



1 **An easy-to-use water vapor sampling approach for stable**  
2 **isotope analysis using affordable membrane valve multi-**  
3 **foil bags**

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10 **Abstract.** Water-stable isotopes are commonly used in hydrological and ecological research.  
11 Until now, measurements were obtained either by taking a destructive sample in the field (such  
12 as a soil or plant sample) and extracting its water in the laboratory, or by directly measuring it  
13 in the field using semi-permeable membranes. These methods, however, present challenges in  
14 achieving high-resolution measurements across multiple sites since they require significant  
15 effort and resources. Gasbag sampling offers the advantage of non-destructive, cost-efficient,  
16 easy to perform, in-situ measurements without the need to bring a Cavity Ring-Down  
17 Spectroscopy (CRDS) analyzer into the field. Gas permeable membranes (GPM) were utilized  
18 to extract samples of water vapor from the soil, which were then stored in specialized gas bags  
19 (multi-layer foil bags). The bags were tested using laboratory isotope standards for their  
20 maximum storage time, potential memory effects, and reusability. To demonstrate their  
21 applicability in field experiments, in-situ measurements using gas bags were compared to  
22 measurements directly connecting a water stable isotope laser. The storage experiment  
23 demonstrated the ability to store water vapor samples for up to seven days while maintaining  
24 acceptable results for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , although the relative uncertainty was higher for  $\delta^{18}\text{O}$ . A  
25 “Memory experiment” revealed that reusing bags can lead to previous samples influencing  
26 subsequent ones. The experiment on “Combined storage and memory” showed that the duration  
27 of storage increases the effect on memory. The field experiment demonstrated an overall  
28 measurement precision of  $0.23 \pm 0.84$  for  $\delta^{18}\text{O}$  [‰] and  $0.94 \pm 2.69$  for  $\delta_2\text{H}$  [‰] using the gas  
29 bags. Together, laboratory and field experiments confirmed that the proposed water vapor  
30 sampling system and procedure for stable water isotope analyses using GPM and re-usable gas  
31 bags is a simple, cost-effective, and versatile approach allowing for various applications. We  
32 were able to demonstrate that both 1) storage is possible, and that 2) gas bags can be reused,  
33 since memory effects caused by previous samples can be prevented by appropriate treatment.  
34 This makes the gas bags suited for field collection of water vapor samples for many  
35 applications.



## 36 1. Introduction

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

44 Traditionally, the isotopic composition of soil and plant water has been measured through  
45 destructive sampling of soil cores or sampled plant material, followed by water extraction e.g.  
46 via cryogenic extraction (see method summary Orłowski et al., 2016a) and measured with  
47 isotope ratio mass spectrometry (IRMS) analyzers (West et al., 2006; Sprenger et al., 2015).  
48 The development of smaller and less expensive cavity ring-down spectroscopy (CRDS)  
49 analyzers has led to an increase in potential applications, including e.g. in-situ measurements  
50 using gas permeable membranes (Rothfuss et al., 2013; Volkmann and Weiler, 2014; Volkmann  
51 et al., 2016; Kübert et al., 2021). Direct measurements are a viable alternative to classic  
52 destructive techniques, especially in small plots, as among other benefits (e.g. high frequency  
53 measurements) they avoid repeated destructive sampling. However, direct, continuous in-situ  
54 field setups are very cost-intensive and technically challenging, requiring a laser spectrometer  
55 (e.g. a CRDS) and permanent power supply in the field as well as a strong expertise to maintain.  
56 To allow an expansion to a wider set of potential study areas and increase the number of  
57 absolute study areas maintainable, scientists are recently trying to develop new simplified  
58 sampling systems. This includes capturing soil moisture as water vapor for subsequent  
59 laboratory analysis (e.g. Jiménez-Rodríguez et al., 2019; Havranek et al., 2020; Magh et al.,  
60 2022; Herbstritt et al. 2023). To do so, primarily glass bottles or gas sampling bags with various  
61 fittings are used, which can cost anywhere from less than 50 euros to a couple of hundred euros  
62 per container. The advantages of these methods include the ability to quickly measure stored  
63 samples in a stable laboratory environment, without the need for time-consuming configuration  
64 for specific samples. In addition, multiple sample containers can be filled at once in the field,  
65 which allows for the simultaneous measurement of multiple probes, and sampling can generally  
66 be performed at a much faster rate. These simplified and more affordable systems could  
67 therefore increase the number of studies on stable water isotopes and provide new insights in  
68 research.



69 In this study, we investigated the use of multi-foil bags with septum valves. These bags had  
70 previously been successfully tested for ambient air storage in the laboratory (Jiménez-  
71 Rodríguez et al., 2019). Our investigation focused on exploring the potential of these affordable  
72 bags (< 30€ per bag) for a wider range of applications and particularly for spanning a wide  
73 isotopic range allowing the use in labelling studies. To ensure easy and reliable bag filling and  
74 measurement, we built an additional connection and a portable dry air supply box system for  
75 easy field measurement. We tested the prepared bags in several experiments in the laboratory  
76 using defined standards and, in the field, using comparison to in-situ measurements with a  
77 CRDS. These results allowed us to find a simple approach to using septum-based gas bags for  
78 field measurements of water stable isotopes, which was then tested over a full growing season.  
79 The focus was to investigate storage capability as well as possible isotopic fractionation effects  
80 due to exchange with the inner surface of the bags. Specific objectives included: 1) determining  
81 the maximum storage time of water vapor for accurate measurement of water stable isotopes,  
82 2) testing the reusability of the prepared bags, and 3) confirming these results in a field  
83 experiment. Four different experiments were performed: 1) a storage experiment up to 7 days,  
84 2) a memory experiment with two different standards, 3) a combined storage and memory  
85 experiment, and 4) a field experiment to compare the bag measurements with in-situ CRDS  
86 measurements followed by gas bag measurements over a full cultivation period.  
87



## 88 **2. Material and methods**

### 89 **2.1 Study area and basics of stable water isotope measurements**

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

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

100

$$101 \quad \delta = \left( \frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1 \right) \times 1000 \quad \text{Eq. 1}$$

102 The in-situ method used is based on the measurement of water vapor in isotopic equilibrium  
103 with the liquid water surrounding the sample probe. To achieve equilibrium between the  
104 sampled water vapor and the liquid water, it is imperative to maintain a sufficiently low air flow  
105 rate. The flow rate depends on the sample probe length, since the carrier gas needs to be  
106 saturated with the sample water. Finally, the isotopic signature between the two phases can then  
107 be calculated as a function of the temperature (T) at the phase transition using equations based  
108 on Majoube (1961).

