Simple water vapor sampling for stable isotope analysis using affordable valves and bags

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Abstract. Water stable isotopes are commonly used in hydrological and ecological research. Until now, most measurements of soil or plant water isotopes have been made by taking a sample from the field and extracting its water in the laboratory. More recently, samples have been collected with ~~semi~~gas-permeable membranes (GPM) and measured in the field. 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-to-perform measurements without the need to bring a Cavity Ring-Down Spectroscopy (CRDS) analyzer into the field. We used gas-permeable membranes ~~(GPM)~~ to extract samples of water vapor from the soil, which were then stored in multi-layer foil bags until analysis. The bags were modified with home-made connections to reduce leakage and simplify gas transfers. The bags were tested using laboratory standards to determine their maximum storage time, potential memory effects, and reusability. The storage experiment with new bags demonstrated the ability to store water vapor samples for up to ~~seven~~7 days while maintaining mostly acceptable ~~results~~trueness for δ^2H, and acceptable to questionable trueness for δ^{18}O. ~~The memory experiment showed that the influence of previous samples increased with duration of storage. 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.~~ Trueness was defined as mean difference between the measured and known water vapor placed into the bags and precision by the standard deviation of ~~repeated~~replicate measurements. The memory experiment using new bags revealed that the influence of previous samples increased with duration of storage. In both experiments, the light standards seemed to result in less accuracy. The reuse experiment confirmed that the bags can be filled repeatedly, provided they are used for similar sample lines and flushed 10 times with dry air. To demonstrate bag applicability in the field, we compared measurements of stored samples to measurements made directly in the field. Storing beyond 24 hours needs further investigation but appears promising. With new

36 gas bags up to 24 hours of storage, we found accuracy of 0.2 ± 0.9 ~~‰, respectively,~~‰ for δ^{18}O

37 and 0.7 ± 2.3 ‰ for δ^2H. When the bags were reused and stored up to 24 hours, they yielded

38 accuracy of 0.1 ± 0.8 ‰ for δ^{18}O and 1.4 ± 3.3 ‰ for δ^2H. ~~This is at least as good as published~~

39 ~~alternative methods.~~ The proposed system is simple, cost-~~effective~~efficient, and versatile for

40 both lab and field applications, however, case-specific testing is necessary given the remaining

41 uncertainties.

42

1. Introduction

44 Water stable isotope measurements are used in a variety of scientific fields, particularly in

45 hydrology, ecohydrology, and meteorology, which focus on aspects of the water cycle. The

46 primary isotopes involved are ^{18}O and ^{2}H (e.g., Gat 1996; Mook 2000), described as δ^{18}O and

47 δ^2H relative to the most abundant isotopes, ^{16}O and ^{1}H (Sodemann, 2006). They serve to

48 investigate processes such as infiltration and groundwater recharge (e.g. Séraphin et al., 2016),

49 evaporation (e.g. Rothfuss et al., 2010), or the plasticity of root water uptake under stress (e.g.

50 Kühnhammer et al., 2021; Kühnhammer et al., 2023).

51 Traditionally, the isotopic composition of soil and plant water has been measured through

52 destructive sampling of soil cores or sampled plant material, followed by water extraction e.g.

53 via cryogenic extraction (see method summary Orlowski et al., 2016a) and measured with

54 isotope ratio mass spectrometry (IRMS) analyzers (West et al., 2006; Sprenger et al., 2015).

55 The development of smaller and less expensive cavity ring-down spectroscopy (CRDS)

56 analyzers has led to an increase in potential applications, including, e.g., in situ measurements

57 using gas permeable membranes (Rothfuss et al., 2013; Volkmann and Weiler, 2014; Volkmann

58 et al., 2016; Kübert et al., 2021; ~~Marshall~~Landgraf et al~~.; 2020~~., 2022). Direct measurements

59 are a viable alternative to classic destructive techniques, especially in small plots, as among

60 other benefits (e.g. high frequency measurements) they avoid repeated destructive sampling.

61 However, direct, continuous in situ field setups are very cost-intensive ~~and~~, technically

62 challenging~~, requiring a laser spectrometer (e.g. a CRDS) and~~ and require a permanent power

63 supply in the field as well as ~~a~~ strong expertise to maintain. Moreover, direct in situ field setups

64 require full-time operation of one laser spectrometer (e.g. a CRDS) each, whereas a vapor

65 storage method could be operated with one CRDS for several field setups. To allow an

66 expansion to a wider set of potential study areas and increase the number of absolute study

67 areas maintainable, scientists are recently trying to develop new simplified sampling systems.

