~~An easy-to-use~~Simple water vapor sampling ~~approach~~ for stable isotope analysis using affordable ~~membrane~~ valves ~~multi-foil~~and ~~-~~bags

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Abstract. Water ~~-~~stable isotopes are commonly used in hydrological and ecological research. Until now, most measurements ~~were obtained either~~have been made by taking a ~~destructive~~ sample from the field ~~(such as a soil or plant sample)~~ and extracting its water in the laboratory~~,~~ ~~or by directly measuring~~. More recently, samples have been collected with semi-permeable membranes and measured in the field ~~it in the field using semi-permeable membranes~~. These new methods, however, present challenges in achieving high-resolution measurements across multiple sites since they require significant effort and resources. Gas bag sampling offers the advantage of non-destructive, cost-efficient, ~~easy~~ easy ~~to~~ to perform~~,~~ ~~in-~~ ~~situ~~ measurements without the need to bring a Cavity Ring-Down Spectroscopy (CRDS) analyzer into the field. ~~Gas~~ We used gas-permeable membranes (GPM) ~~were utilized~~ to extract samples of water vapor from the soil, which were then stored in ~~specialized~~ multi-layer foil~~gas~~ bags ~~(multi-layer foil bags)~~until analysis. The bags were modified with home-made ~~membrane valves~~connections to reduce leakage and simplify gas transfers. The bags were tested using laboratory ~~isotope~~ standards ~~for~~ to determine their maximum storage time, potential memory effects, and reusability. ~~To demonstrate their applicability in field experiments, in-situ measurements using gas bags were compared to measurements directly connecting a water stable~~ CRDS~~isotope laser.~~ The storage experiment demonstrated the ability to store water vapor samples for up to seven days while maintaining acceptable results for δ^2H and $\delta^{18}O$~~,~~ ~~although the relative uncertainty was higher for $\delta^{18}O$. A "Memory experiment"~~The following ~~experiments revealed~~ ~~that reusing bags can will lead to~~The memory experiment showed that the influence of previous samples ~~influencing subsequent ones. The experiment on "Combined storage and memory" showed that the~~ , increaseds with ~~the~~ duration of storage ~~increases the effect on memory~~. The reuse experiment showed that samples can be filled repeatedly, provided they are filled and evacuated ten times with dry air between ~~-~~measured samples. To demonstrate bag applicability in the field, we compared accuracy and precision of stored samples to measurements made directly in the field. ~~Accuracy~~Trueness was defined as mean difference ~~from~~between the

measured and known water vapor placed into the bags and precision by the standard deviation of repeated measurements. ~~The field experiment demonstrated an~~With new gas bags, we found ~~overall measurement precision~~ accuracy ~~and precision~~of 0.2 ± 0.9 ‰, respectively, for $\delta^{18}O$ and 0.7 ± 2.3 ‰ for $\delta^{2}H$. ~~0.23 ± 0.84 for $\delta^{18}O$ [‰] and 0.94 ± 2.69 for $\delta_{2}H$ [‰] using the new gas bags~~When the bags were reused, they yielded ~~accuracy~~accuracy ~~precision~~ of 0.1 ± 0.8 ‰ for $\delta^{18}O$ and 1.4 ± 3.3 ‰ for $\delta^{2}H$ ~~using reused gas bags~~. This is at least as good as published alternative methods.~~Together, laboratory and field experiments confirmed that the proposed water vapor sampling system and procedure for stable water~~ stable isotope analyses using GPM and combined with re-usable gas bags is a simple, cost-effective, and versatile approach allowing for various applications. We were able to demonstrate that both 1) storage is possible, and that 2) gas bags can be reused, since memory effects caused by previous samples can be prevented by appropriate treatment.~~ The proposed system is simple, cost-effective, and versatile for both lab and field applications.

~~This makes the gas bags suited~~ suitable for field collection of water vapor samples for many ~~applications~~scientific fields~~.~~

1. Introduction

~~Stable w~~Water stable isotope measurements are used in a variety of scientific fields, particularly in hydrology, ecohydrology, and meteorology, which focus on aspects of the water cycle ~~within the biosphere~~. The primary isotopes involved are ^{18}O and ^{2}H (e.g., Gat 1996; Mook ~~2001~~2000), described as $\delta^{18}O$ and $\delta^{2}H$ relative to the most abundant isotopes, ^{16}O and ^{1}H (Sodemann, 2006). They serve to investigate processes such as infiltration and groundwater recharge (~~e.g~~e.g. Séraphin et al., 2016), evaporation (e.g. Rothfuss et al., 2010), or the plasticity of root water uptake under stress (e.g. Kühnhammer et al., 2021; Kühnhammer et al., 2023).

Traditionally, the isotopic composition of soil and plant water has been measured through destructive sampling of soil cores or sampled plant material, followed by water extraction e.g. via cryogenic extraction (see method summary Orlowski et al., 2016a) and measured with isotope ratio mass spectrometry (IRMS) analyzers (West et al., 2006; Sprenger et al., 2015). The development of smaller and less expensive cavity ring-down spectroscopy (CRDS) analyzers has led to an increase in potential applications, including, e.g., in- situ measurements using gas permeable membranes (Rothfuss et al., 2013; Volkmann and Weiler, 2014; Volkmann et al., 2016; Kübert et al., 2021; Marshall et al.; 2020). Direct measurements are a viable

alternative to classic destructive techniques, especially in small plots, as among other benefits (e.g. high frequency measurements) they avoid repeated destructive sampling. However, direct, continuous in- situ field setups are very cost-intensive and technically challenging, requiring a laser spectrometer (e.g. a CRDS) and permanent power supply in the field as well as a strong expertise to maintain. To allow an expansion to a wider set of potential study areas and increase the number of absolute study areas maintainable, scientists are recently trying to develop new simplified sampling systems. This includes capturing soil moisture as water vapor for subsequent laboratory analysis (e.g. Jiménez-Rodríguez et al., 2019; Havranek et al., 2020; Magh et al., 2022; Herbstritt et al. 2023). To do so, primarily glass bottles or gas sampling bags with various fittings are used, which can cost anywhere from less ~than 50 1.2 200 euros to a couple of hundred euros per container. The advantages of these methods include the ability to quickly measure stored samples in a temperature-stable laboratory environment., without the need for time-consuming configuration for specific samples. In addition, multiple sample containers can be filled at once in the field, which allows for the simultaneous measurement of multiple probes, and sampling can generally be performed at a much faster rate. These simplified and more affordable systems could therefore increase the number of studies on stable water stable isotopes and provide new insights in research by increasing the number of possible experimental sites and samples and provide new insights in research.

In this study, we investigated the use of multi-foil bags with septum valves. These bags had previously been successfully tested for ambient air storage in the laboratory (Jiménez-Rodríguez et al., 2019). Our investigation focused on exploring the potential of these commercially available but affordable bags (< 30€ per bag) for a wider range of applications (~ 20€ per bag plus ~ 15€ for the connection) and particularly for spanning a wide isotopic range allowing the use in labelling studies. To ensure easy and reliable bag filling and measurement, we built an additional connection and a portable dry air supply box system for easy field measurement. We tested the prepared bags in several experiments in the laboratory using defined standards and, in the field, using comparison to in- situ measurements with a CRDS. These results allowed us to find a simple approach to using septum-based gas bags for field measurements of water stable isotopes, which was then tested over a full growing season. The focus was to investigate storage capability as well as possible isotopic fractionation effects due to exchange with the inner surface of the bags. Specific objectives included: 1) determining the maximum storage time of water vapor for accurate measurement of water stable isotopes, 2) testing the reusability of the prepared bags, and 3) confirming these results in a field experiment. Four Five different experiments were performed: i1) a storage experiment up to 7 days, 2ii) a

memory experiment without sample storage and two quite different standards, iii~~3~~) a memory experiment with one day of storage of the initial standard followed by ~~a combined storage and memory~~sample replacement ~~experiment~~ exploring duration effects on memory setting and ~~and flushing effects on memory erasure~~, ~~and 4~~iv) a field filling and bag reuse experiment to compare the bag measurements with in~~-~~ situ CRDS measurements. These were followed by v) a gas bag measurement sequence~~s~~ over a full cultivation period.

2. Material and methods

2.1 Study area and basics of ~~stable~~ water stable isotope measurements

The laboratory experiments were carried out ~~in the laboratories of~~at the Leibniz Centre for Agricultural Landscape Research (ZALF). The field experiments took place at the AgroFlux experimental platform of ZALF, located in the northeast of Germany, near Dedelow in the Uckermark region (N 53°22′45", E 13°47′11"; ~50-60 m a.s.l.).

During the experiments, the δ^2H and $\delta^{18}O$ values were recorded using a ~~cavity ring down spectroscopy (~~CRDS~~)~~ analyzer (L2130-i, Picarro Inc., Santa Clara, CA, USA). ~~Water vapor from standards and soil samples was transferred to the CRDS analyzer and either measured directly or using the selected gas bags.~~ The hydrogen and oxygen stable isotopes in the sampled water vapor (δ^2H and $\delta^{18}O$) are ~~detailed~~ given in ~~parts~~ per ~~million~~ mil (‰), relative to the Vienna Standard Mean Ocean Water (VSMOW) ~~through the~~using δ-notation ~~scale~~ (Eq. 1; Craig, 1961).

$$\delta = \left(\frac{R_{sample}}{R_{VSMOW}} - 1\right) \times 1000 \qquad \text{Eq. 1}$$

During all experiments, water stable isotope signatures (δ^2H and $\delta^{18}O$ in ‰) were measured with the method of Rothfuss et al. (2013), using gas permeable membranes (GPM, Accurel GP V8/2HF, 3M, Germany; 0.155 cm wall thickness, 0.55 cm i.d., 0.86 cm o.d.~~)~~; e.g. as used in~~.~~ ~~following the approach~~ ~~The method has already been used several times such as in~~ Kübert et al., ~~(~~2020~~)~~ or Kühnhammer et al., ~~(~~202~~2~~1). In the laboratory experiments, we attached ~~the~~two ~~GPM~~membranes to the cap of a 100 ml glass bottle with two stainless steel fittings (CUA-2, Hy-Lok D Vertriebs GmbH, Germany) to directly measure standard water vapor and to fill the bags. The glass bottle was filled with approx. ~ 60 - 80 ml of standard water. The first ~~GPM serves as a dry air~~membrane ~~supply that is is~~was submerged in the stand~~a~~dard water, where it bubbles the dry air through, resulting in equilibration of water vapo~~u~~r in the headspace with the standard water ~~passing through the water, and t~~. The second membrane, in the headspace, collects ~~for sampling~~ saturated sample air and supplies it ~~transporting the sample~~ to the analyzer. Both ~~GPMs~~membranes were sealed with adhesive. ~~Here, the GPMs~~The second membrane (< 5 cm) ~~are more of~~served as a safety mechanism to prevent liquid water from entering the tubing.

A gas cylinder was used to induce dry gas at a low flow rate of 50 - 80 ml per minute (257-6409, RS Components GmbH, Germany). ~~To ensure~~We ensured that the isotopic signature of

the vapour would be at equilibrium with liquid water ~~stable vapor concentrations at the given temperature, i.e. water stable isotope signatures~~at this flow rate. We tested~~, the standard bottles were tested~~flows from the minimum ~~flow~~ required for Picarro operation (approximately 35 ml/min) to 300 ml/min ~~with~~and found accurate results to 100 ml/min. ~~Due to the~~At the lower ~~low~~ flow rates, the water vapor passing through the ~~GPM reaches an~~membrane reached isotopic thermodynamic equilibrium ~~. This means that it has an isotopic signature that exclusively depends on that of the liquid water and the surrounding temperature~~ (Majoube, 1971; Horita and Wesolowski, 1994).

In the field experiments, we used approx. 12 cm ~~GPM~~membranes (comparable to soil GPM in e.g. Kühnhammer et al., 2021) attached to PTFE tubing to sample the four different soil depths (see section 2.7). ~~A gas cylinder was used to induce dry gas at a low flow rate of 50 - 80 ml per minute. Due to the low flow rate, the water vapor passing through the GPM reaches an isotopic thermodynamic equilibrium. This means that it has an isotopic signature that depends on that of the liquid water and the surrounding temperature (Majoube, 1971; Horita and Wesolowski, 1994).~~

The in~~-~~ situ method ~~used is, similar to the standard measurements, is~~was likewise based on the measurement of water vapor with the assumption that the vapor ~~is~~was in isotopic equilibrium with the liquid water surrounding the sample probe (Rothfuss et al., 2013). ~~To achieve equilibrium between the sampled water vapor and the liquid water, it is imperative to maintain a sufficiently low air flow rate. The possible flow rate depends on the sample probe length, since the carrier gas needs to be saturated with the sample water.~~ Finally, the isotopic ~~signature~~ fractionation ~~between the two phases can then be~~was calculated as a function of the temperature (T) at the phase transition using equations based on Majoube (~~1961~~1971).