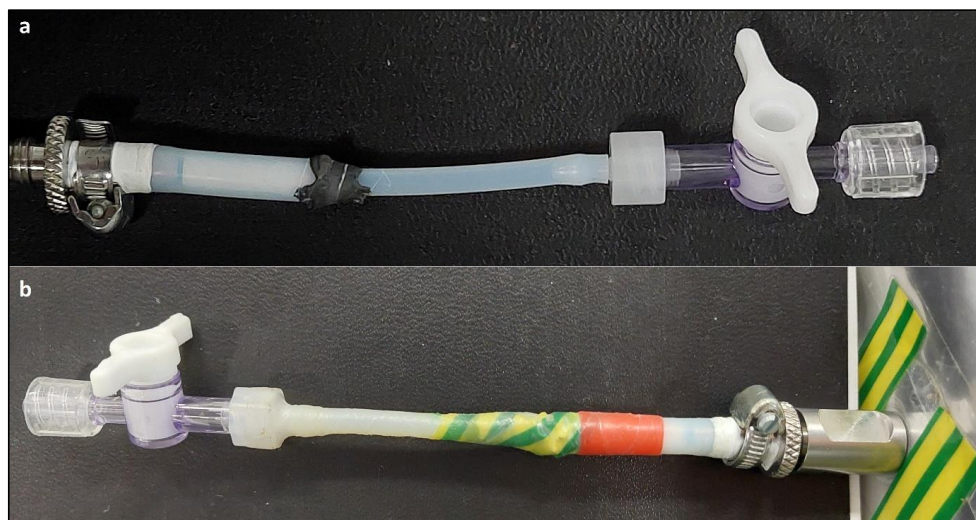
109

### 110 **2.2 Storage and sampling design**

111 The sampling and measurement concept is designed as simply as possible. The storage system  
112 is based on multi-layer foil gas sample bags (see table S1 for details) with a membrane-based  
113 valve (Multi-Layer Foil Bags, Sense Trading B.V., Netherlands) and an additional self-  
114 constructed connector with a valve. The bags have a Water Vapor Transmission Rate (WVTR)  
115 of 0.09 g m<sup>-2</sup> d<sup>-1</sup> (Jiménez-Rodríguez et al., 2019). The connection (Fig. 1) consists of two  
116 short PTFE tubes (PTFE-tubing (natural), Wolf-Technik eK, Germany) and an additional luer-  
117 lock stopcock (1-way Masterflex™ Stopcocks with Luer Connection, Avantor, USA). A hose  
118 clamp (TORRO SGL 5mm, NORMA Group Holding GmbH, Germany) is used to directly  
119 connect a ¼-inch tube to the valve and the other 4 mm tube is glued into the ¼ inch tube using  
120 2-component-adhesive (DP8005, 3M Deutschland GmbH, Germany). To protect the adhesive



121 and ensure proper sealing, electrical isolation tape is wrapped around the splice. Then, a luer-  
122 lock connection (LF-1.5NK-QC, GMPTEC GmbH, Germany) is used to connect the luer-lock  
123 stopcock. The additional connection is necessary to reliably connect the storage system to the  
124 specific experimental setup and to increase reusability.



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

126 During all experiments, water stable isotope signatures ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in ‰) were measured  
127 with the method of Rothfuss et al. (2013), using gas permeable membranes (GPM, Accurel GP  
128 V8/2HF, 3M, Germany; 0.155 cm wall thickness, 0.55 cm i.d., 0.86 cm o.d.). The method has  
129 already been used several times such as in Kübert et al. (2020) or Kühnhammer et al. (2022).  
130 In the laboratory experiments, we attached the GPM to the cap of a 100 ml glass bottle with  
131 two stainless steel fittings (CUA-2, Hy-Lok D Vertriebs GmbH, Germany) to directly measure  
132 standard water vapor and to fill the bags. A gas cylinder was used to induce dry gas at a low  
133 flow rate of 50 - 80 ml per minute. Due to the low flow rate, the water vapor passing through  
134 the GPM reaches an isotopic thermodynamic equilibrium. This means that it has an isotopic  
135 signature that depends on that of the liquid water and the surrounding temperature (Majoube,  
136 1971; Horita and Wesolowski, 1994).

137 For the 1) direct standard measurements, the sample thus generated is passed directly to the  
138 laser spectrometer to determine its isotopic signature. Since the laser spectrometer only has a  
139 flow rate of approx. 35 to 40 ml per minute, an open outlet was added to ensure a constant flow  
140 and to avoid pressure differences. In addition, the outgoing flow was also measured  
141 continuously, thus ensuring that no ambient air could flow back. A 5-minute average was taken  
142 at the end of a minimum 10-minute measurement for direct standard measurements.



143 For the 2) field measurements, the GPMs were installed at four different depths (5 cm, 15 cm,  
144 45 cm and 150 cm) and water vapor was transported out of the ground using 4 mm PTFE tubing.  
145 The open ends were fitted with Luer connectors for later connection of gas sample bags and the  
146 dry air supply. To protect these open ends from environmental influences, waterproof outdoor  
147 boxes (outdoor.case type 500, B&W International GmbH, Germany) were installed 20 to 30  
148 cm above the ground. Holes were drilled in the boxes to keep the tubes with cable glands (PG  
149 screw set, reichelt elektronik GmbH, Germany) watertight in the boxes.

150 A separate box was built to  
151 supply dry air to the  
152 measuring system during  
153 the field experiments (Fig.  
154 2). This contains a pump  
155 (NMP850KPDC-B, KNF  
156 DAC GmbH, Germany)  
157 including a power supply  
158 (DPP50-24, TDK-Lambda  
159 Germany, Germany),  
160 which can transport the dry  
161 air in 3 tubes

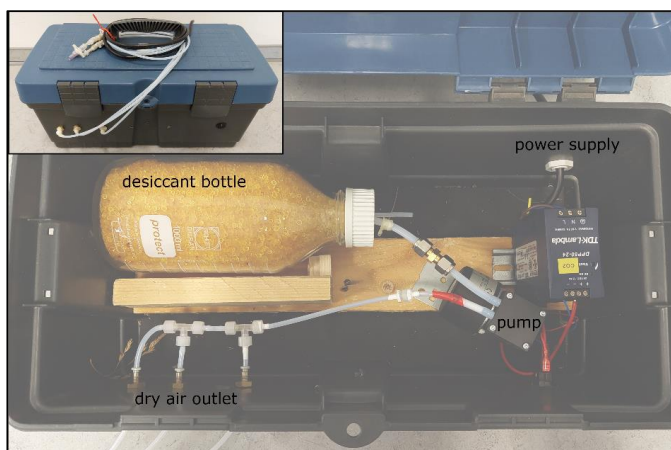


Figure 2: Self-constructed box for field dry air supply (top left) including a bottle with desiccant, power supply and a pump for up to three dry air outlet lines.

162 simultaneously through the sample tubes (i.e. can fill three gas bags at the same time). The air  
163 is ambient air which is dried by a desiccant (Silica Gel Orange, Carl Roth GmbH + Co. KG,  
164 Germany) contained in a 1-liter bottle (Screw top bottle DURAN®, DWK Life Science, USA).  
165 To regulate the flow of individual sample lines, fixed valves were used (AS1002F-04, SMC  
166 Deutschland GmbH, Germany). As recommended by the manufacturer, care was taken when  
167 filling the bags to ensure that the maximum volume did not exceed 90% of capacity.

168

### 169 2.3 Laboratory standards

170 The water stable isotope measurements were  
171 calibrated against six water vapor standards (see  
172 Table 1) that were manually measured during  
173 the experiments. The standards were each  
174 measured for at least 10 minutes, and a 5-minute  
175 average was documented. Temperature (T) was  
176 recorded continuously every 30 seconds with a thermometer (EBI 20-TH1, Xylem Analytics

Table 1: Standards used during the experiments.

Standard	$\delta^{18}\text{O}_{\text{liquid}} [\text{‰}]$	$\delta^2\text{H}_{\text{liquid}} [\text{‰}]$
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





177 Germany Sales GmbH & Co. KG, Germany) placed directly next to the standard container.  
178 This allowed us to measure the standards in the vapor phase during the laboratory experiments  
179 as well as the later soil samples during the field measurements. Of the six standards with  
180 different  $\delta$  values, approximately 60 ml were filled into the prepared 100 ml standard bottles as  
181 described in 2.2 (storage and sampling design) and measured directly on the CRDS.

182

#### 183 **2.4 Experimental design: storage test**

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

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

198

#### 199 **2.5 Experimental design: memory test**

200 Within our memory experiment, we conducted two distinct sample tests, maintaining a  
201 consistent methodology similar to that employed during the storage experiment, utilizing newly  
202 prepared bags.

203 In the first test, we followed a structured sequence: starting with a direct standard measurement  
204 of the initial standard to ensure carrier gas equilibrium, then filling gas bags with this standard  
205 for subsequent measurements. After emptying the bags, we performed another direct standard  
206 measurement of the initial standard and proceeded to measure the opposite standard. We



207 repeated the process (fill, measure, empty) with the opposite standard until our measurements  
208 aligned within the required accurate range (defined in 2.8). In the first experiment, L23 was  
209 used as the initial standard and H23 as the opposite standard, in the second experiment, the  
210 standards were used in reverse order. We used five gas bags per standard during the experiments  
211 and the temperature was continuously monitored and documented throughout the filling  
212 process.