68 This includes capturing soil moisture as water vapor for subsequent laboratory analysis (e.g.

69 Havranek et al., 2020; Magh et al., 2022; Herbstritt et al. 2023). To do so, primarily glass bottles

70 or gas sampling bags with various fittings are used, which cost from ~1-200 euros per container.

71 The advantages of these methods include the ability to quickly measure stored samples at

72 elevated temperatures relative to the source in a temperature-stable laboratory environment. In

73 addition, multiple sample containers can be filled at once in the field, which allows for the

74 simultaneous measurement of multiple probes, and sampling can generally be performed at a

75 much faster rate. These simplified and more affordable systems could therefore increase the

76 number of studies on water stable isotopes and provide new insights in research by increasing

77 the number of possible experimental sites and samples.

78 In this study, we investigated the use of multi-foil bags with septum valves. Our investigation

79 focused on exploring the potential of these commercially available but affordable bags for a

80 wider range of applications (~ 20€ per bag plus ~ 15€ for the connection). To ensure easy and

81 reliable bag filling and measurement, we built an additional connection and a portable dry air

82 supply box system for easy field measurement. We tested the prepared bags in several

83 experiments in the laboratory using defined standards and, in the field, using comparison to in

84 situ measurements with a CRDS. These results allowed us to find a simple approach to using

85 septum-based gas bags for field measurements of water stable isotopes. The focus was to

86 investigate storage capability as well as possible isotopic fractionation effects due to exchange

87 with the inner surface of the bags. Five different experiments were performed: i) a storage

88 experiment up to 7 days, ii) a memory experiment without sample storage and two quite

89 different standards, iii) a memory experiment with one1 day of storage of the initial standard

90 followed by sample replacement exploring duration effects on memory setting and, iv) a field

91 filling and bag reuse experiment to compare the bag measurements with in situ CRDS

92 measurements. These were followed by v) a gas bag measurement sequence over a full

93 cultivation period. These results allowed us to find a simple approach to using septum-based

94 gas bags for field measurements of water stable isotopes.

2. Material and methods

2.1 Study area and basics of water stable isotope measurements

97 The laboratory experiments were carried out at the Leibniz Centre for Agricultural Landscape

98 Research (ZALF). The field experiments took place at the AgroFlux experimental platform of

99 ZALF, (see Dahlmann et al., 2023 for further details), located in the northeast of Germany, near

100 Dedelow in the Uckermark region (N 53°22′45″, E 13°47′11″; ~50-60 m a.s.l.).

101   During the experiments, the δ^2H and δ^{18}O values were recorded using a CRDS analyzer (L2130-

102   i, Picarro Inc., Santa Clara, CA, USA). The hydrogen and oxygen stable isotopes in the sampled

103   water vapor (δ^2H and δ^{18}O) are given in per mil (‰), relative to the Vienna Standard Mean

104   Ocean Water (VSMOW) using δ-notation (Eq. 1; Craig, 1961).

105   $$\delta = \left(\frac{R_{sample}}{R_{VSMOW}} - 1 \right) \times 1000 \hspace{3cm} \text{Eq. 1}$$

106   During all experiments, water stable isotope signatures (δ^2H and δ^{18}O in ‰) were measured

107   with the method of Rothfuss et al. (2013), using gas permeable membranes (GPM, Accurel GP

108   V8/2HF, 3M, Germany; 0.155 cm wall thickness, 0.55 cm i.d., 0.86 cm o.d.; e.g. as used in

109   Kübert et al., 2020 or Kühnhammer et al., 2021). In the laboratory experiments, we attached

110   two membranes to the cap of a 100 ml glass bottle with two stainless steel fittings (CUA-2, Hy-

111   Lok D Vertriebs GmbH, Germany) to directly measure standard water vapor and to fill the bags.

112   The glass bottle was filled with approx. ~~~~60 - 80 ml of standard water. The first membrane was

113   submerged in the standard water, where it bubbles the dry air through, resulting in equilibration

114   of water vapor in the headspace with the standard water. The second membrane, in the

115   headspace, collects saturated sample air and supplies it to the analyzer. Both membranes were

116   sealed with adhesive. The second membrane ($<$ 5 cm) served as a safety mechanism to prevent

117   liquid water from entering the tubing.