~~W~~The ~~sampled~~ water vapor from the standards and soil ~~samples~~ was then either transferred immediately to the CRDS analyzer and ~~either~~ measured directly or it was stored ~~and measured using the selected gas bags.~~in the gas bags and measured later. In laboratory experiments I, II and III, the temperatures were around 20°C during filling and around 24°C during storage and bag measurement to avoid condensation. In field experiments IV and V, great care was taken to measure the bags at elevated temperatures relative to the source temperatures.

2.2 Storage and sampling design

2.2.1 Gas bag design

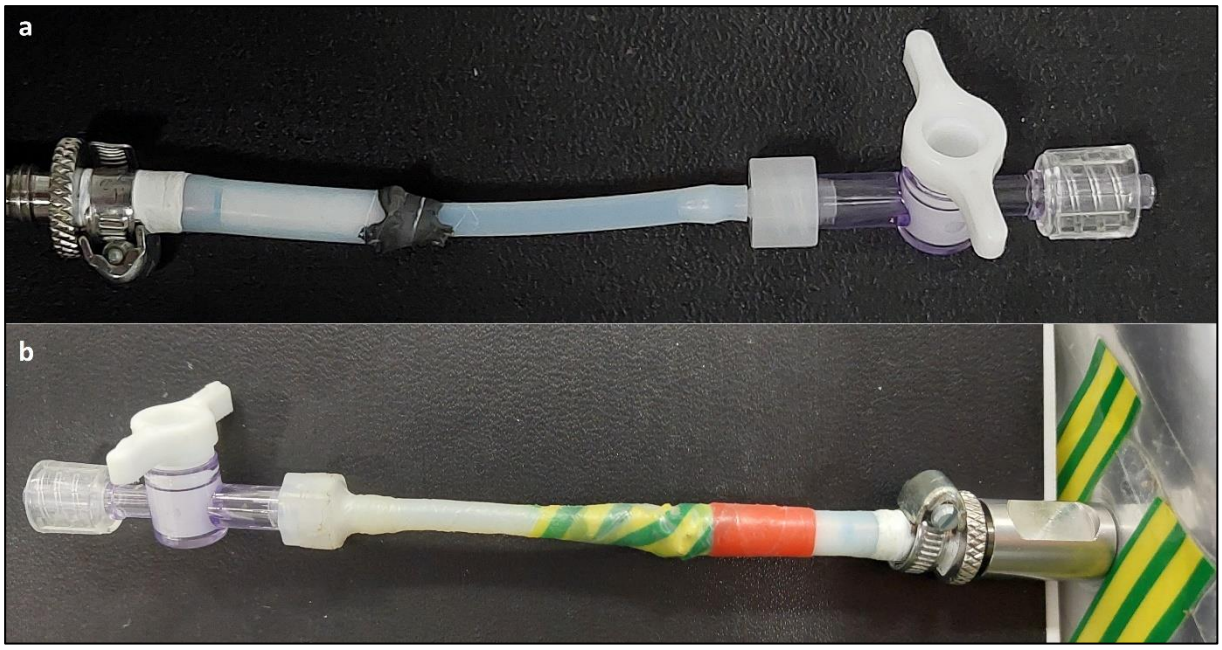


Figure 1: Self-constructed luer-lock connector with the splice exposed (a) and stabilized with tape attached to the bag on the right (b).

The sampling and measurement concept was intended to be as simple as possible, while still providing high accuracy and precision. Water vapor samples were stored in 1-L multi-layer foil bags with a septum-based valve (1l Multi-Layer Foil Bags with stainless steel fitting, Sense Trading B.V., Netherlands; see Table S1 for more details; Sense Trading B.V., 2024). The stainless steel 2-in-1 fitting combined the valve and septum, with the septum acting as a seal, allowing air to flow around it when the valve was open, and sealing when the valve was closed. As recommended by the manufacturer, care was taken when filling the bags to ensure that the maximum volume did not exceed 90% of capacity, which could cause material damage. The connection (Fig. 1) was built to easily attach the bags with the sample setup. It consisted of two short PTFE tubes (PTFE-tubing, Wolf-Technik eK, Germany) and an additional luer-lock stopcock (1-way Masterflex™ Stopcocks with Luer Connection, Avantor, USA). A hose clamp (TORRO SGL 5mm, NORMA Group Holding GmbH, Germany) was used to directly connect a quarter-inch tube to the valve and the other 4 mm tube was glued into the quarter-inch tube using 2-component-adhesive (DP8005, 3M Deutschland GmbH, Germany). Since the adhesive contact with the PTFE tube could break under tension and cause leakage, we wrapped electrical insulation tape around the splice to reinforce the connector. This tape was not essential for sealing. Then, a luer-lock connection (LF-1.5NK-QC, GMPTEC GmbH, Germany) was used to connect the luer-lock stopcock.

~~The sampling and measurement concept is designed as simply as possible~~was intended to be as simple as possible, while still providing high accuracy and precision~~. The storage system is based on~~Water vapor samples were stored in 1-L multi-layer foil gas sample bags (see table S1 for details) with a

membrane-based valve (Multi-Layer Foil Bags, Sense Trading B.V., Netherlands) and an additional. As recommended by the manufacturer, care was taken when filling the bags to ensure that the maximum volume did not exceed 90% of capacity, which could cause material damage.. The valve was attached to a self-constructed connector, which served to simplify filling and minimize leakager with a valve. The valve was based on a(Sense Trading B.V.,), which which As recommended by the manufacturer, care was taken when filling the bags to ensure that the maximum volume did not exceed 90% of capacity.The bags have a Water Vapor Transmission Rate (WVTR) of 0.09 g m-2 d-1 (Jiménez-Rodríguez et al., 2019). The connection (Fig. 1) consisteds of two short PTFE tubes (PTFE tubing (natural), Wolf-Technik eK, Germany) and an additional luer-lock stopcock (1-way Masterflex™ Stopcocks with Luer Connection, Avantor, USA). A hose clamp (TORRO SGL 5mm, NORMA Group Holding GmbH, Germany) wais used to directly connect a ¼ inch tube to the valve and the other 4 mm tube is glued into the ¼ inch tube using 2-component adhesive (DP8005, 3M Deutschland GmbH, Germany). contactTo protect the adhesive and ensure proper sealing, electrical insusolation tape reinforceis wrapped around the splice. Then, a luer-lock connection (LF-1.5NK-QC, GMPTEC GmbH, Germany) wasis used to connect the luer-lock stopcock. The additional connection is necessary to reliably connect the storage system to the specific experimental setup and to increase reusability.

2.2.2 Sampling design

Figure 1: Self-constructed luer-lock connector with the splice exposed (a) and stabilized with tape (b).

During all experiments, water stable isotope signatures ($\delta^{2}H$ and $\delta^{18}O$ in ‰) were measured with the method of Rothfuss et al. (2013), using gas permeable membranes (GPM, Accurel GP V8/2HF, 3M, Germany; 0.155 cm wall thickness, 0.55 cm i.d., 0.86 cm o.d.). The method has already been used several times such as in Kübert et al. (2020) or Kühnhammer et al. (2022). In the laboratory experiments, we attached the GPM to the cap of a 100 ml glass bottle with two stainless steel fittings (CUA-2, Hy-Lok D Vertriebs GmbH, Germany) to directly measure standard water vapor and to fill the bags. A gas cylinder was used to induce dry gas at a low flow rate of 50 - 80 ml per minute. Due to the low flow rate, the water vapor passing through the GPM reaches an isotopic thermodynamic equilibrium. This means that it has an isotopic signature that depends on that of the liquid water and the surrounding temperature (Majoube, 1971; Horita and Wesolowski, 1994).

For the 1) direct standard measurements, the sample thus generated ~~is~~ was passed directly to the laser spectrometer to determine its isotopic signature. Since the laser spectrometer only has

a flow rate of approx. 35 to 40 ml per minute, an open ~~outlet~~ split was added to ensure a constant flow and to avoid pressure differences. T~~In addition, t~~he ~~outgoing~~ open split ~~flow~~ was ~~also~~ measured ~~continuously,~~ continuously t~~hus~~o ensur~~eing~~ that no ambient air could flow back. A 5-minute average was taken at the end of a minimum 10-minute measurement for direct standard measurements.

For the 2) field measurements, the ~~GPMs~~ membranes were installed at the four different depths of~~(~~ 5 cm, 15 cm, 45 cm and 150 cm~~,)~~ and water vapor was transported out of the ~~ground~~ soil using 4 mm PTFE tubing. The open ends were fitted with Luer connectors for later connection of gas sample bags and the dry air supply. To protect these open ends from environmental influences, waterproof outdoor boxes ~~(outdoor.case type 500, B&W International GmbH, Germany)~~ were installed 20 to 30 cm above the ground (outdoor.case type 500, B&W International GmbH, Germany). ~~Holes were drilled in the boxes to~~Cable glands ~~tubes (PG screw set, reichelt elektronik GmbH, Germany)~~were used to keep the boxes ~~tubes with cable glands (PG screw set, reichelt elektronik GmbH, Germany)~~ watertight (PG screw set, reichelt elektronik GmbH, Germany) ~~in the boxes~~.

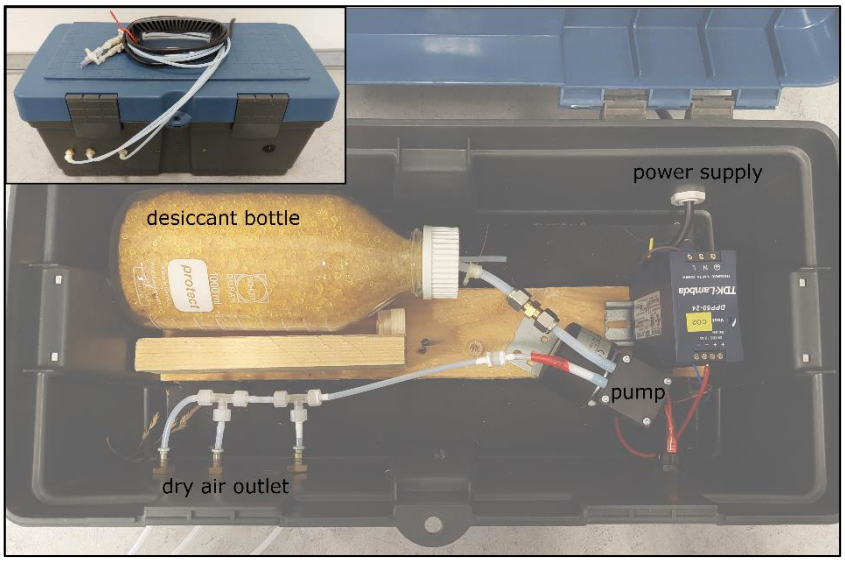


Figure 2: Self-constructed box for field dry air supply (top left) including a bottle with desiccant, power supply and a pump for up to three dry air outlet lines.

A separate box was built to supply pressurized dry air to the measuring system during the field experiments (Fig. 2). This containeds a pump (NMP850KPDC-B, KNF DAC GmbH, Germany) including a power supply (DPP50-24, TDK-Lambda Germany, Germany), which couldan transport the dry air in 3 three tubes simultaneously through the up to three sample tubes lines(i.e. can fill three gas bags at the same time). The air is ambient air which is dried by a desiccant (Silica Gel Orange, Carl Roth GmbH + Co. KG, Germany) contained in a 1-liter bottle (Screw top bottle DURAN®, DWK Life Science, USA). To regulate the flow of individual sample lines, fixed valves were used (AS1002F-04, SMC Deutschland GmbH, Germany). The dry air supply box was tested prior to our experiments by measuring the outlet concentration of the dry box over the course of one day. However, the use of such a system should always be tested for the specific application, as a very high flow rate combined with very humid air could greatly affect the duration of possible use. During the experiments, we periodically tested the water concentration before and after the field campaigns and could not detect any increase after one day in the field. The water concentration of the dry air produced was approximately 200 ppm. As recommended by the manufacturer, care was taken when filling the bags to ensure that the maximum volume did not exceed 90% of capacity.

Table 1: Standards Liquid water standards used during the experiments.