213

## 214 **2.6 Experimental design: combined storage and memory experiment**

215 In the combined storage and memory experiment, we followed a similar procedure to the  
216 memory experiments with one notable difference: after filling the gas bags with the first  
217 standard (L22:  $-19.9\text{‰}$   $\delta^{18}\text{O}$  and  $-148.1\text{‰}$   $\delta^2\text{H}$ ) and conducting measurements, we allowed  
218 the standard to remain in the bags for a one-day storage period and refilled the bags again on  
219 the second day. We then proceeded with the second standard (H22:  $2\text{‰}$   $\delta^{18}\text{O}$  and  $12.9\text{‰}$   $\delta^2\text{H}$ )  
220 following the usual steps until our measurements aligned within the accurate range again.  
221 Between the second and third measurement cycle, the experiment was interrupted due to the  
222 long duration (1h) of each measurement cycle and continued the next day. The bags were  
223 emptied during this second night to avoid any effects. Due to the length of each measurement  
224 cycle, we used 3 repetitions during the experiment and the temperature was consistently  
225 monitored and documented throughout the filling process.

226

## 227 **2.7 Experimental design: field test**

228 To validate results gained during the laboratory experiments under field conditions, thus testing  
229 the applicability of our proposed system, we compared measurements using the gas bags and  
230 subsequent laboratory analyses with direct in-situ CRDS measurements. The experiment took  
231 place at the area of the AgroFlux sensor platform. We measured once a month during the winter  
232 and once a week starting in the spring resulting in 18 measurement campaigns. During two  
233 measurement campaigns, a total of 50 samples were collected at four different depths: 5cm ( $n$   
234 = 14), 15cm ( $n$  = 14), 45cm ( $n$  = 7), and 150cm ( $n$  = 15). Due to permeability issues, for the  
235 depth of 45cm could only be taken during one measurement campaign, resulting in only 7  
236 samples. For direct CRDS measurements and gas bag sampling, carrier gas was passed through





237 the GPM soil probe using the described pump system at a flow rate of approximately 50 ml per  
238 minute. First, we connected the CRDS to the outlet valve to determine the time required to  
239 reach a stable value indicating equilibrium. Subsequently, a 2-minute average was recorded for  
240 comparison with the subsequent bag measurement. Second, we connected the bags and filled  
241 them for 15 minutes. The source temperature at the corresponding depth was logged using a  
242 datalogger (CR1000, Campbell Scientific Ltd., Germany) at 20-minute averages.

243 The field applicability test was followed by gas bag sampling and subsequent stable water  
244 isotope analyses for the same soil depths during a full winter wheat (variety: "Ponticus";  
245 sowing: September 26, 2022; harvest: July 18, 2023) cropping period. We measured once a  
246 month during the winter and once a week starting in the spring resulting in 18 additional  
247 measurement campaigns using only our gas bags. Precipitation was collected within lysimeters  
248 as two-week bulk samples.

249

## 250 **2.8 Calculation of isotope ratios, evaluation of uncertainty and data correction**

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

256

$$257 \quad \delta_{liquid} = (\delta_{vapor} + 1) \times \alpha^+ - 1 \quad \text{Eq. 2}$$

258

$$259 \quad \ln \alpha^+ = a \frac{10^6}{T^2} + b \frac{10^3}{T} + c \quad \text{Eq. 3}$$

260

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

264 To assess the accuracy of our measurements, we calculated z-scores for each sample and water  
265 stable isotope ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ). Z-scores indicate the normalized deviation of the extracted water  
266 isotopic ratios from the benchmark isotopic signature of the referenced standard water, and can  
267 be calculated following the method (Eq. 4) described by Wassenaar et al. (2012):



268

269 
$$z - score = \frac{S - B}{\mu} \quad \text{Eq. 4}$$

270

271 Where  $S$  is the isotope signature ( $\delta^2\text{H}$  or  $\delta^{18}\text{O}$ ) measured with our gas bag,  $B$  is the benchmark  
272 isotope signature and  $\mu$  is the target standard deviation. To assess the performance of each  
273 extraction method, we set a target standard deviation (SD) of 2‰ for  $\delta^2\text{H}$  and 0.4‰ for  $\delta^{18}\text{O}$   
274 for measuring water vapor samples. The target SD was selected based on CRDS measurements  
275 using the bag method and considering standard deviations from previous studies, such as those  
276 by Wassenaar et al. (2012), Orłowski et al. (2016a), and Jiménez-Rodríguez et al. (2019). A  $z$ -  
277 score  $< 2$  represents an accurate sample range, a  $z$ -score between 2 and 5 describes the  
278 questionable range, and a  $z$ -score  $> 5$  representing an unacceptable range (Wassenaar et al.,  
279 2012, Orłowski et al., 2016a, and Jiménez-Rodríguez et al., 2019).



## 280 3. Results and discussion

### 281 3.1 Storage experiment

282 Used laboratory standards, "L22" and "M22", span an isotopic gradient of  $-9.0$  to  $-19.9$  ‰ in  
283  $\delta^{18}\text{O}$  and  $-63.3$  to  $-148.1$  ‰ in  $\delta^2\text{H}$  (Fig. 3a; filled symbols: "M22", empty symbols: "L22").  
284 In average, a difference of  $-0.7 \pm 0.6$  ‰  $\delta^{18}\text{O}$  and  $-0.1 \pm 2$  ‰  $\delta^2\text{H}$  after 1 day,  $-0.3 \pm 0.6$  ‰  $\delta^{18}\text{O}$   
285 and  $4.3 \pm 5.2$  ‰  $\delta^2\text{H}$  after 3 days and,  $0.4 \pm 1$  ‰  $\delta^{18}\text{O}$  and  $0.1 \pm 2$  ‰  $\delta^2\text{H}$  after 7 days of storage  
286 was obtained for "L22" and "M22". All samples were measured following filling of the bags  
287 on day 0 (grey). Except for one sample during the "M22" experiment, deviations from the true  
288 standard values in these measurements were all in the range of  $\pm 0.4$  for  $\delta^{18}\text{O}$  and  $2$  ‰ for  $\delta^2\text{H}$   
289 and thus bias associated with filling of the bags could be excluded.