118   A gas cylinder was used to induce dry gas at a low flow rate of 50 - 80 ml per minute (257-

119   6409, RS Components GmbH, Germany). We ensured that the isotopic signature of the vapor

120   would be at equilibrium with liquid water at this flow rate. We tested flows from the minimum

121   required for Picarro operation (~~approximately~~approx. 35 ml/min) to 300 ml/min and found

122   ~~accurate~~consistent results up to 100 ml/min. At the lower flow rates, the water vapor passing

123   through the membrane reached isotopic thermodynamic equilibrium (Majoube, 1971; Horita

124   and Wesolowski, 1994).

125   In the field experiments, we used approx. 12 cm membranes (comparable to soil GPM in e.g.

126   Kühnhammer et al., 2021) attached to PTFE tubing to sample the four different soil depths (see

127   section 2.7). The in situ method was likewise based on the measurement of water vapor with

128   the assumption that the vapor was in isotopic equilibrium with the liquid water surrounding the

129   sample probe (Rothfuss et al., 2013). Finally, the isotopic fractionation was calculated as a

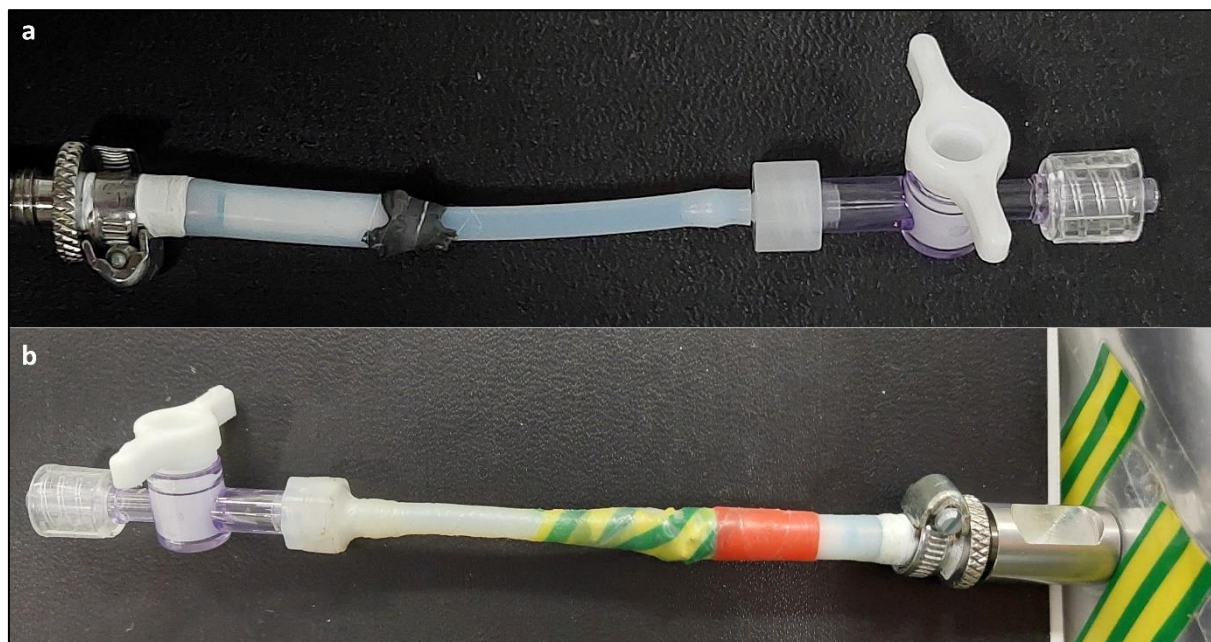
130   function of the temperature (T) at the phase transition using equations based on Majoube

131   (1971).

132 The water vapor from the standards and soil was then either transferred immediately to the
133 CRDS analyzer and measured directly or it was stored in the gas bags and measured later. In
134 laboratory experiments I, II and III, the temperatures were around 20°C during filling and
135 around 24°C during storage and bag measurement to avoid condensation. In field experiments
136 IV and V, great care was taken to measure the bags at elevated temperatures relative to the
137 source temperatures.
138 In laboratory experiments, calibration was performed by measuring the described glass bottles
139 before the start of the measurement and the used standard during and after the experiment for
140 drift correction. In field experiments, the standards covering the expected sampled isotopic
141 range were filled into bags and treated similarly to the samples. Calibration was then performed.

142

2.2 Storage and sampling design

2.2.1 Gas bag design

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 nominal 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.