Standard	$\delta^{18}O_{liquid}$ [‰]	$\delta^{2}H_{liquid}$ [‰]
L22	- 19.9	- 148.1
M22	- 9	- 63.3
H22	2	12.9
L23	- 16	- 108.2
M23	- 9.2	- 63.9
H23	- 1.3	- 32

2.3 Laboratory standards

The water stable isotope measurements were calibrated against six water vapor standards (see Table 1) that were manually measured during the experiments. The standards were each measured for at least 10 minutes, and a 5-minute average was documented. Temperature (T) was recorded continuously every 30 seconds with a thermometer (EBI 20-TH1, Xylem Analytics Germany Sales GmbH & Co. KG, Germany) placed directly next to the standard container. This allowed us to measure the standards in the vapor phase during the laboratory experiments as well as the later soil samples during the field measurementsand infer the values in a liquid phase at equilibrium (Sec. 2.95). Of the six standards with different δ values, approximately 60

Standard	$\delta^{18}O_{liquid}$ [‰]	$\delta^{2}H_{liquid}$ [‰]
L22	- 19.9	- 148.1
M22	- 9	- 63.3
H22	2	12.9
L23	- 16	- 108.2
M23	- 9.2	- 63.9
H23	- 1.3	- 32

ml were filled into the prepared 100 ml standard bottles as described in section 2.~~2~~ 1 ~~(storage and sampling design)~~ and measured directly on the CRDS.

2.4 Experimental design

2.4.1 Experimental design I: ~~storage~~ Storage ~~test~~duration

In our storage experiment, we ~~conducted testing of~~tested our gas sample bags for water vapor storage using water sources of known isotopic composition. New bags, including the self-made connections ~~underwent initial preparation before being filled with the sample~~were prepared t~~.~~ ~~T~~o eliminate any production artifacts~~, e~~. Each bag was cycled with dry air, filled, and emptied ~~for~~ five times in a row. Following this preparation, five bags per storage period were filled with two standards, L22 and M22 (15 min. at 50 ml/min). ~~Throughout the filling process, temperature was consistently monitored and documented.~~

Upon filling, the gas bags were promptly measured to ensure that no isotopic fractionation occurred during the filling process. Subsequently, the gas bags were stored in the laboratory ~~under stable temperatures (24-25.5°C). Three distinct)~~ for three storage durations - 1 day, 3 days, and 7 days ~~were chosen before conducting subsequent measurements on the samples~~. After the designated storage periods, the samples were measured for 4 to 5 minutes, and a stable 2-minute average was recorded. ~~To prevent condensation d~~During bag measurement, ~~the laboratory temperature was raised to 25°C prior to each assessment.prevent condensation~~

2.~~5~~ 4.2 Experiment II~~al design~~: ~~memory~~Memory ~~test~~

~~Within our memory experiment,~~ W~~w~~e conducted two ~~distinct sample~~memory tests, maintaining a consistent methodology similar to that employed during the storage experiment, both utilizing newly prepared bags.

In the first test, we followed a structured sequence: ~~starting with a direct standard measurement of the initial standard to ensure carrier gas equilibrium~~that the water vapor in the headspace had reached equilibrium. W~~w~~e ~~, then~~ fill~~ed~~~~ing~~ gas bags with this standard~~,~~ emptied them, and switched to another standard and refilled the bags. ~~for subsequent measurements. After emptying the bags, we performed another direct standard measurement of the initial standard and proceeded to measure the opposite standard.~~ We repeated the process (fill, measure, empty) with the opposite standard until our measurements ~~aligned~~ fell within the required accurate range (defined in 2.~~8~~5). In the first experiment, L23 was used as the initial standard and H23 as

the opposite standard, in the second experiment, the standards were used in reverse order. We used five gas bags per standard during the experiments. ~~and the temperature was continuously monitored and documented throughout the filling process.~~

2.4.3~~6~~ Experiment III~~al design~~: ~~combined storage and memory~~sample replacement ~~experimenttestm~~Memory test with storage

This laboratory experiment was ~~conducted as a combined storage and memory effect test in which we replaced a water vapor sample in a bag with a highly different isotopic vapor sample in numerous steps without dry air rinsing~~conceived after we observed the effect of a short delay on memory in Experiment II. ~~In the combined storage and memory experiment, w~~We followed a similar procedure ~~similar procedure to the memory experiments with one notable difference: after filling the gas bags with the first initial standard L22 (L22: -19.9 ‰ δ^{18}O and -148.1 ‰ δ^{2}H) and conducting measurements~~except that the initial standard was allowed to stand in the bags for one day prior to replacement with the second standard. ~~, we allowed the initial standard to remained in the bags for a one-day storage period and . On the second day, the bag was measured, then refilled and measured again with the initial standard to make sure there was no storage effect on the same standard. refilled the bags again on the second day.~~ We then proceeded with the second standard ~~(H22: 2 ‰ δ^{18}O and 12.9 ‰ δ^{2}H)~~ following the ~~usual~~ repe~~titive~~ated steps (fill, measure, empty) until our measurements ~~aligned~~ fell within the accurate range again. Between the second and third measurement cycle, the experiment was interrupted due to the long duration (1h) of each measurement cycle and continued the next day (after 15.5 hours). The bags were ~~emptied~~ left empty during this second night to avoid any effects. Due to the length of each measurement cycle, we used 3 repetitions during the experiment ~~and the temperature was consistently monitored and documented throughout the filling process~~.

2.4.4 Experiment IV~~imental design~~: Field filling and bag reuse~~ability test~~

To validate results gained during the laboratory experiments under field conditions, ~~thus testing the applicability of our proposed system,~~ we compared measurements using the gas bags with direct in situ CRDS measurements. To do so, we conducted two measuring campaigns, the first using new bags and the second using reused bags. During the first one ~~in October 2022~~, we focused on the applicability of bag filling in the field ~~and possible errors~~ by ~~directly measuring~~comparing direct measurements of the soil water isotopes with the CRDS in the field ~~followed by filling and measurement of the bags~~measurement of bagged samples. In the second

campaign ~~in February 2023~~, we ~~tested the full applicability by comparing~~again compared direct field measurements ~~with field-filled~~to bagged measurements, but this time using re-used bags measured in the laboratory within 24 hours. To exclude any memory effects, as we saw in experiment III, the reused bags were rinsed 10 times with dry air (approx. 10 x 10 min). Identical sample bags were utilized for the identical sample probe to minimize changes in isotopic composition and reduce the impact of memory effects.~~es in both campaigns.~~ During each of the two measurement campaigns, a total of 48 samples were collected at four different depths: 5cm (n = 14), 15cm (n = 13), 45cm (n = 7), and 150cm (n = 14). Due to low soil permeability ~~issues~~, the depth of 45cm could only be sampled during one measurement campaign, resulting in only 7 samples ~~(see discussion for more details)~~. ~~For direct CRDS measurements and gas bag sampling,~~Dry carrier gas was passed through the home-built ~~GPM~~membrane soil probes ~~in the four different depth following the original developments of Rothfuss et al. (2013) and as used similar in Kübert et al. (2020) or Kühnhammer et al. (2021) using the described pump system~~ at a flow rate of approximately 50 ml per minute. First, we connected the CRDS to the outlet valve to determine the time required to reach a ~~stable~~steady-state value ~~value indicating equilibrium with the given low flow rate~~ (compared to e.g. Kühnhammer et al., 2021). Subsequently, a 2-minute average was recorded ~~from~~at the end of a 15-minute measurement for comparison with the subsequent bag measurement. Second, we connected the bags and filled them for 15 minutes (approx. 750 mL). The ~~source~~ temperature at the ~~corresponding~~sampled soil depth (TEROS 21, Meter Group, USA) was logged using a datalogger (CR1000, Campbell Scientific Ltd., Germany) at 20-minute averages and used to correct for equilibrium fractionation. Furthermore, it was used to determine the saturated water concentration to control the concurrent measured concentration in the probe.~~s.~~

2.~~7~~ 4.5 Experiment V~~al design~~: ~~measuring a f~~FObservation over a full cultivation period~~field test~~

~~To validate results gained during the laboratory experiments under field conditions, thus testing the applicability of our proposed system, we compared measurements using the gas bags and subsequent laboratory analyses with direct in-situ CRDS measurements. The experiment took place at the area of the AgroFlux sensor platform. We measured once a month during the winter and once a week starting in the spring resulting in 18 measurement campaigns. During two measurement campaigns, a total of 50 samples were collected at four different depths: 5cm (n~~

~~= 14), 15cm (n = 14), 45cm (n = 7), and 150cm (n = 15). Due to permeability issues, for the depth of 45cm could only be taken during one measurement campaign, resulting in only 7 samples. For direct CRDS measurements and gas bag sampling, carrier gas was passed through the GPM soil probe using the described pump system at a flow rate of approximately 50 ml per minute. First, we connected the CRDS to the outlet valve to determine the time required to reach a stable value indicating equilibrium. Subsequently, a 2-minute average was recorded for comparison with the subsequent bag measurement. Second, we connected the bags and filled them for 15 minutes. The source temperature at the corresponding depth was logged using a datalogger (CR1000, Campbell Scientific Ltd., Germany) at 20-minute averages.~~

The field applicability test was followed by gas bag sampling and subsequent ~~stable~~ water stable isotope analyses in the laboratory for the same soil depths during a full winter wheat cropping period (variety: "Ponticus"; sowing: September 26, 2022; harvest: July 18, 2023) ~~cropping period~~. We measured once a month during the winter and once a week starting in the spring resulting in 18 ~~additional~~ measurement campaigns using only our gas bags. For calibration, three laboratory standards were bagged and treated in the same manner as the samples. As was the case with experiment IV, identical sample bags were used for the identical sample probes throughout all campaigns. Sample bags were replaced with new ones if they were damaged. ~~The a~~To provide context for the soil isotopic data, additional p~~P~~recipitation samples ~~taken~~ w~~ereas~~ collected ~~within lysimeters as two-week bulk samples.~~at the site over a two-year period.

2.5~~8~~ Calculation of isotope ratios, evaluation of uncertainty and data correction

~~The water vapor samples were recorded as 5-minute averages for standards, while bag measurements were recorded as 2-minute averages, including standard deviation.~~ The isotope signatures of the collected water vapor water sample were converted to liquid water isotope signatures using Majoube's method (Majoube, 1971; Kübert et al., 2020). This conversion was based on equilibrium fractionation at the~~the~~ source temperature ~~and assumed thermodynamic equilibrium~~ (Eq. 2 and 3).

$$\delta_{liquid} = \left(\delta_{vapor} + 1\right) \times \alpha^{+} - 1 \qquad \text{Eq. 2}$$

$$\ln \alpha^{+} = a\,\frac{10^6}{T^2} + b\,\frac{10^3}{T} + c \qquad \text{Eq. 3}$$

The equilibrium fractionation factor α+ was determined based on Majoube's (1971) experimental results, using the coefficients a, b and c (a = 1.137, b = -0.4156 and c = -2.0667 for ^{18}O and a = 24.844, b = -76.248 and c = 52.612 for ^{2}H ~~and a = 1.137, b = -0.4156 and c = -2.0667 for ^{18}O~~).

To assess the accuracy of our laboratory measurements, we calculated z-scores for each sample and water stable isotope ($\delta^{18}O$~~$\delta^{2}H$~~ and $\delta^{2}H$ ~~$\delta^{18}O$~~). Z-scores ~~, which are shown on the right side of many of the figures,~~ indicate the normalized deviation of the ~~extracted~~ measured water isotopic ratios from the ~~benchmark~~ known isotopic signature of the ~~referenced standard water~~added water vapor, and can be calculated following the method (Eq. 4) described by Wassenaar et al. (2012):

$$z - score = \frac{S - B}{\mu} \qquad \text{Eq. 4}$$

Where S is the isotope signature ($\delta^{18}O$~~$\delta^{2}H$~~ or $\delta^{2}H$ ~~$\delta^{18}O$~~) measured with our gas bag, B is the benchmark isotope signature and μ is the target standard deviation. To assess the performance of each extraction method, we set a target standard deviation (SD) of 2‰ for $\delta^{2}H$ and 0.4‰ for $\delta^{18}O$ for measuring water vapor samples. The target SD was selected based on CRDS measurements using the bag method and considering standard deviations from previous studies, such as those by Wassenaar et al. (2012~~),)~~ or Orlowski et al. (2016a)~~., and Jiménez-Rodríguez et al. (2019).~~ A z-score < 2 represents an accurate sample range, a z-score between 2 and 5 describes the questionable range, and a z-score > 5 representing an unacceptable range (Wassenaar et al., 2012~~;~~, Orlowski et al., 2016a~~, and Jiménez-Rodríguez et al., 2019~~).

3. Results ~~and discussion~~

The experimental results will be described using the following figure design: the defined standard deviation will be shown as a dashed blue box in plots of the true water vapor isotope values, which will be predominantly shown on the left side. The accurate z-scores are shown as a dashed black box and the questionable z-scores are shown as a black box, predominantly on the right side. Both standard deviation and z-scores were defined in section 2.5.