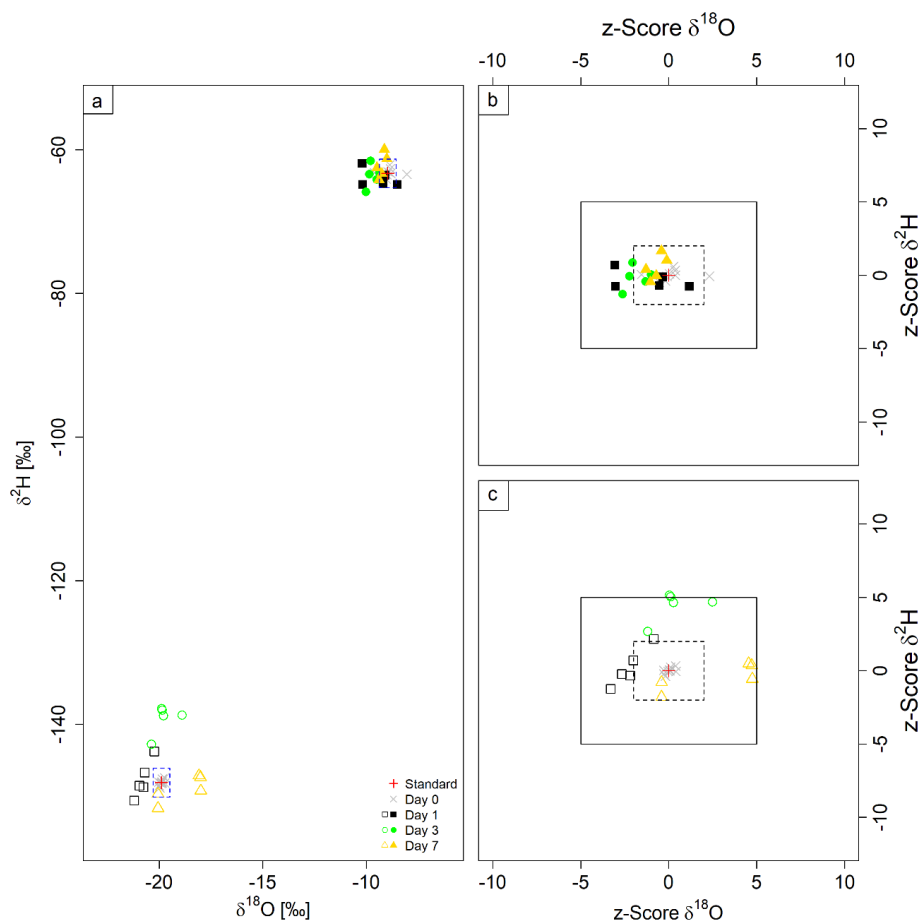


Figure 3: Dual isotope plots showing variation over several days of water-vapor storage in gas bags. The separate panels show results from both experiments (a) and z-score plots for standard "M22" (filled symbols, b) and "L22" (open symbols, c). The black box describes the questionable range while the box delineated with a dashed line describes the accurate range.



290 All samples were measured following filling of the bags on day 0 (grey). Errors associated with  
291 filling of the bags could be largely ruled out since day 0 measurements were all in the range of  
292  $\pm 0.4 \text{ ‰ } \delta^{18}\text{O}$  and  $\pm 2 \text{ ‰ } \delta^2\text{H}$  from the deviation of the true standard values. Only one sample  
293 during the “M22” experiment showed an increased deviation.

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

300 The second storage test using “L22”, showed a higher deviation from the true value (which was  
301  $-19.9 \text{ ‰ } \delta^{18}\text{O}$  and  $-148.1 \text{ ‰ } \delta^2\text{H}$ ) being  $-0.1 \pm 1.1 \text{ ‰}$  for  $\delta^{18}\text{O}$  and  $2.8 \pm 4.9 \text{ ‰}$  for  $\delta^2\text{H}$ . No  
302 trend could be observed as in the previous experiment. The increased deviation was mostly  
303 caused by the high imprecision after three days, as all gas bags showed a significant enrichment  
304 ( $8.9 \pm 2 \text{ ‰}$  on average). The higher inaccuracy after three days of storage must be due to an  
305 error during the measurement, as better measurement results were again obtained after 7 days.  
306 The z scores show the same result with accurate values for  $\delta^2\text{H}$  (except after 3 days) and a larger  
307 scatter with questionable values for  $\delta^{18}\text{O}$ . The average z-score was  $0.3 \pm 2.7$  for  $\delta^{18}\text{O}$  and  $1.4$   
308  $\pm 2.5$  for  $\delta^2\text{H}$  (see Table 3 for detailed values).

309 In comparison to prior studies, testing storage of water vapor samples, our results are generally  
310 of slightly higher accuracy for  $\delta^2\text{H}$  and comparable for  $\delta^{18}\text{O}$ . The Soil Water Isotope Storage  
311 System (SWISS) introduced by Havranek et al. (2020) showed a high accuracy within the  
312 overall system uncertainty ( $\pm 0.5 \text{ ‰ } \delta^{18}\text{O}$  and  $\pm 2.4 \text{ ‰ } \delta^2\text{H}$ ) during a 30-day storage period in  
313 a laboratory experiment. This accuracy is not directly transferable to field experiments, and  
314 several follow up experiments revealed a actual precision of  $0.9 \text{ ‰}$  and  $3.7 \text{ ‰}$  for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$   
315 (Havranek et al., 2023). Their system is based on 750 ml glass vials, which are more expensive  
316 and require an offset correction. Magh et al., 2022 developed the VSVS system, which is based  
317 on crimp neck vials in combination with a PTFE/butyl membrane and has a similar accuracy  
318 compared to our results after one day of storage but requires a linear correction for longer  
319 measurement periods. Moreover, although the mean isotopic composition remained the same  
320 throughout the measurement, it increasingly led to very high scatter of the measured isotopic  
321 signatures. Both systems are more difficult to handle compared to inflatable bags as they must



322 be filled with the same amount of dry gas mixture during the measurement due to the static  
323 properties of the glass vials and the glass vials might also be prone to break during field work.

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

343



### 344 3.2 Memory experiment

345 In the first part of the memory experiment (Fig. 4a and b), the initial standard filled into the  
346 bags was L23 (-16 ‰  $\delta^{18}\text{O}$  and -108.2 ‰  $\delta^2\text{H}$ ), followed by cycles of filling and emptying with  
347 standard H23 (-1.3 ‰  $\delta^{18}\text{O}$  and -32 ‰  $\delta^2\text{H}$ ). This standard sequence was reversed in the second  
348 part of the experiment (initially H23, then cycles of L23). No clear memory effect was found  
349 in the first part of the experiment, whereas a clear memory effect was observed in the first  
350 repetition (L1) of the second part of the experiment (Fig. 4c), which, however, almost  
351 disappeared again in the next repetition (L2). There was an interruption (approx. 45 minutes)  
352 between the three measurements with a clear memory effect and the two measurements without  
353 a memory effect, so we suspect a connection between storage time and memory effect. The

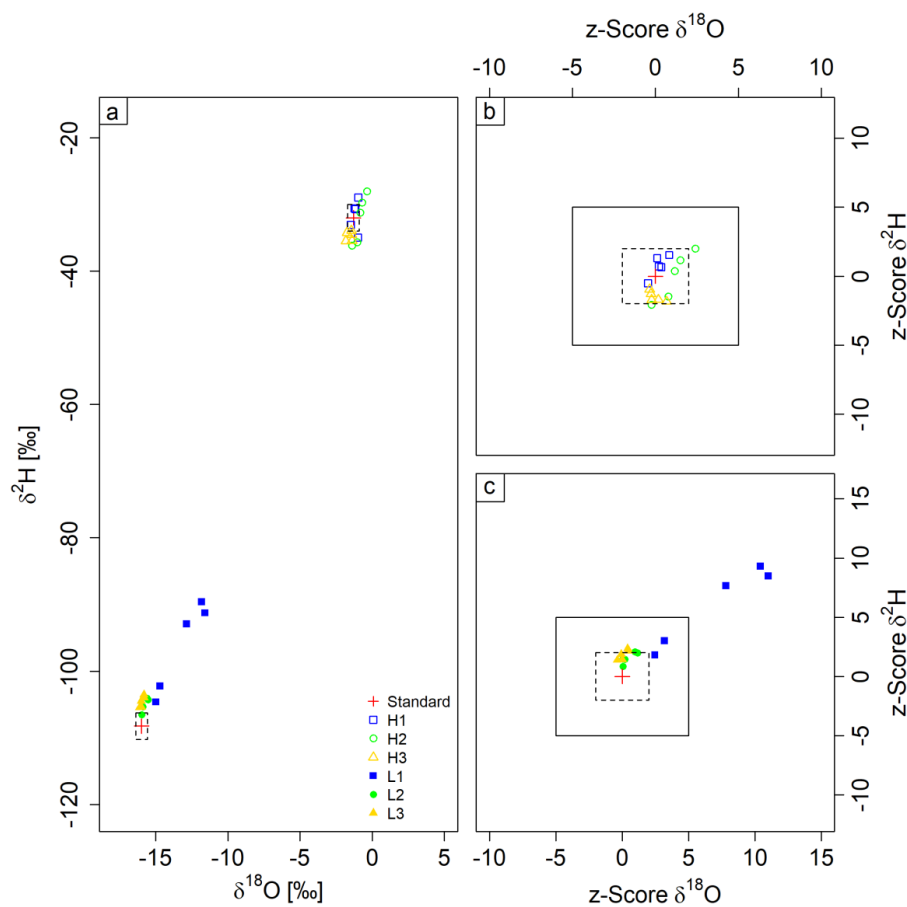


Figure 4: Memory experiment results with dual isotope plot for both experiments (a) and z-score plots for L23 to H23 (b) and H23 to L23 (c). The bags were filled first with standard H, then repeatedly (1-3) with standard L. The memory effect is evident only for measurement L1, the first to follow the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