2.2.2 Sampling design

For the 1) direct standard measurements, the sample ~~thus~~ generated 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 split was added to ensure a constant flow and to avoid pressure differences. ~~The~~Flow at the open split was measured continuously to ensure 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 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 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 were installed 20 to 30 cm above the ground (outdoor.case type 500, B&W International GmbH, Germany). Cable glands were used to keep the boxes watertight (PG screw set, reichelt elektronik GmbH, Germany).

A separate box was built to supply pressurized dry air to the measuring system during the field experiments (Fig. 2). This contained a pump (NMP850KPDC-B, KNF DAC GmbH, Germany) including a power supply (DPP50-24, TDK-Lambda Germany, Germany), which could transport the

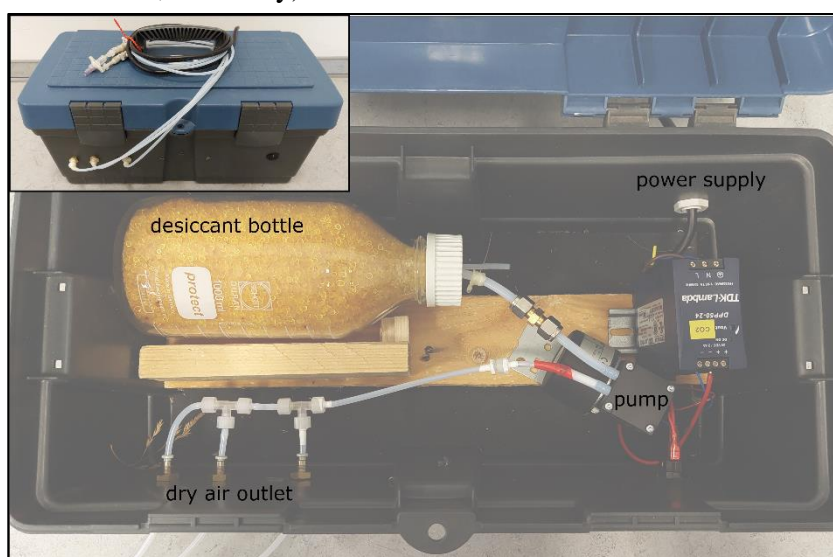



Figure 2: Self-constructed box for field dry air supply (top left) including a bottle with desiccant, power supply and a pump for up to three dry air outlet lines.

dry air in three tubes simultaneously through up to three sample lines. 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~~1 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,

199 we periodically tested the water concentration before and after the field campaigns and could
200 not detect any increase after ~~one~~1 day in the field. The water concentration of the dry air
201 produced was ~~approximately~~approx. 200 ppm.

202

2.3 Laboratory standards

204 The water stable isotope measurements were
205 calibrated against six water vapor standards
206 (see Table 1) that were manually measured
207 during the experiments. Temperature (T) was
208 recorded continuously every 30 seconds with a
209 thermometer (EBI 20-TH1, Xylem Analytics
210 Germany Sales GmbH & Co. KG, Germany)

Table 1: Liquid water standards used during the experiments.

Standard	$\delta^{18}O_{liquid}$ [‰]	δ^2H_{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

211 placed directly next to the standard container. This allowed us to measure the standards in the
212 vapor phase and infer the values in a liquid phase at equilibrium (Sec. 2.5). Of the six standards
213 with different δ values, ~~approximately~~approx. 60 ml were filled into the prepared 100 ml
214 standard bottles as described in section 2.1 and measured directly on the CRDS.

2.4 Experimental design

2.4.1 Experiment I: Storage duration

217 In our storage experiment, we tested our gas sample bags for water vapor storage using water
218 sources of known isotopic composition. New bags, including the self-made connections, were
219 prepared to eliminate any production artifacts. Each bag was cycled with dry air, filled, and
220 emptied five times in a row. Following this preparation, five bags per storage period were filled
221 with two standards, L22 and M22 (15 min. at 50 ml/min).
222 Upon filling, the gas bags were promptly measured to ensure that no isotopic fractionation
223 occurred during the filling process. Subsequently, the gas bags were stored in the laboratory for
224 three storage durations - 1 day, 3 days, and 7 days. After the designated storage periods, the
225 samples were measured for 4 to 5 minutes, and a stable 2-minute average was recorded.