3.1 Experiment I: Storage ~~experiment~~ duration

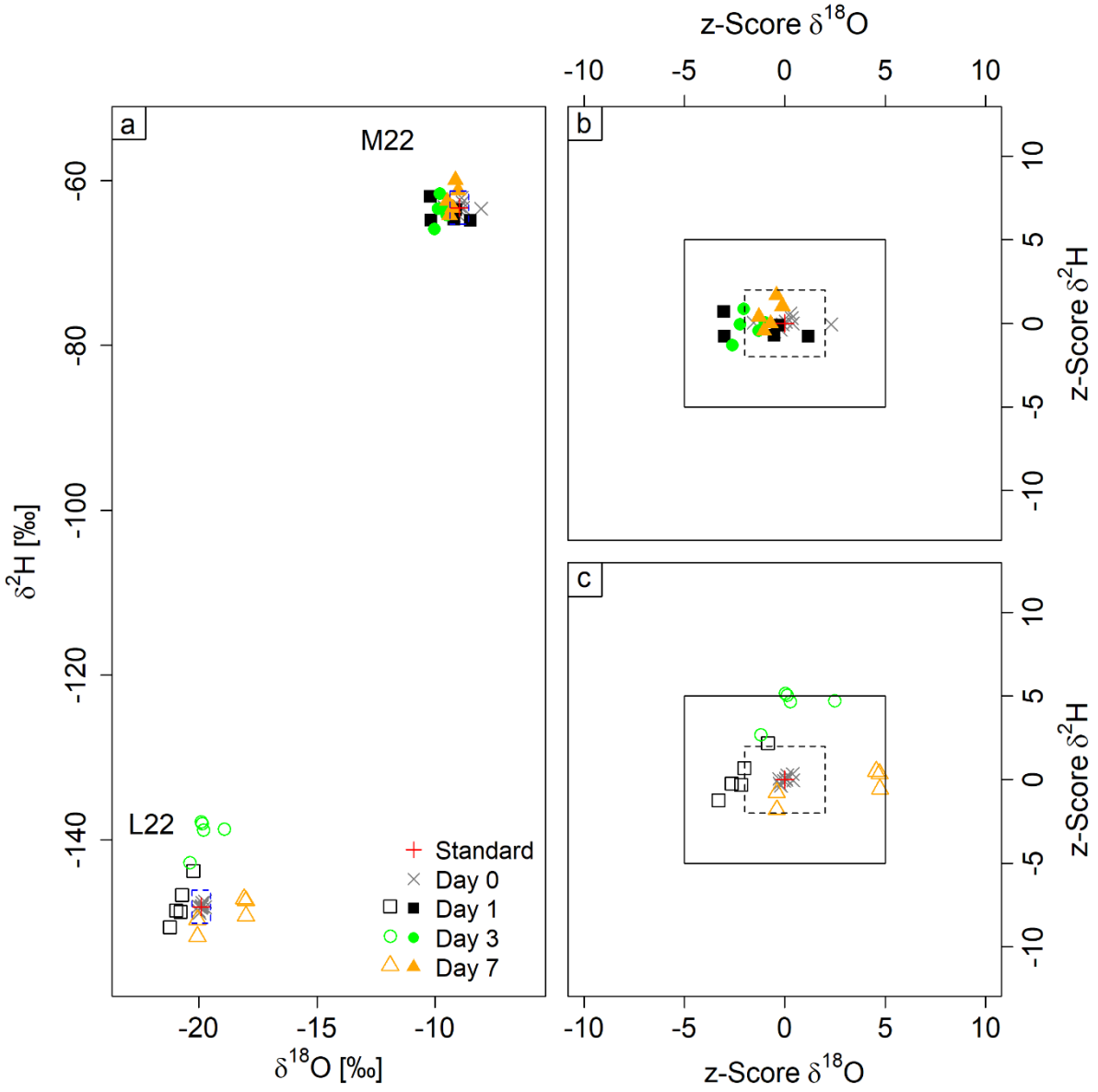
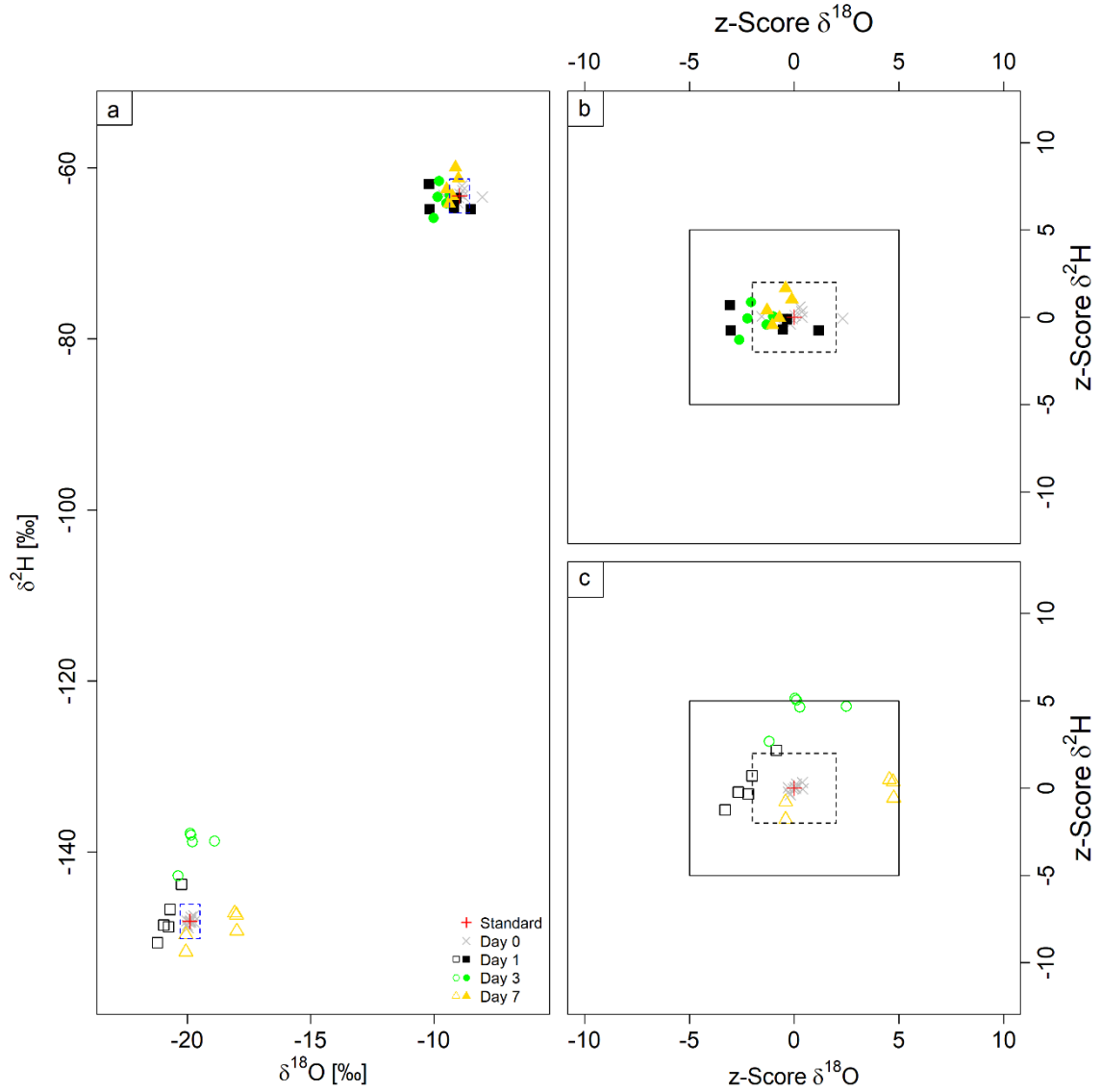


Figure 3: Dual isotope plots showing variation over several days of water-vapor storage in gas bags. ~~-~~ The ~~separate~~ panel on the left~~s~~ shows~~w~~ results from both experiments (a) and those on the right show ~~z~~z-score plots for standard "M22" (filled symbols, b) and "L22" (open symbols, c). The black boxes describe~~s~~ the questionable range while the boxes delineated with a dashed line describes the accurate range (b, c). The blue dashed line (a) describes the defined standard deviation for measurements.

Used laboratory standards, "L22" and "M22", spanned an isotopic gradient of – 9.0 to - 19.9 ‰ in $\delta^{18}O$ and - 63.3 to - 148.1 ‰ in $\delta^{2}H$ (Fig. 3a; filled symbols: "M22", empty symbols: "L22"). On average, ~~a difference of~~measured values differed from known values by -0.7 ± 0.6 ‰ $\delta^{18}O$ and -0.1 ± 2 ‰ $\delta^{2}H$ after 1 day, -0.3 ± 0.6 ‰ $\delta^{18}O$ and +4.3 ± 5.2 ‰ $\delta^{2}H$ after 3 days and, +0.4 ± 1 ‰ $\delta^{18}O$ and +0.1 ± 2 ‰ $\delta^{2}H$ after 7 days of storage ~~was obtained for "L22" and "M22 (for more details, see~~ Table S2/S3~~, supplement)~~". ~~All samples were measured following filling of the bags on day 0 (grey).~~ Except for one sample during the "M22" experiment, deviations from the true standard values in these measurements were all in the range of ± 0.4 for $\delta^{18}O$ and 2 ‰ for $\delta^{2}H$ and thus no bias was associated with filling of the bags ~~could be excluded~~.



~~All samples were measured following filling of the bags on day 0 (grey). Errors associated with filling of the bags could be largely ruled out since day 0 measurements were all in the range of~~

~~± 0.4 ‰ $\delta^{18}O$ and ± 2 ‰ $\delta^{2}H$ from the deviation of the true standard values. Only one sample during the "M22" experiment showed an increased deviation.~~

The experiment using standard ~~"~~M22~~"~~ resulted in an overall high accuracy for all measurements of the three storage durations ~~with average deviation from the true value (which was - 9 ‰ $\delta^{18}O$ and - 63.3 ‰ $\delta^{2}H$)~~ being – 0.5 ± 0.5 ‰ for $\delta^{18}O$ and 0 ± 1.6 ‰ for $\delta^{2}H$. In addition, no trend in isotopic signature could be observed over storage duration for ~~both~~ either $\delta^{18}O$ ~~and~~ or $\delta^{2}H$. Consequently, z-scores were either within the accurate range or close to it, again with no trend of decreasing accuracy over storage time.

The second storage test using ~~"~~L22~~"~~, showed a lower accuracy due to ~~due to a decreased~~lower precision for $\delta^{2}H$, ~~higher deviation from the true value (which was - 19.9 ‰ $\delta^{18}O$ and - 148.1 ‰ $\delta^{2}H$)~~ being – 0.1 ± 1.1 ‰ for $\delta^{18}O$ and 2.8 ± 4.9 ‰ ~~for $\delta^{2}H$~~. ~~No~~ However, no time trend wasnd ~~could be~~ observed ~~as in the previous experiment~~. The ~~increased~~ decreased ~~deviation~~ accuracy was mostly caused by the ~~high imprecision~~samples after three days, as all gas bags showed a significant enrichment (8.9 ± 2 ‰ on average). The higher inaccuracy after three days of storage must be due to an error during the measurement, as ~~samples from better measurement results were~~accuracy improved again ~~obtained~~ after 7 days. The overall higher scatter (particularly for $\delta^{18}O$), which has a different isotopic signature than the ambient air, led to initial concern over potential exchange with ambient air. However, we do not think that is likely as the visible scatter already appeared within one day of storage, was not directed towards isotopic signatures of ambient air and did not increase over time. ~~-~~The z scores show ~~the same result with~~ accurate values for $\delta^{2}H$ (except after 3 days) and ~~a larger scatter with~~more questionable values for $\delta^{18}O$. The average z-score was 0.3 ± 2.7 for $\delta^{18}O$ and 1.4 ± 2.5 for $\delta^{2}H$ ~~(see Table 3 for detailed values)~~.

~~In comparison to prior studies, testing storage of water vapor samples, our results are generally of slightly higher accuracy for $\delta^{2}H$ and comparable for $\delta^{18}O$. The Soil Water Isotope Storage System (SWISS) introduced by Havranek et al. (2020) showed a high accuracy within the overall system uncertainty (± 0.5 ‰ $\delta^{18}O$ and ± 2.4 ‰ $\delta^{2}H$) during a 30-day storage period in a laboratory experiment. This accuracy is not directly transferable to field experiments, and several follow up experiments revealed a actual precision of 0.9 ‰ and 3.7‰ for $\delta^{18}O$ and $\delta^{2}H$ (Havranek et al., 2023). Their system is based on 750 ml glass vials, which are more expensive and require an offset correction. Magh et al., 2022 developed the VSVS system, which is based on crimp neck vials in combination with a PTFE/butyl membrane and has a similar accuracy compared to our results after one day of storage but requires a linear correction for longer~~

measurement periods. Moreover, although the mean isotopic composition remained the same throughout the measurement, it increasingly led to very high scatter of the measured isotopic signatures. Both systems are more difficult to handle compared to inflatable bags as they must be filled with the same amount of dry gas mixture during the measurement due to the static properties of the glass vials and the glass vials might also be prone to break during field work.