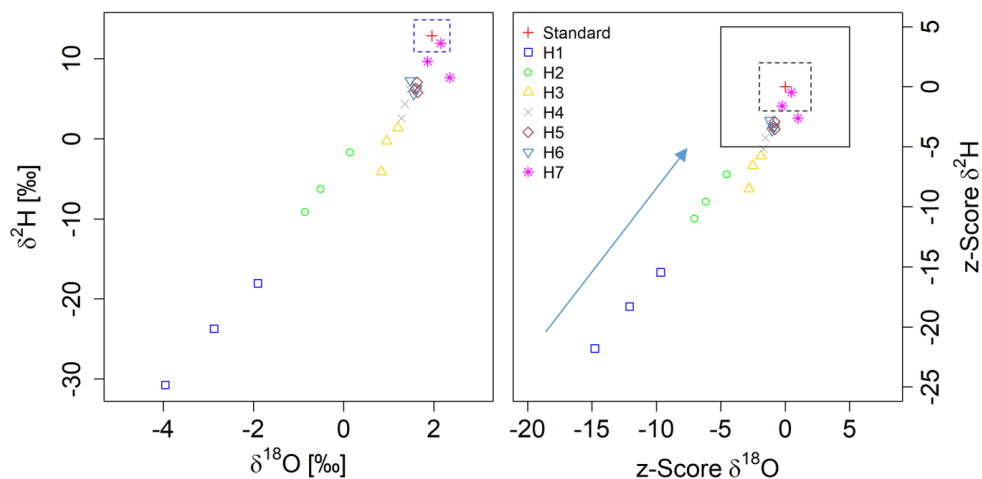


354 results therefore show that a memory effect caused by the sample previously contained in the  
355 gas bag is possible.

356 As depicted in Fig. 4 (a and c), except for L1, almost all measurements fall within the standard  
357 deviation for  $\delta^{18}\text{O}$ , while  $\delta^2\text{H}$  values are more scattered around the standard deviation (see table  
358 2). The same pattern can be seen for the z-scores (Fig. 4 b and d). While almost all the z-scores  
359 are in the accurate range or in the questionable range at the threshold of the accurate range, the  
360 values of L1 are clearly outside with values in the unacceptable range. These high z-scores for  
361 L1 are an indication of the memory effect with this first fill. This type of memory effect in the  
362 direction of the last sample contained agrees with the results of Herbstritt et al. (2023). In their  
363 study, the bags were additionally pre-flushed with saturated air of a known isotopic signature.  
364 Some influence in the direction of the water vapor used for rinsing was observed. However,  
365 since we could not detect this effect to a high degree with a traceable direction for a short storage  
366 time in the bag, we performed a combined storage and memory experiment.

367

### 368 3.3 Combined storage and memory experiment



369

Figure 5: Combined storage and memory effect test 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 black box describes the accurate range. The arrow indicates the direction from strong to weak memory effect.

370 The final laboratory experiment was conducted as a combined storage and memory effect test.  
371 The bags were stored for 1 day using the initial standard L22 ( $-19.9\text{‰ } \delta^{18}\text{O}$ ;  $-148.1\text{‰ } \delta^2\text{H}$ ).  
372 On the second day, the bags were first measured and cycled again with L22 and then with the  
373 opposite standard H22 ( $2\text{‰ } \delta^{18}\text{O}$ ;  $-12.9\text{‰ } \delta^2\text{H}$ ). No significant storage effect was observed



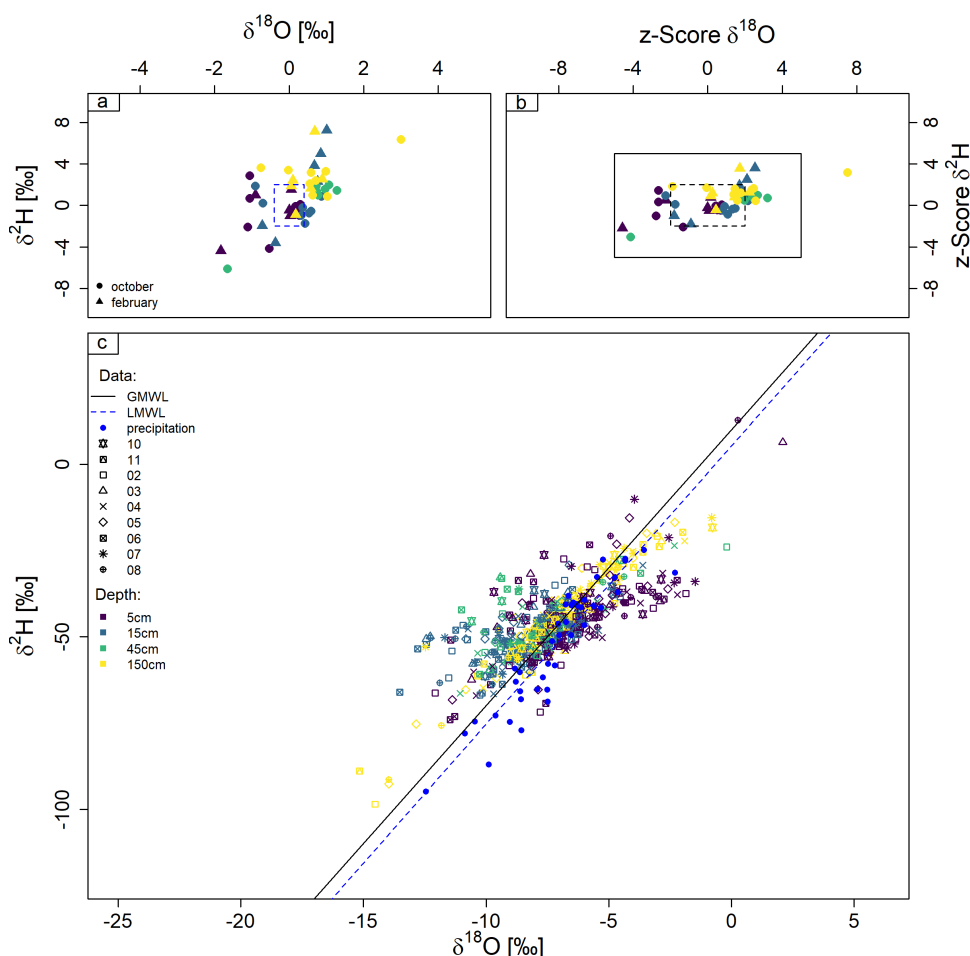
374 during this one-day storage period, and there was no noticeable difference between the two  
375 repetitions (mean difference between days:  $0.4 \pm 0.4$  ‰  $\delta^{18}\text{O}$  and  $0.1 \pm 1.9$  ‰  $\delta^2\text{H}$ ). However,  
376 when the water source was changed to H, there was a clear memory effect of a magnitude that  
377 has not been described in the literature before (Fig. 5). Measurements H1 to H6 are notably  
378 influenced by the initial standard (table 3). After filling with the opposing standard, H22 (2 ‰  
379  $\delta^{18}\text{O}$ ; 12.9 ‰  $\delta^2\text{H}$ ), the first measurements (H1) revealed a high deviation from the true standard  
380 isotopic value. This high deviation was reduced by around 50% with each repetition until the  
381 average result of H7 is close to the target standard value. The z-scores follow a similar trend  
382 from H1 to H5, gradually decreasing. Although H1 and H2 showed unacceptable z-scores for  
383  $\delta^{18}\text{O}$ , and H3 fell within the questionable range, all subsequent measurements have z-scores  
384 within the accurate range. The  $\delta^2\text{H}$  z-scores follow a similar trend to the z-scores for  $\delta^{18}\text{O}$ ,  
385 indicating a clear memory effect. However, this effect persisted for a longer duration, requiring  
386 more cycles in the case of  $\delta^2\text{H}$ . The measurements H1 to H3 are in the unacceptable range,  
387 while the results for H4 to H6 are questionable. Accurate values are only observed at H7. On  
388 average, H7 showcase highly accurate results with one measurement at H7 has a z-score within  
389 the questionable range. The transition between the two measurement days, between H2 and H3,  
390 is notably evident in the shift in  $\delta^{18}\text{O}$  z-scores. The difference of  $\delta^2\text{H}$  is smaller, but this cannot  
391 be attributed to the overnight break of the measurement, as there is also hardly any difference  
392 between the measurements H4 and H6, which were measured directly one after the other.  
393 However, it is clearly visible that a memory effect is significantly increased by the previous  
394 sample during a longer storage period and remains visible over significantly more fillings.  
395 These results are highly relevant for potential usage of storage bags in especially labelling  
396 experiments. Based on our results, we advise only use the presented method and used bags for  
397 measurements of the natural abundance or samples within the isotopic range of our experiments  
398 or performing additional experiments on labeled water vapor samples. If reused, gas bags  
399 should be repeatedly filled and emptied at least seven times ( $n \geq 7$ ) prior to actual sampling.

