collected with a low-budget rain collector, Rapid communications in mass spectrometry : RCM, 28, 879-885, 10.1002/rcm.6852, 2014.

Radtke, C. F., Yang, X., Müller, C., Rouhiainen, J., Merz, R., Lutz, S. R., Benettin, P., Wei, H., and Knöller, K.: Nitrate and Water Isotopes as Tools to Resolve Nitrate Transit Times in a Mixed Land Use Catchment, Hydrol. Earth Syst. Sci. Discuss., 2024, 1-32, 10.5194/hess-2024-109, 2024.

Romañach, R., Castro, A., and Esbensen, K.: WHAT are sampling errors—and WHAT can we do about them? Part 1, Spectroscopy Europe, 36, 10.1255/sew.2021.a11, 2021.

Schürch, M., Kozel, R., Schotterer, U., and Tripet, J.-P.: Observation of isotopes in the water cycle—the Swiss National Network (NISOT), Environmental Geology, 45, 1-11, 10.1007/s00254-003-0843-9, 2003.

Sevruk, B.: Evaporation losses from storage gauges, Distribution of precipitation in mountainous areas, 96-102, 1972.

Terzer-Wassmuth, S., Araguás-Araguás, L. J., Copia, L., and Wassenaar, L. I.: High spatial resolution prediction of tritium (3H) in contemporary global precipitation, Scientific Reports, 12, 10271, 10.1038/s41598-022-14227-5, 2022.

Terzer-Wassmuth, S., Wassenaar, L. I., Welker, J. M., and Araguás-Araguás, L. J.: Improved high-resolution global and regionalized isoscapes of O, H and -excess in precipitation, Hydrological Processes, 35, e14254, https://doi.org/10.1002/hyp.14254, 2021.

von Freyberg, J., Knapp, J. L. A., Rücker, A., Studer, B., and Kirchner, J. W.: Technical note: Evaluation of a low-cost evaporation protection method for portable water samplers, Hydrol. Earth Syst. Sci., 24, 5821-5834, 10.5194/hess-24-5821-2020, 2020.

Weaver, J. and Talma, S.: Cumulative rainfall collectors – A tool for assessing groundwater recharge, Water SA, 31, 10.4314/wsa.v31i3.5216, 2007.