To the best of our knowledge there are two studies testing different bags for water vapor storage, and only one using standardized water with different isotopic signatures. Jiménez-Rodríguez et al. (2019) conducted an experiment in which they filled bags of different material with ambient laboratory air and measured them after 3 hours, 1 day, 2 days, 9 days, and 16 days. Among the different bag materials, the MPU gas sample bags – the same bags we used in the present study – showed the best results with mostly accurate z-scores over the entire measurement period. In the present study the experiment using standard M22 is best comparable to their result, having an isotopic signature very similar to the ambient air in our laboratory, yielding comparable results to Rodriquez et al. (2019) with z-scores in the accurate range. The overall higher scatter (particularly for $\delta^{18}O$) visible in the experiment using standard L22, which has a different isotopic signature than the ambient air, led to initial concern over potential exchange with ambient air. However, we do not think that is likely as the visible scatter already appeared within one day of storage, was not directed towards isotopic signatures of ambient air and did not increase over time. We believe the most obvious explanation for this is the previous flushing with dry air, which was reported by Herbstritt et al. (2023) to lead to an undirected scattering of the measured values. This non-directional scattering is more a question of conditioning and can therefore be attributed to material effects, for example, rather than to an exchange with the ambient air. Consequently, the memory experiment was performed, to assess potential impacts of the preconditioning of the bags on the water vapor isotopic measurement results.

3.2 ~~Memory e~~Experiment II: Memory

In this~~e first part of the memory~~ experiment, the initial standard filled into the bags was L23, followed by cycles of filling and emptying with standard H23. This standard sequence was reversed in the second part of the experiment (initially H23, then cycles of L23). No clear memory effect was found in the first part of the experiment (Fig. 4b), whereas a clear memory effect was observed ~~in~~after the first ~~repetition~~filling (L1) of the second part of the experiment (Fig. 4c). H~~, which, h~~owever, this memory almost disappeared again in the next repetition (L2). ~~There was an interruption (approx. 45 minutes) between the three measurements with a clear memory effect and the two measurements without a memory effect, so we suspect a connection between storage time and memory effect.~~

As depicted in Fig. 4 (a and c), except for L1, almost all measurements f~~a~~ell within the target standard deviation for $\delta^{18}O$, while $\delta^{2}H$ values are more scattered. The same pattern can be seen for the z-scores (Fig. 4 b and c). While almost all the z-scores are in the accurate range or in the

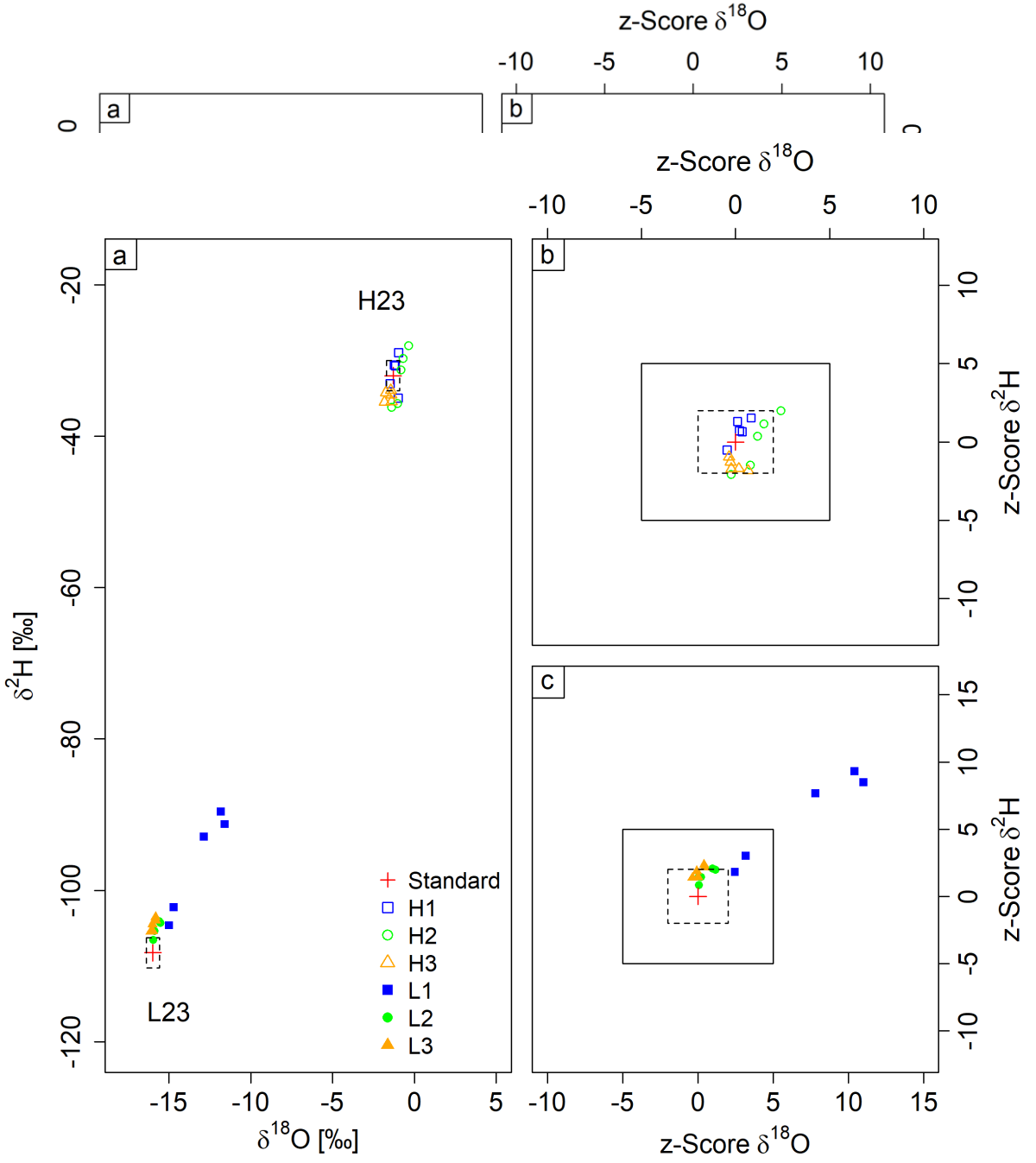


Figure 4: Memory experiment results with dual isotope plot for both experiments (a) and z-score plots for L23 to H23 (b) and H23 to L23 (c). The bags were filled first with standard H, then repeatedly (1-3) with standard L. The memory effect is evident only for measurement L1, the first to follow the change of source water vapor. The black box describes the questionable range while the scatter black box describes the accurate range (b, c). The blue dashed line (a) describes the defined standard deviation for measurements.

questionable range at the threshold of the accurate range, the values of L1 are clearly outside with values in the unacceptable range. ~~These high z-scores for L1 are an indication of the memory effect with this first fill in the direction of the last sample. However, since we could not detect this effect to a high degree with a traceable direction for a short storage time in the bag, we performed a sample replacement experiment with one day of storage of the initial standard.~~

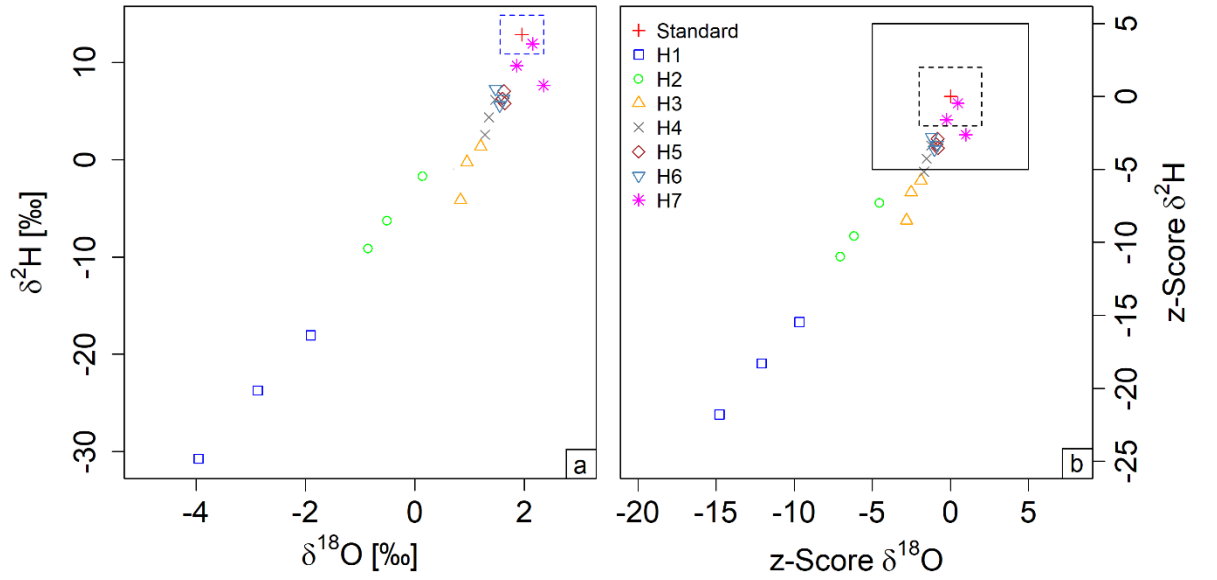
~~In the first part of the memory experiment (Fig. 4a and b), the initial standard filled into the bags was L23 (-16 ‰ $\delta^{18}O$ and -108.2 ‰ $\delta^{2}H$), followed by cycles of filling and emptying with standard H23 (-1.3 ‰ $\delta^{18}O$ and -32 ‰ $\delta^{2}H$). This standard sequence was reversed in the second part of the experiment (initially H23, then cycles of L23). No clear memory effect was found in the first part of the experiment, whereas a clear memory effect was observed in the first repetition (L1) of the second part of the experiment (Fig. 4c), which, however, almost disappeared again in the next repetition (L2). There was an interruption (approx. 45 minutes) between the three measurements with a clear memory effect and the two measurements without a memory effect, so we suspect a connection between storage time and memory effect. The results therefore show that a memory effect caused by the sample previously contained in the gas bag is possible.~~

~~As depicted in Fig. 4 (a and c), except for L1, almost all measurements fall within the standard deviation for $\delta^{18}O$, while $\delta^{2}H$ values are more scattered around the standard deviation (see table 2). The same pattern can be seen for the z-scores (Fig. 4 b and d). While almost all the z-scores are in the accurate range or in the questionable range at the threshold of the accurate range, the values of L1 are clearly outside with values in the unacceptable range. These high z-scores for L1 are an indication of the memory effect with this first fill. This type~~

Figure 5: ~~Combined storage and memory effect test~~~~Sample replacement~~Memory test with storage experiment: ~~with~~ dual isotope plot on the left and z-score plot on the right. The red cross describes the target standard value. The black box describes the questionable range while the ~~scatter~~ dashed black box describes the accurate range, based ~~*either on the CRDS's reported accuracy (a) or*~~ on our classification of z-values (b) ~~(b)~~ (Sec. 2.5~~9~~). The arrow indicates the direction

~~of memory effect in the direction of the last sample contained agrees with the results of Herbstritt et al. (2023). In their study, the bags were additionally pre-flushed with saturated air of a known isotopic signature. Some influence in the direction of the water vapor used for rinsing was observed. However, since we could not detect this effect to a high degree with a traceable direction for a short storage time in the bag, we performed a combined storage and memory experiment.~~

3.3 ~~Combined storage and memory~~~~Sample replacement e~~Experiment III: Memory test with storage



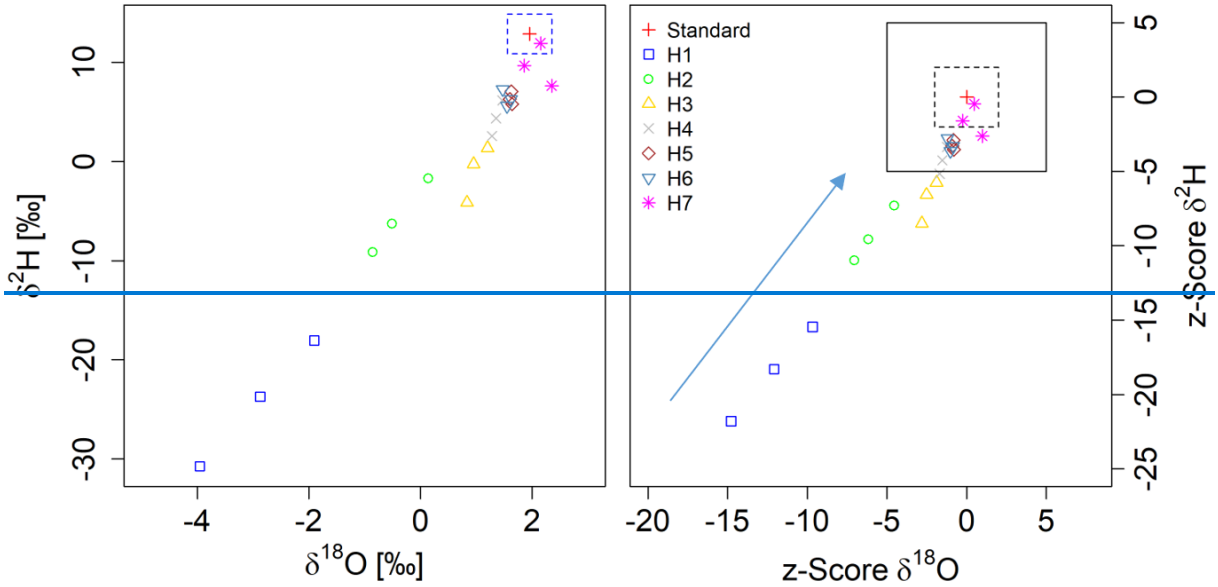


Table 2: Mean differences between measured and known isotopic signatures (S-B, eq. 4) ~~and z-scores~~ of the different repetitions of the combined storage and memory experiment.