Table 2: Mean isotopic signature and z-scores of the different repetitions of the combined storage and memory experiment.

Repetition	Diff. $\delta^{18}\text{O}$ [‰]	Diff. $\delta^2\text{H}$ [‰]	Z-score $\delta^{18}\text{O}$	Z-score $\delta^2\text{H}$
H1	$-4.9 \pm 1$	$-37 \pm 6.4$	$-12.2 \pm 2.6$	$-18.5 \pm 3.2$
H2	$-2.4 \pm 0.5$	$-18.6 \pm 3.7$	$-5.9 \pm 1.3$	$-9.3 \pm 1.9$
H3	$-1 \pm 0.2$	$-13.9 \pm 2.8$	$-2.4 \pm 0.5$	$-6.9 \pm 1.4$
H4	$-0.6 \pm 0.1$	$-8.5 \pm 1.8$	$-1.5 \pm 0.2$	$-4.3 \pm 0.9$
H5	$-0.3 \pm 0$	$-6.5 \pm 0.7$	$-0.8 \pm 0.1$	$-3.2 \pm 0.3$
H6	$-0.4 \pm 0.1$	$-6.5 \pm 0.9$	$-1 \pm 0.2$	$-3.2 \pm 0.4$
H7	$0.2 \pm 0.3$	$-3.1 \pm 2.2$	$0.4 \pm 0.6$	$-1.6 \pm 1.1$



### 400 3.4 Field test - Comparison between gas bag sampling and direct measurements



401 Figure 6: Comparison between in-situ and bag measurements (a) and related z-scores (b). The dual isotope plot  
402 (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.

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



409 The average difference between direct measurement and bag measurement was  $0.2 \pm 0.9$  ‰ for  
 410  $\delta^{18}\text{O}$  and  $0.7 \pm 2.3$  ‰ for  $\delta^2\text{H}$  during the first sampling campaign in October, 2022 and  $0.1 \pm$   
 411  $0.8$  ‰ for  $\delta^{18}\text{O}$  and  $1.4 \pm 3.3$  ‰ for  $\delta^2\text{H}$  for the second sampling campaign in February, 2023  
 412 (Fig. 6a). The deviation of the bag method from direct in-situ measurements was thus mostly  
 413 within the uncertainty range of the in-situ method and yielded in highly accurate z-scores (Fig.  
 414 6b). However, the  $\delta^{18}\text{O}$  z-scores exhibit a larger scatter compared to  $\delta^2\text{H}$ , consistent with the  
 415 results of the laboratory storage experiment. In comparison to other methods determining the  
 416 isotopic signature of soil water, the tested gas bag method competed well. In the past,  
 417 destructive

418 measurements of soil  
 419 water have relied  
 420 predominantly on  
 421 cryogenic vacuum  
 422 extraction (CVE). The  
 423 accuracy of CVE can  
 424 vary greatly for soil  
 425 samples, as shown by a  
 426 comparative study by  
 427 Orłowski et al. (2018), in

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

Depth [cm]	Diff. $\delta^{18}\text{O}$ [‰]	Diff. $\delta^2\text{H}$ [‰]	Z-score $\delta^{18}\text{O}$	Z-score $\delta^2\text{H}$
<b>25.10.2022</b>				
5	$-0.3 \pm 0.6$	$-0.6 \pm 1.9$	$-0.7 \pm 1.6$	$-0.3 \pm 1$
15	$0.2 \pm 0.6$	$-0.2 \pm 1.1$	$0.5 \pm 1.6$	$-0.1 \pm 0.6$
45	$0.6 \pm 1$	$0.4 \pm 2.9$	$1.4 \pm 2.5$	$0.2 \pm 1.5$
150	$0.8 \pm 1$	$2.9 \pm 1.6$	$1.9 \pm 2.5$	$1.5 \pm 0.8$
<b>21.02.2023</b>				
5	$-0.5 \pm 0.8$	$-0.6 \pm 2.3$	$-1.3 \pm 2.1$	$-0.3 \pm 1.2$
15	$0.4 \pm 0.7$	$2.13 \pm 4.2$	$0.9 \pm 1.8$	$1.1 \pm 2.1$
150	$0.4 \pm 0.4$	$2.5 \pm 2.6$	$1 \pm 0.9$	$1.2 \pm 1.3$

428 which the results of 16 laboratories showed a mean difference compared to the reference water  
 429 ranging from  $+18.1$  to  $-108.4$ ‰ for  $\delta^2\text{H}$  and  $+11.8$  to  $-14.9$ ‰ for  $\delta^{18}\text{O}$  across all laboratories.  
 430 In addition, CVE is associated with co-extraction of organic compounds, significantly  
 431 interfering with the isotopic quantification (Orłowski et al., 2018). In comparison, methods  
 432 using in-situ soil or xylem probes based on semi permeable tubing have reported high accuracy  
 433 (Volkman and Weiler, 2014; Volkman et al., 2016; Rothfuss et al., 2013; Kübert et al., 2020).

434 Among the few previous experiments that tested water vapor storage of soil or plant water in  
 435 controlled or field conditions, Herbstritt et al. (2023) sampled prepared sandboxes and achieved  
 436 an accuracy of  $0.2 \pm 0.8$  ‰  $\delta^{18}\text{O}$  and  $0.8 \pm 2.9$  ‰  $\delta^2\text{H}$  after calibration, while Havranek et al.  
 437 (2023) achieved an accuracy of  $\pm 0.9$  ‰ in  $\delta^{18}\text{O}$  and  $\pm 3.7$  ‰ in  $\delta^2\text{H}$  during several experiments,  
 438 comparable to our findings ( $0.2 \pm 0.9$  ‰ for  $\delta^{18}\text{O}$  and  $0.7 \pm 2.3$  ‰ for  $\delta^2\text{H}$  in the first sampling  
 439 campaign and  $0.1 \pm 0.8$  ‰ for  $\delta^{18}\text{O}$  and  $1.4 \pm 3.3$  ‰ for  $\delta^2\text{H}$  in the second sampling campaign).  
 440 In the field experiment of Magh et al. (2022), xylem water samples were taken using the  
 441 borehole equilibration method (Marshall et al. 2020). In general, the VSVS system did not differ



442 significantly from the in-situ measured data but resulted in a higher uncertainty with 0.6 ‰ to  
443 0.8 ‰ for  $\delta^{18}\text{O}$  and 0.6 ‰ to 4.4 ‰ for  $\delta^2\text{H}$  after.