Repetition	Diff. $\delta^{18}O$ [‰]	Diff. $\delta^{2}H$ [‰]
H1	-4.9 ± 1	-37 ± 6.4
H2	-2.4 ± 0.5	-18.6 ± 3.7
H3	-1 ± 0.2	-13.9 ± 2.8
H4	-0.6 ± 0.1	-8.5 ± 1.8
H5	-0.3 ± 0	-6.5 ± 0.7
H6	-0.4 ± 0.1	-6.5 ± 0.9
H7	0.2 ± 0.3	-3.1 ± 2.2

~~The final laboratory experiment was conducted as a combined storage and memory effect test. The bags were stored for 1 day using the initial standard L22 (-19.9 ‰ $\delta^{18}O$; -148.1 ‰ $\delta^{2}H$). On the second day, the bags were first measured and cycled again with L22 and then with the opposite standard H22 (2 ‰ $\delta^{18}O$; -12.9‰ $\delta^{2}H$).~~ No significant storage effect was observed ~~during~~ ~~at the end of~~over ~~this~~ the one-day storage period, and there was no noticeable difference between the two repetitions (mean difference between days: 0.4 ± 0.4 ‰ $\delta^{18}O$ and 0.1 ± 1.9 ‰ $\delta^{2}H$). However, when the water

source was changed to H, there was a clear memory effect of a magnitude up to -4.9 ± 1 ‰ $\delta^{18}O$ in and -37 ± 6.4 in ‰ $\delta^{2}H$ ~~that has not been described in the literature before~~ (Fig. 5 and Tab. 2). ~~Measurements H1 to H6 are notably influenced by the initial standard (Ttable 32).~~ After filling with the opposite~~ng~~ standard, H22 ~~(2 ‰ $\delta^{18}O$; 12.9 ‰ $\delta^{2}H$)~~, the first measurements (H1) revealed a ~~high~~ low ~~deviation~~ accuracy due to low precision and trueness~~from the true standard isotopic value. This high deviation~~ , which was improved~~reduced~~ by around 50% with each repetition until the average result of H7 wa~~i~~s close to the target standard value. The z-scores follow~~ed~~ a similar trend from H1 to H5, gradually decreasing. Although H1 and H2 showed unacceptable z-scores for $\delta^{18}O$, and H3 fell within the questionable range, all subsequent measurements ha~~v~~d e~~-~~z-scores within the accurate range. The $\delta^{2}H$ z-scores follow a similar trend to the z-scores for $\delta^{18}O$, thus also ~~indicating~~ indicating a clear memory effect. However, this effect persisted for ~~a longer duration, requiring~~ more cycles in the case of $\delta^{2}H$. The measurements H1 to H3 we~~a~~re in the unacceptable range, while the results for H4 to H6 ~~are~~ were questionable. ~~Accurate values are only observed at H7. On average, H7 showcase highly accurate results with one measurement at H7 has a z-score within the questionable range. The transition between the two measurement days, between H2 and H3, is notably evident in the shift in $\delta^{18}O$ z-scores. The difference of $\delta^{2}H$ is smaller, but this cannot be attributed to the overnight break of the measurement, as there is also hardly any difference between the measurements H4 and H6, which were measured directly one after the other. However, it is clearly visible that a memory effect is significantly increased by the previous sample during a longer storage period and remains visible over significantly more fillings.~~

~~These results are highly relevant for potential usage of storage bags in especially labelling experiments. Based on our results, we advise only use the presented method and used bags for measurements of the natural abundance or samples within the isotopic range of our experiments or performing additional experiments on labeled water vapor samples. If reused, gas bags should be repeatedly filled and emptied at least seven times (n≥7) prior to actual sampling.~~

3.4 Experiment IV: Field filling and bag reuse

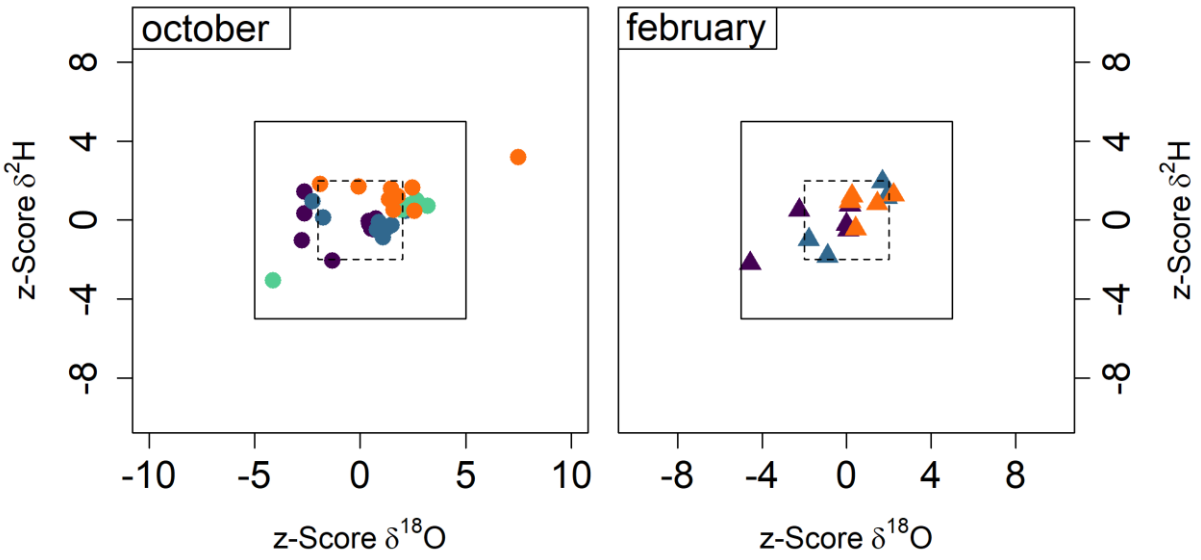


Figure 6: ~~Comparison between in-situ and bag measurements (a) and related z-scores (b). The dual isotope plot (c) shows all 603 measurements taken during the cultivation period. The black box describes the questionable range while the dashed black box describes the accurate range.~~

To compare the measurements during the two campaigns and calculate the Z-scores (Eq. 4), we considered the measured isotopic value ~~of the direct in-situ measurements~~made by the CRDS in the field as the benchmark value (B) and the measurements from the gas bags as the sample (S). The average difference between direct measurement and bag measurement was 0.2 ± 0.9 ‰ for $\delta^{18}O$ and 0.7 ± 2.3 ‰ for $\delta^{2}H$ during the first sampling campaign in October, 2022 and 0.1 ± 0.8 ‰ for $\delta^{18}O$ and 1.4 ± 3.3 ‰ for $\delta^{2}H$ for the second sampling campaign with reused bags in February, 2023 (Fig. 6). The deviation of the bag

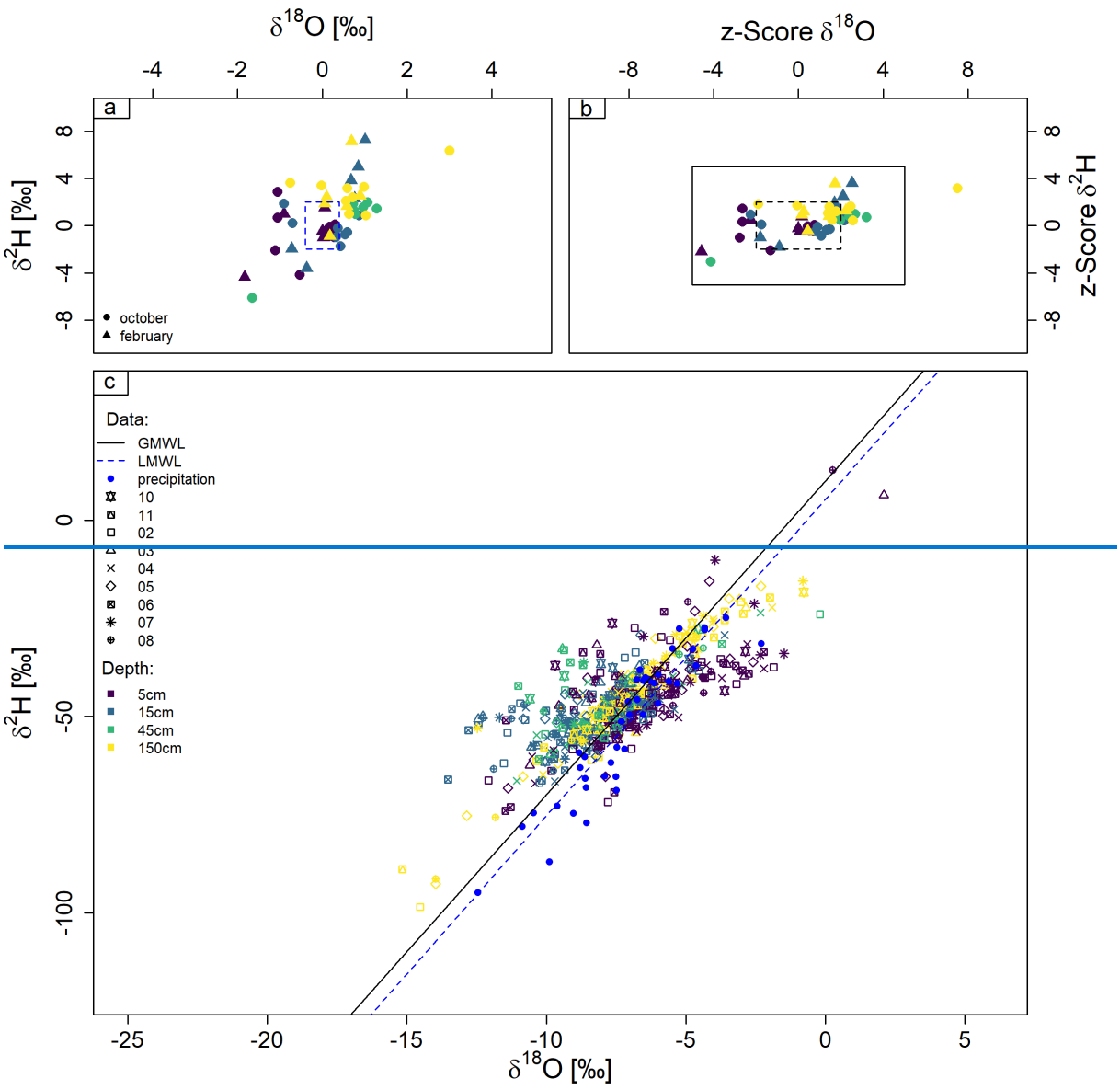
~~New bagsReused bags~~method from direct in situ measurements was thus mostly within the uncertainty range of the in situ method and yielded in highly accurate z-scores for $\delta^{2}H$. However, the $\delta^{18}O$ z-scores exhibit a larger scatter compared to $\delta^{2}H$, consistent with the results of the laboratory storage experiment (Exp. I).