444 Measurements of soil water isotope profiles over the full season field experiment (Fig. 6c)  
445 revealed a wide range of isotopic signatures. The isotopic signature of precipitation is  
446 represented by the local meteoric water line (LMWL) shown here for the period of ... to ....  
447 The LMWL reveals a slightly different offset but equal increase between  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$   
448 compared to the Global Meteoric Water Line (GMWL). The isotopic signature of soil water  
449 can vary strongly from precipitation, as it is a mixture of different precipitation events  
450 containing different isotopic signatures and magnitude. Furthermore, its isotopic signature can  
451 change significantly as evaporated soil vapor is depleted in heavy isotopes, leaving the  
452 remaining soil water enriched in  $^{18}\text{O}$  and  $^2\text{H}$  (Dubbert and Werner, 2018). This results in a wide  
453 range of isotopic signatures throughout the complete cultivation season, as can be seen in the  
454 wide scatter around the LMWL. In general, the measurements show isotopic signatures similar  
455 to precipitation immediately after rain events and a trend toward evaporative enrichment in  
456 during droughts. As expected, evaporative enrichment is particularly evident in the upper 5 cm  
457 depth, while there are only slight trends in evapotranspiration enrichment at lower depths (e.g.  
458 Sprenger et al., 2016). These results are consistent with the environmental conditions, as the  
459 measurements were taken during a rather wet cultivation season with only short droughts.  
460 Overall, our findings from the field trial suggest a good agreement with GPM probe and bag-  
461 based soil water isotope measurements with the LMWL and are plausible in terms of seasonal  
462 variability (e.g. compare offsets between cryogenically extracted bulk soil water isotope  
463 measurements and LMWL; e.g. Zhao and Wang, 2021). Notably, there is increased variability  
464 and higher rate of discarded samples at 45 cm depth. This coincides with the placement of the  
465 GPM probes just below the lower boundary of the plow layer. This typically leads to a layer of  
466 increased soil compaction underneath, which we suspect had deteriorating consequences for  
467 the functionality of the GPM probes that should be considered in future experiments in  
468 agricultural settings.

#### 469 **4. Conclusion**

470 Our laboratory and field experiments have confirmed that GPM combined with gas bags for in-  
471 situ soil water vapor sampling and subsequent stable water isotope analyses is a reliable, cost-  
472 effective, and easy to handle method allowing for many future applications. We were able to  
473 demonstrate that both 1) storage is possible and 2) memory effects caused by previous samples  
474 can be prevented by appropriate preconditioning, allowing the gas bags to be reused. When



475 reusing the bags, it was important that 1) the bags were rinsed ten times with dry air, 2) the  
476 additional connection including valve was built and 3) the bags and their valves (especially the  
477 seals) were regularly checked for damage. In addition, great care must be taken to open the bag  
478 valves only minimally for filling and not to fill the bags more than 90% (as specified by the  
479 manufacturer). Regarding the isotopic signature during the experiment, reuse is easier to carry  
480 out with smaller differences between the consecutive samples in the bags, e.g. in the natural  
481 abundance range. However, if a strong labeling experiment is performed, the bags may need to  
482 be handled differently (e.g. better flushing between samples or no reuse). Through the  
483 conducted field experiment, we were able to show that the bags could be used in our case with  
484 an accuracy of  $0.23 \pm 0.84 \delta^{18}\text{O} [\text{‰}]$  and  $0.94 \pm 2.69 \delta^2\text{H} [\text{‰}]$ , which allows a wide  
485 applicability. The possibility to take and store samples easily and without permanent power  
486 supply extends the usability of stable water isotope measurements in the field. Finally, the bags  
487 should not be measured at a temperature that is lower than the temperature measured at the  
488 GPM (source temperature) during the measurement. If the gas bags are measured below the  
489 source temperature, condensation will occur in the bag, which can greatly distort the  
490 measurement result.

#### 491 **5. Data availability**

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

#### 493 **6. Author contribution**

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

#### 497 **7. Competing interests**

498 The authors declare that they have no conflict of interest.

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503 **9. References**

- 504 Craig, H.: Standard for Reporting Concentrations of Deuterium and Oxygen-18 in Natural  
505 Waters, *Science*, 133, 1833–1834, <https://doi.org/10.1126/science.133.3467.1833>, 1961.
- 506 Dubbert, M., and Werner, C.: Water fluxes mediated by vegetation: emerging isotopic insights  
507 at the soil and atmosphere interfaces. *New Phytol*, 221(4), 1754–1763,  
508 <https://doi.org/10.1111/nph.15547>, 2019.
- 509 Gat, J. R.: Oxygen and hydrogen isotopes in the hydrologic cycle. *Ann Rev Earth Pl Sc*, 24(1),  
510 225–262, <https://doi.org/10.1146/annurev.earth.24.1.225>, 1996.
- 511 Havranek, R. E., Snell, K. E., Davidheiser-Kroll, B., Bowen, G. J., and Vaughn, B.: The Soil  
512 Water Isotope Storage System (SWISS): An integrated soil water vapor sampling and  
513 multiport storage system for stable isotope geochemistry. *Rapid Commun Mass Sp*, 34(12),  
514 e8783, <https://doi.org/10.1002/rcm.878>, 2020.
- 515 Havranek, R. E., Snell, K., Kopf, S., Davidheiser-Kroll, B., Morris, V., and Vaughn, B.:  
516 Lessons from and best practices for the deployment of the Soil Water Isotope Storage  
517 System. *Hydrol Earth Syst Sc*, 27(15), 2951–2971, [https://doi.org/10.5194/hess-27-2951-](https://doi.org/10.5194/hess-27-2951-2023)  
518 [2023](https://doi.org/10.5194/hess-27-2951-2023), 2023.
- 519 Herbstritt, B., Gralher, B., Seeger, S., Rinderer, M., and Weiler, M.: Discrete in situ vapor  
520 sampling for subsequent lab-based water stable isotope analysis. *Hydrol Earth Syst Sc*,  
521 27(20), 3701–3718, <https://doi.org/10.5194/hess-27-3701-2023>, 2023.
- 522 Horita, J., and Wesolowski, D. J.: Liquid-vapor fractionation of oxygen and hydrogen isotopes  
523 of water from the freezing to the critical temperature. *Geochim Cosmochim Ac*, 58(16),  
524 3425–3437, [https://doi.org/10.1016/0016-7037\(94\)90096-5](https://doi.org/10.1016/0016-7037(94)90096-5), 1994.
- 525 Jiménez-Rodríguez, C. D., Coenders-Gerrits, M., Bogaard, T., Vatiéro, E., and Savenije, H.:  
526 Comparison of water vapor sampling techniques for stable isotope analysis. [preprint],  
527 *Hydrol Earth Syst Sc Discussions*, 1–15, <https://doi.org/10.5194/hess-2019-344>, 2019.
- 528 Kübert, A., Paulus, S., Dahlmann, A., Werner, C., Rothfuss, Y., Orłowski, N., and Dubbert,  
529 M.: Water stable isotopes in ecohydrological field research: comparison between in situ and  
530 destructive monitoring methods to determine soil water isotopic signatures. *Front plant sci*,  
531 11, 497124, <https://doi.org/10.3389/fpls.2020.00387>, 2020.
- 532 Kühnhammer, K., Dahlmann, A., Iraheta, A., Gerchow, M., Birkel, C., Marshall, J. D., and  
533 Beyer, M.: Continuous in situ measurements of water stable isotopes in soils, tree trunk and  
534 root xylem: Field approval. *Rapid Commun Mass Sp*, 36(5), e9232,  
535 <https://doi.org/10.1002/rcm.9232>, 2022.



- 536 Kühnhammer, K., van Haren, J., Kübert, A., Bailey, K., Dubbert, M., Hu, J., Ladd, N. S.,  
537 Meridith, L. K., Werner, C., and Beyer, M.: Deep roots mitigate drought impacts on tropical  
538 trees despite limited quantitative contribution to transpiration. *Sci Total Environ*, 893,  
539 164763, <https://doi.org/10.1016/j.scitotenv.2023.164763>, 2023.
- 540 Marshall, J.D., Cuntz, M., Beyer, M., Dubbert, M., Kuehnhammer, K.: Borehole equilibration:  
541 Testing a new method to monitor the isotopic composition of tree xylem water in situ. *Front*  
542 *Plant Sci.*, 11, 508657, <https://doi.org/10.3389/fpls.2020.00358>, 2020.
- 543 Magh, R. K., Gralher, B., Herbstritt, B., Kübert, A., Lim, H., Lundmark, T., and Marshall, J.:  
544 Conservative storage of water vapour–practical in situ sampling of stable isotopes in tree  
545 stems. *Hydrol Earth Syst Sc*, 26(13), 3573-3587, [https://doi.org/10.5194/hess-26-3573-](https://doi.org/10.5194/hess-26-3573-2022)  
546 [2022](https://doi.org/10.5194/hess-26-3573-2022), 2022.
- 547 Majoube M. Fractionnement en oxygene 18 et en deuterium entre l'eau et sa vapeur. *J Chim*  
548 *Phys*, 68, 1423-1436, <https://doi.org/10.1051/jcp/1971681423>, 1971.
- 549 Millar, C., Pratt, D., Schneider, D. J., and McDonnell, J. J.: A comparison of extraction systems  
550 for plant water stable isotope analysis. *Rapid Commun Mass Sp*, 32(13), 1031-1044,  
551 <https://doi.org/10.1002/rcm.8136>, 2018.
- 552 Mook, W. G. (Eds.): *Environmental isotopes in the hydrological cycle: principles and*  
553 *applications*. UNESCO/IAEA, Volume 1, Centre for Isotope Research, Groningen,  
554 Netherlands, 280 pp., 2000.
- 555 Orłowski, N., Frede, H. G., Brüggemann, N., and Breuer, L.: Validation and application of a  
556 cryogenic vacuum extraction system for soil and plant water extraction for isotope analysis.  
557 *Journal of Sensors and Sensor Systems*, 2(2), 179-193, [https://doi.org/10.5194/jsss-2-179-](https://doi.org/10.5194/jsss-2-179-2013)  
558 [2013](https://doi.org/10.5194/jsss-2-179-2013), 2013.
- 559 Orłowski N., Pratt D.L., and McDonnell J.J.: Intercomparison of soil pore water extraction  
560 methods for stable isotope analysis. *Hydrol Process*, 30(19), 3434-3449,  
561 <https://doi.org/10.1002/hyp.10870>, 2016a.
- 562 Orłowski N., Breuer L., McDonnell J.J.: Critical issues with cryogenic extraction of soil water  
563 for stable isotope analysis. *Ecohydrology*, 9(1), 3-10, <https://doi.org/10.1002/eco.1722>,  
564 2016b.
- 565 Orłowski, N., Breuer, L., Angeli, N., Boeckx, P., Brumbt, C., Cook, C. S., Dubbert M.,  
566 Dyckmans J., Gallagher B., Gralher B., Herbstritt B., Hervé-Fernández P., Hissler C.,  
567 Koeniger P., Legout A., Macdonald C. J., Oyarzún C., Redelstein R., Seidler C., Siegwolf  
568 R., Stumpp C., Thomsen S., Weiler M., Werner C., and McDonnell, J. J.: Inter-laboratory



- 569 comparison of cryogenic water extraction systems for stable isotope analysis of soil water.  
570 Hydrol Earth Syst Sc, 22(7), 3619-3637, <https://doi.org/10.5194/hess-22-3619-2018>, 2018.
- 571 Rothfuss, Y., Biron, P., Braud, I., Canale, L., Durand, J. L., Gaudet, J. P., Richard P., Vauclin  
572 M., and Bariac, T.: Partitioning evapotranspiration fluxes into soil evaporation and plant  
573 transpiration using water stable isotopes under controlled conditions. Hydrol Process,  
574 24(22), 3177-3194, <https://doi.org/10.1002/hyp.7743>, 2010.
- 575 Rothfuss, Y., Vereecken, H., and Brüggemann, N.: Monitoring water stable isotopic  
576 composition in soils using gas-permeable tubing and infrared laser absorption spectroscopy.  
577 Water resour res, 49(6), 3747-3755, <https://doi.org/10.1002/wrcr.20311>, 2013.
- 578 Séraphin, P., Vallet-Coulomb, C., and Gonçalves, J.: Partitioning groundwater recharge  
579 between rainfall infiltration and irrigation return flow using stable isotopes: The Crau  
580 aquifer. J Hydrol, 542, 241-253, <https://doi.org/10.1016/j.jhydrol.2016.09.005>, 2016.
- 581 Sodemann, H. (Eds.): Tropospheric transport of water vapour: Lagrangian and Eulerian  
582 perspectives. Swiss. ETH Zurich, No. 16623, 225 pp., ISBN 978-3832513849, 2006.
- 583 Sprenger M, Herbstritt B, Weiler M. Established methods and new opportunities for pore water  
584 stable isotope analysis. Hydrol Process. 29(25), 5174-5192,  
585 <https://doi.org/10.1002/hyp.10643>, 2015.
- 586 Sprenger, M., Leistert, H., Gimbel, K., and Weiler, M.: Illuminating hydrological processes at  
587 the soil-vegetation-atmosphere interface with water stable isotopes. Rev Geophys, 54(3),  
588 674-704, <https://doi.org/10.1002/2015RG000515>, 2016.
- 589 Volkmann, T. H., and Weiler, M.: Continual in situ monitoring of pore water stable isotopes in  
590 the subsurface. Hydrol Earth Syst Sc, 18(5), 1819-1833, [https://doi.org/10.5194/hess-18-](https://doi.org/10.5194/hess-18-1819-2014)  
591 [1819-2014](https://doi.org/10.5194/hess-18-1819-2014), 2014.
- 592 Volkmann, T. H., Haberer, K., Gessler, A., and Weiler, M.: High-resolution isotope  
593 measurements resolve rapid ecohydrological dynamics at the soil-plant interface. New  
594 Phytol, 210(3), 839-849, <https://doi.org/10.1111/nph.13868>, 2016.
- 595 Wassenaar, L. I., Ahmad, M., Aggarwal, P., Van Duren, M., Pölsenstein, L., Araguas, L., and  
596 Kurttas, T.: Worldwide proficiency test for routine analysis of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in water by  
597 isotope-ratio mass spectrometry and laser absorption spectroscopy. Rapid Commun Mass  
598 Sp, 26(15), 1641-1648, <https://doi.org/10.1002/rcm.6270>, 2012.
- 599 West, A. G., Patrickson, S. J., and Ehleringer, J. R.: Water extraction times for plant and soil  
600 materials used in stable isotope analysis. Rapid Commun Mass Sp, 20(8), 1317-1321,  
601 <https://doi.org/10.1002/rcm.2456>, 2006.



602 Zhao, Y., and Wang, L.: Insights into the isotopic mismatch between bulk soil water and Salix  
603 matsudana Koidz trunk water from root water stable isotope measurements. Hydrol Earth  
604 Syst Sc, 25(7), 3975-3989, <https://doi.org/10.5194/hess-25-3975-2021>, 2021.