Table 3:~~ Absolute measurement values ($\delta^{18}O$ and $\delta^{2}H$), differences of water stable isotopes (direct vs. bag measurement) and z-scores of the different depth during the two field experiments.~~Mean *differences between direct and bag measurement (S-B, eq. 4)*

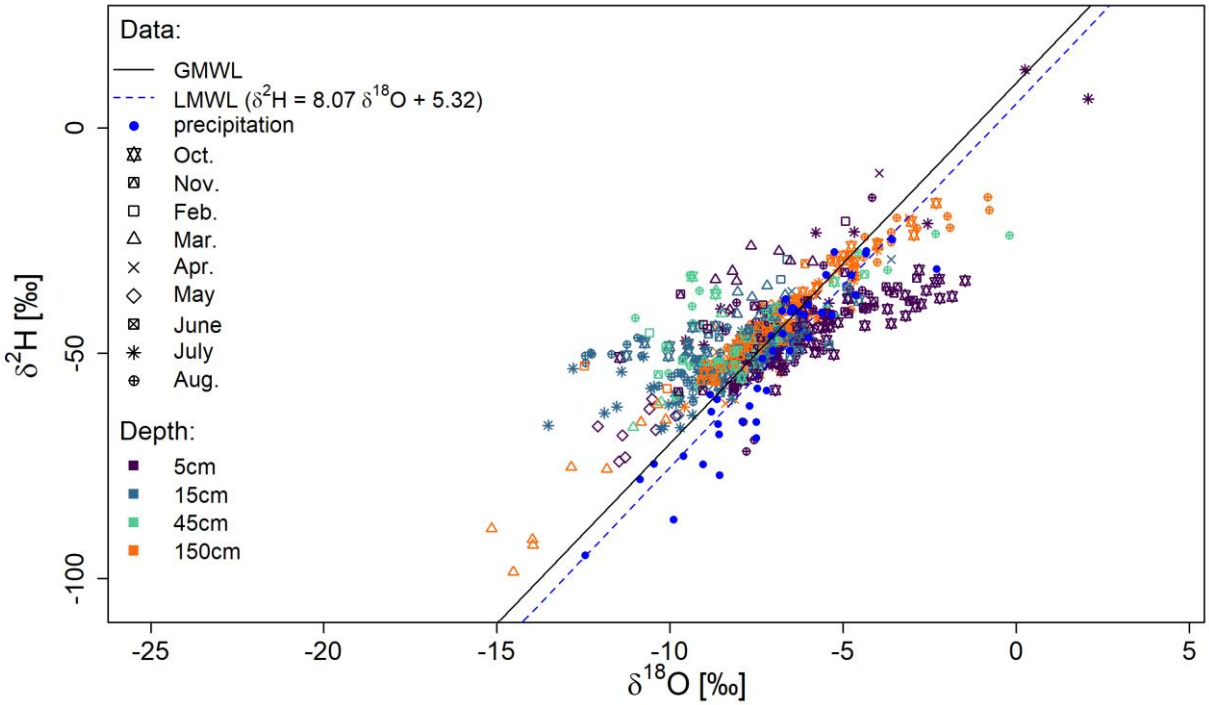
Depth [cm]	Diff. $\delta^{18}O$ [‰]	Diff. $\delta^{2}H$ [‰]	Z-score $\delta^{18}O$	Z-score $\delta^{2}H$
New bags				
5	- 0.3 ± 0.6	- 0.6 ± 1.9	- 0.7 ± 1.6	- 0.3 ± 1
15	0.2 ± 0.6	- 0.2 ± 1.1	0.5 ± 1.6	- 0.1 ± 0.6
45	0.6 ± 1	0.4 ± 2.9	1.4 ± 2.5	0.2 ± 1.5
150	0.8 ± 1	2.9 ± 1.6	1.9 ± 2.5	1.5 ± 0.8
Reused bags				
5	- 0.5 ± 0.8	- 0.6 ± 2.3	- 1.3 ± 2.1	- 0.3 ± 1.2
15	0.4 ± 0.7	2.13 ± 4.2	0.9 ± 1.8	1.1 ± 2.1
150	0.4 ± 0.4	2.5 ± 2.6	1 ± 0.9	1.2 ± 1.3

3.~~4~~ 5 ~~Measuring a~~Experiment V: Observation over a full cultivation period~~Field test - Comparison between gas bag sampling and direct measurements~~

Figure ~~6~~7: ~~Comparison between in-situ and bag measurements (a) and related z-scores (b).~~ The dual isotope plot ~~(c)~~ shows all 603 measurements taken during the cultivation period, including the Global Meteoric Water Line (GMWL; black line), the Local Meteoric Water Line (LMWL; blue dashed line) and the bag method measurements at 5, 15, 45



~~To compare the measurements during the two campaigns and calculate the Z-scores, we considered the measured isotopic value of the direct in-situ measurements as the benchmark value (B) and the measurements from the gas bags as the sample (S). Of the 623 measurements taken, 3.2% had to be discarded due to damaged bags, filling errors, or condensation during the measurement and are therefore not shown. To exclude any memory effects, as we saw in the combined experiment for up to seven repetitions, the reused bags were rinsed 10 times.~~



15	0.2 ± 0.6	-0.2 ± 1.1	0.5 ± 1.6	-0.1 ± 0.6
45	0.6 ± 1	0.4 ± 2.9	1.4 ± 2.5	0.2 ± 1.5
150	0.8 ± 1	2.9 ± 1.6	1.9 ± 2.5	1.5 ± 0.8
21.02.2023				
5	-0.5 ± 0.8	-0.6 ± 2.3	-1.3 ± 2.1	-0.3 ± 1.2
15	0.4 ± 0.7	2.13 ± 4.2	0.9 ± 1.8	1.1 ± 2.1
150	0.4 ± 0.4	2.5 ± 2.6	1 ± 0.9	1.2 ± 1.3

The average difference between direct measurement and bag measurement was 0.2 ± 0.9 ‰ for $\delta^{18}O$ and 0.7 ± 2.3 ‰ for δ^2H during the first sampling campaign in October, 2022 and 0.1 ± 0.8 ‰ for $\delta^{18}O$ and 1.4 ± 3.3 ‰ for δ^2H for the second sampling campaign in February, 2023 (Fig. 6a). The deviation of the bag method from direct in-situ measurements was thus mostly within the uncertainty range of the in-situ method and yielded in highly accurate z-scores (Fig. 6b). However, the $\delta^{18}O$ z-scores exhibit a larger scatter compared to δ^2H, consistent with the results of the laboratory storage experiment. In comparison to other methods determining the isotopic signature of soil water, the tested gas bag method competed well. In the past, destructive measurements of soil water have relied predominantly on cryogenic vacuum extraction (CVE). The accuracy of CVE can vary greatly for soil samples, as shown by a comparative study by Orlowski et al. (2018), in which the results of 16 laboratories showed a mean difference compared to the reference water ranging from +18.1 to -108.4‰ for δ^2H and +11.8 to -14.9‰ for $\delta^{18}O$ across all laboratories. In addition, CVE is associated with co-extraction of organic compounds, significantly interfering with the isotopic quantification (Orlowski et al., 2018). In comparison, methods using in-situ soil or xylem probes based on semi permeable tubing have reported high accuracy (Volkmann and Weiler, 2014; Volkmann et al., 2016; Rothfuss et al., 2013; Kübert et al., 2020).

~~Among the few previous experiments that tested water vapor storage of soil or plant water in controlled or field conditions, Herbstritt et al. (2023) sampled prepared sandboxes and achieved an accuracy of 0.2 ± 0.8 ‰ $\delta^{18}O$ and 0.8 ± 2.9 ‰ $\delta^{2}H$ after calibration, while Havranek et al. (2023) achieved an accuracy of ± 0.9 ‰ in $\delta^{18}O$ and ± 3.7 ‰ in $\delta^{2}H$ during several experiments, comparable to our findings (0.2 ± 0.9 ‰ for $\delta^{18}O$ and 0.7 ± 2.3 ‰ for $\delta^{2}H$ in the first sampling campaign and 0.1 ± 0.8 ‰ for $\delta^{18}O$ and 1.4 ± 3.3 ‰ for $\delta^{2}H$ in the second sampling campaign). In the field experiment of Magh et al. (2022), xylem water samples were taken using the borehole equilibration method (Marshall et al. 2020). In general, the VSVS system did not differ significantly from the in-situ measured data but resulted in a higher uncertainty with 0.6 ‰ to 0.8 ‰ for $\delta^{18}O$ and 0.6 ‰ to 4.4 ‰ for $\delta^{2}H$ after.~~

Measurements of soil water isotope profiles over the full season ~~field experiment~~ (Fig. 7~~Fig. 6c~~) revealed a wide range of isotopic signatures with 2.1 ‰ to -15.2 ‰ for $\delta^{18}O$ and 12.9 ‰ to -98.5 ‰ for $\delta^{2}H$. Of the 623 measurements taken, 20 measurements or 3.2% had to be discarded due to damaged bags, filling errors, or condensation during the measurement and are therefore not shown (see "Handling Recommendations" in the supplement for further details). The isotopic signature of precipitation is represented by the local meteoric water line (LMWL), shown here for the period of ~~…~~ September 2021 to ~~….~~ September 2023. The LMWL ~~reveals a slightly different offset but equal increase between $\delta^{18}O$ and $\delta^{2}H$ compared~~ is nearly parallel to the Global Meteoric Water Line (GMWL). ~~The isotopic signature of soil water can vary strongly from precipitation, as it is a mixture of different precipitation events containing different isotopic signatures and magnitude. Furthermore, its isotopic signature can change significantly as evaporated soil vapor is depleted in heavy isotopes, leaving the remaining soil water enriched in ^{18}O and ^{2}H (Dubbert and Werner, 2018). This results in a wide range of isotopic signatures throughout the complete cultivation season, as can be seen in the wide scatter around the LMWL.~~ In general, the measurements show isotopic signatures similar to precipitation immediately after rain events and a trend toward evaporative ~~enrichment in~~enrichment during droughts (see Fig. S1, supplement), but with distinct differences between months (e.g., Mar vs. Oct, at the 5 cm depth~~.~~). ~~As expected, evaporative enrichment is particularly evident in the upper 5 cm depth, while there are only slight trends in evapotranspiration enrichment at lower depths (e.g. Sprenger et al., 2016). These results are consistent with the environmental conditions, as the measurements were taken during a rather wet cultivation season with only short droughts.~~ Overall, our findings from the field trial suggest a good agreement ~~with GPM probe and bag based soil water isotope measurements~~ with the LMWL and are plausible in terms of seasonal variability. ~~(e.g. compare offsets between~~

~~cryogenically extracted bulk soil water isotope measurements and LMWL; e.g. Zhao and Wang, 2021).~~ ~~Notably, there is increased variability and higher rate of discarded samples at 45 cm depth. This coincides with the placement of the GPM probes just below the lower boundary of the plow layer. This typically leads to a layer of increased soil compaction underneath, which we suspect had deteriorating consequences for the functionality of the GPM probes that should be considered in future experiments in agricultural settings.~~

4. Discussion

~~destructivecontinue~~~~In general, it is difficult to compare the few different approaches to water vapor sampling for isotopic analysis because they vary in complexity and application (e.g., storage time or price per sample). However, when we try to, o~~Our results are generally comparable in accuracy to previous studies of water vapor storage~~for δ^2H and for δ^{18}O~~. For example, the Soil Water Isotope Storage System (SWISS) introduced by Havranek et al. (2020) showed a high accuracy ~~within the overall system uncertainty~~ during a 30-day storage period in a laboratory experiment (± 0.5 ‰ δ^{18}O and ± 2.4 ‰ δ^2H). This result was followed by several experiments, which showed an actual precision of 0.9 ‰ and 3.7‰ for δ^{18}O and δ^2H in field applications ~~and~~with a storage time of 14 days (Havranek et al., 2023). Their system is based on custom~~–~~made 750 ml glass vials with stainless steel connections. Magh et al. (2022)~~,~~ developed the vapor storage vial system (VSVS), which is based on crimp neck vials in combination with a PTFE/butyl membrane and has a similar accuracy compared to our results after one day of storage, but, like the static vials used by Havranek et al. (2020), requires a linear correction. Moreover, although the mean isotopic composition remained the same throughout the measurement, it increasingly led to ~~very~~ high scatter of the measured isotopic signatures. Both systems are more difficult to handle during the measurement compared to inflatable bags as they must be filled with the same amount of dry gas mixture during the measurement due to the static ~~properties~~volume of the glass vials.

~~To the best of our knowledge there is only one study testing~~A recent paper compared different types of ~~storage~~ affordable food storage bags for water vapor sampling ~~storage~~ using

standardized water with different isotopic signatures~~.~~ ~~(~~Herbstritt et al.; ~~(~~2023). These authors conducted rigorous tests of ~~first tested the~~ diffusion tightness and inertness of various ~~gas bags~~bag types. T~~followed by a variety of experiments using the best performing bags with the, recently commercially available, in situ water isotope probes (WIPs; Volkmann and Weiler, 2014). The WIP system dilutes the sample flow by reducing the water vapor concentration in the probe, hence enabling measurements with relatively constant water vapor concentrations. In comparison, home-built systems with GPMs, such as those used in our study (following the original developments of Rothfuss et al.,2013), typically measure the saturated airflow without dilution in the GPM. One of the main differences is that the water vapor concentration of a sample from the WIP system is usually lower than that of the self-built systems due to the dilution. This has the advantage of reducing the risk of condensation, but also leads to a lower water concentration and thus a reduction in sample volume.~~ hey detected significant memory in all bag types, even after flushing with dry N_2. To circumvent these memory effects, they explored preconditioning of the bags with a known moist air sample where the goal was not to eliminate the memory effect, but to make it predictable and remove it. After one storage day, the accuracy was 0.25 ± 0.41‰ and 0.41 ± 1.93 ‰ for $\delta^{18}O$ and $\delta^{2}H$. ~~In this sense, it~~This preconditioning resembles the pre-treatment of feathers (Hobson *et al.*, 1999) and hair (Ehleringer *et al.*, 2020) to fill exchange sites with known water vapor prior to analysis, followed by post-processing to remove the pre-treatment effect~~(Hobson *et al.*, 1999; Ehleringer *et al.*, 2020).~~

Our study differs from ~~(~~Herbstritt et al.~~;~~ ~~(~~2023) paper in several important ways. First, we have used different bags, which are more expensive, but have better control over suppliers and better description of specifications. Second, we have modified the valve inlets to the bags in a way that may reduce leakage and simplify gas transfers both in the lab and in the field. ~~Third, we tested our bags under a wider range of isotopic composition, which provides a more rigorous test. Fourth~~Third, we have suggested a means by which multiple flush~~ings~~es of the bags with dry air may eliminate, or at least minimize, the memory effect. ~~Fifth~~Fourth, we have identified a time-dependent memory effect, which is consistent with the notion that some diffusion/adsorption process occurs over many hours within the walls of the bag, setting an isotopic signal that requires multiple ~~flushings~~flushes to remove. This time-dependent process does not seem to require slow flushing to reverse the memory effect (Expt. IV~~3???~~). These results call for the automation of bag flushing protocols in order to make these techniques routinely useful. Since the isotopic range in the experiment was relatively narrow (< 20 ‰ for $\delta^{2}H$ between first and second sampling), we additionally performed a small reuse experiment

using two laboratory standards with higher differences in isotopic signatures and ten-times flushing with dry air (Fig. S2). As expected, results were unaffected for both $\delta^{18}O$ and $\delta^{2}H$ directly after bag filling. While storing did not influence the $\delta^{18}O$ signature, a clear but consistent effect was visible after one day regarding $\delta^{2}H$, which, contrary to the results of Herbstritt et al. (2023), did not increase over three days storage. Since this effect was stable and we know the previous sample signature, this effect may be correctable like the moist conditioning approach described by Herbstritt et al. (2023) or erasable by increasing the number of flushes. ~~In the meantime, we have demonstrated that our bags met the expected level of performance already, provided that they were flushed multiple times between uses, they are reused for the same sample probes, and that standards are taken through the whole sample collection, transport, and analysis process. Most importantly, we recommend rapid dry-air flushing rather than the slow pre-conditioning with humid air recommended by Herbstritt et al., (2023).~~

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~~With sample bags, a reduced sample volume can be a disadvantage, as they are not completely sealed and an exchange with the ambient air takes place, which is described by the WVTR. The WVTR is mainly dependent on temperature and humidity, so sample bags should generally be stored and transported under as constant conditions as possible. Even though the multilayer gas bags have a low WVTR, we conducted the storage experiments using different standards to avoid a possible error. The experiment using standard M22 showed the best results, having an isotopic signature closest to the ambient air in our laboratory. The overall higher scatter (particularly for $\delta^{18}O$) visible in the experiment using standard L22, which has a slightly higher difference in isotopic signature to the ambient air (compared to M22), led to initial concern over potential exchange with ambient air. However, we do not think that is likely as the visible scatter already appeared within one day of storage, was not directed towards isotopic signatures of ambient air and did not increase over time. In addition, Herbstritt et al. (2023) conducted a storage experiment with pure N_2, which resulted in a relatively low exchange for most bag types~~

for short durations, and only mean vapor content readings of approx. 1450 ppmv after 4 weeks of storage for their best tested bags. We believe the most obvious explanation for the slightly lower accuracy is the previous flushing with dry air. This non-directional scattering is more a question of conditioning and can therefore be attributed to material effects, for example, rather than to an exchange with the ambient air.

Regarding the reusability of gas bags, our memory experiment results confirm a possible memory effect caused by the previous sample in the gas bag (Herbstritt et al. 2023). To enable the reuse of gas bags and quantify a possible memory effect, we performed the sample replacement experiment followed by the field reusability experiment. On average, a very accurate result was achieved after replacing the sample 7 times. However, it is clearly visible that a memory effect is significantly increased by the previous sample during a longer storage period and remains visible over significantly more fillings. These results are highly relevant to the potential storage of water vapor samples in gas bags, particularly in labelling experiments. Following these results, we have obtained our field reusability experiment using 10x dry air rinsed bags, resulting in unaffected values compared to in situ CRDS measurements. In comparison, Herbstritt et al. (2023) first tried to flush the bags with pure nitrogen. After flushing three times, all bags showed a proportional shift towards the previous sample independent of ambient air values. They then tested two conditioning methods, flushing the bags up to five times with dry synthetic air or moist air with a known isotopic signature, with one day of storing time between the flushing steps. The dry conditioning resulted in a decline in precision and accuracy, whereas the moist conditioning showed a bias towards the conditioning value (increasing over time), overall resulting in a higher accuracy but a necessary correction. In contrast, our rinsing approach was performed by filling and emptying the bags sequentially, which took approximately 10 minutes, resulting in approximately 2 hours to rinse all the bags. With this approach, our field reusability experiment showed a high accuracy with reused bags indicating the possibility of reusing the bags after flushing them with dry air. However, since the isotopic range in the field reusability experiment was relatively narrow (range of… between first and second sampling), we additionally performed a small experiment using two laboratory standards with higher differences in isotopic signatures (difference of 14.7 ‰ in $\delta^{18}O$ and 76.2‰ in $\delta^{2}H$): we stored our standard L23 in the bags for one day, rinsed them 10 times, and filled them with the opposite standard H23 (see Fig. S2 supplement). Directly after bag filling, results were unaffected for both $\delta^{18}O$ and $\delta^{2}H$. While storing did not have an effect on the $\delta^{18}O$ signature a clear but consistent effect was visible after one day regarding $\delta^{2}H$, which, contrary to the results of Herbstritt et al. (2023), did not increase over time (three days storage). Since

~~this effect is stable over three days of storage and we know the previous sample signature, this effect may be correctable similar to the moist conditioning approach described by Herbstritt et al. (2023). Therefore, we recommend to reuse bags according to the presented approach (10x rinsing and ideally similar samples for reused bags) only for natural abundance measurements. In order to recommend our bag approach over a larger range of isotopic signatures, it should be examined whether the effect observed on the δ^2H signature is stable over changing ranges of previous and current samples stored in the bag that can be corrected to enable additional experiments with labeled water vapor samples. Otherwise, a possible solution to avoid the memory effect of these samples in δ^2H could be to increase the number of rinse cycles (further tests required), which would be fairly easy if it were automated.~~

To the best of our knowledge, a campaign of measuring soil water isotopes using gas bags over an entire cultivation period, as shown in this study, has not been done before. However, such studies have been done with other data collection techniques. For example the isotopic composition of water in surface soils ~~The isotopic signature of soil water can vary strongly from precipitation, as it is a mixture of different precipitation events containing different isotopic signatures and magnitude. Furthermore, its isotopic signature~~ can change significantly as evaporated soil vapor is depleted in heavy isotopes, leaving the remaining soil water enriched in ^{18}O and ^{2}H (Dubbert and Werner, 2018). This results in a wide range of isotopic signatures throughout the complete cultivation season, as can be seen in the scatter around the LMWL (Fig. 7). As expected, evaporative enrichment is evident following precipitation free periods in the upper 5 cm depth (e.g. April period in Fig. S1), but not after the rainy winter period. ~~while~~ In contrast, there are only slight trends in evaporative enrichment at lower depths (compare e.g. Sprenger et al., 2016). ~~These results are consistent with the environmental conditions, as the measurements were taken during a rather wet cultivation season with only short droughts.~~

~~***Move this to supplement:***~~

~~***Add final paragraph about alternative methods….costs, precision, conditions, open questions…***~~In the past, destructive measurements of soil water have relied predominantly on cryogenic vacuum extraction (CVE). The accuracy of CVE can vary greatly for soil samples and is associated with co-extraction of organic compounds, significantly interfering with the isotopic quantification using CRDS (Orlowski et al., 2016b). In comparison, methods using in situ soil or xylem probes based on semi permeable tubes have been reported to be highly accurate but complex to handle and set up (Volkmann and Weiler, 2014; Volkmann et al., 2016;

Rothfuss et al., 2013; Kübert et al., 2020). Therefore, development efforts to combine destructive with in-situ sampling continue.

Recent studies showed that sampling of water vapor with subsequent analysis in the laboratory is possible with both glass bottles and different types of bags. Glass containers revealed the advantage of less material effects and higher diffusion tightness while gas bags were easier to measure due to their flexible structure. Nevertheless, further experiments should investigate the detected interaction of water samples within the gas bag wall. The cost for the commercially available gas bags we used was relatively low. To classify the costs per sample container, the SWISS-System was clearly more expensive while the other methods were less expensive per sample container with 1-2€ but produced running cost (Magh et. al, 2022) or additional cost and effort to attach the valve and built the final bag (Herbstritt et. al, 2023). We have demonstrated that commercially available our bags met the expected level of performance already, provided that they were flushed multiple times between uses, they are reused for the same sample probes, and that standards are taken through the whole sample collection, transport, and analysis process. Following the described conditions, we were able to reliably measure soil water over a full cultivation period under natural abundance conditions.

4. Conclusion

Our laboratory and field experiments have confirmed that ~~GPM~~ soil membranes combined with gas bags for in- situ soil water vapor sampling and subsequent ~~stable~~ water stable isotope analyses ~~is~~ was a reliable, cost-effective, and easy to handle method allowing for many future applications. We were able to demonstrate that both 1) storage is possible and 2) memory effects caused by previous samples can be prevented by appropriate preconditioning, allowing the gas bags to be reused. ~~When reusing the bags, it was important that 1) the bags were rinsed ten times with dry air, 2) the additional connection including valve was built and 3) the bags and their valves (especially the seals) were regularly checked for damage. In addition, great care must be taken to open the bag valves only minimally for filling and not to fill the bags more than 90% (as specified by the manufacturer).~~ Most importantly, we recommend rapid dry-air flushing rather than the slow pre-conditioning with humid air recommended by Herbstritt et al. (2023). Regarding the isotopic signature during the experiment, reuse is easier to carry out with smaller differences between the consecutive samples in the bags, e.g. in the natural abundance range. However, ~~if a strong labeling experiment is performed~~for larger differences in isotopic signatures, the bags ~~may~~ need to be handled differently (e.g. better flushing between samples or no reuse). Through the conducted field experiment (two campaigns with CRDS and bag measurements), we were able to show that the bags could be used in our case with an accuracy of 0.23 ± 0.84 $\delta^{18}O$ [‰] and 0.94 ± 2.69 $\delta^{2}H$ [‰], which allows a wide applicability. The

possibility to take and store samples easily and without permanent power supply extends the usability of ~~stable~~ water stable isotope measurements in the field. ~~Finally, the bags should not be measured at a temperature that is lower than the temperature measured at the GPM (source temperature) during the measurement. If the gas bags are measured below the source temperature, condensation will occur in the bag, which can greatly distort the measurement result.~~

5. Data availability

The data will be available in the BonaRes repository upon publication.

6. Author contribution

AD and MD designed the study. AD conducted the experiments and analyzed the data. JM, DD, and MH provided support for the experimental setup and analysis methods. AD prepared the paper with supervision from MD and contributions from all co-authors.

7. Competing interests

The authors declare that they have no conflict of interest.

8. Acknowledgements

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