2.4.2 Experiment II: Memory

227 We conducted two memory tests, maintaining a consistent methodology similar to that
228 employed during the storage experiment, both utilizing five newly prepared bags~~.~~ per standard.
229 In the first test, we followed a structured sequence: we filled gas bags with ~~this~~the initial
230 standard, emptied them, and switched to ~~another~~the opposite standard and refilled the bags. We

231 repeated the process three times (fill, measure, empty) with the opposite standard until our

232 measurements fell within the required ~~accurate~~acceptable range (defined in 2.5). In the first

233 experiment, L23 was used as the initial standard and H23 as the opposite standard, in the second

234 experiment, the standards were used in reverse order. ~~We used five gas bags per standard during~~

235 ~~the experiments.~~

2.4.3 Experiment III: Memory test with storage

237 This laboratory experiment was conceived after we observed the effect of a short delay on

238 memory in Experiment II. We followed a similar procedure except that the initial standard L22

239 was allowed to stand in the bags for ~~one~~1 day prior to replacement with the second standard

240 H22. We then proceeded with the second standard following the repeated steps (fill, measure,

241 empty) until our measurements fell within the ~~accurate~~acceptable range again. Between the

242 second and third measurement cycle, the experiment was interrupted due to the long duration

243 (1h) of each measurement cycle and continued the next day (after 15.5 hours). The bags were

244 left empty during this second night to avoid any effects. Due to the length of each measurement

245 cycle, we used 3 repetitions during the experiment.

2.4.4 Experiment IV: Field filling and bag reuse

247 To validate results gained during the laboratory experiments under field conditions, we

248 compared measurements using the gas bags with direct in situ CRDS measurements. To do so,

249 we conducted two measuring campaigns, the first using new bags and the second using reused

250 bags. During the first one, we focused on the applicability of bag filling in the field by

251 comparing direct measurements of the soil water isotopes with the CRDS in the field

252 measurement of bagged samples. In the second campaign, we again compared direct field

253 measurements to bagged measurements, but this time using re-used bags measured in the

254 laboratory within 24 hours. To exclude any memory effects, as we saw in experiment III, the

255 reused bags were ~~rinsed~~flushed 10 times with dry air (approx. 10 x 10 min). Identical sample

256 bags were utilized for the identical sample probe to minimize changes in isotopic composition

257 and reduce the impact of memory effects. During each of the two measurement campaigns, a

258 total of 48 samples were collected at four different depths: ~~5cm~~5 cm (n = 14), ~~15cm~~15 cm (n =

259 13), ~~45cm~~45 cm (n = 7), and ~~150cm~~150 cm (n = 14). Due to low soil permeability, the depth of

260 45cm could only be sampled during one measurement campaign, resulting in only 7 samples.

261 Dry carrier gas was passed through the home-built membrane soil probes at a flow rate of

262 ~~approximately~~approx. 50 ml per minute. First, we connected the CRDS to the outlet valve to

263 determine the time required to reach a steady-state value (compared to e.g. Kühnhammer et al.,

2021). Subsequently, a 2-minute average was recorded 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 temperature at the 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.

2.4.5 Experiment V: Observation over a full cultivation period

The field applicability test was followed by gas bag sampling and subsequent 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). We measured once a month during the winter and once a week starting in the spring resulting in 18 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. To provide context for the soil isotopic data, additional precipitation samples were collected at the site over a two-year period.

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

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 source temperature (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).

To assess the ~~accuracy~~uncertainty of our laboratory measurements, we calculated z-scores for each sample and water stable isotope (δ^{18}O and δ^2H). Z-scores indicate the normalized deviation

296 of the measured water isotopic ratios from the known isotopic signature of the added water
297 vapor, and can be calculated following the method (Eq. 4) described by Wassenaar et al. (2012):
298
299 $$z - score = \frac{S - B}{\mu}$$ Eq. 4
300
301 Where S is the isotope signature ($\delta^{18}O$ or δ^2H) measured with our gas bag, B is the benchmark
302 isotope signature and μ is the target standard deviation. To assess the performance of each
303 extraction method, we set a target standard deviation (SD) of 2‰ for δ^2H and 0.4‰ for $\delta^{18}O$
304 for measuring water vapor samples. The target SD was selected based on CRDS measurements
305 using the bag method and considering standard deviations from previous studies, such as those
306 by Wassenaar et al. (2012) or Orlowski et al. (2016a). A z-score < 2 represents an ~~accurate~~
307 ~~sample~~acceptable range, a z-score between 2 and 5 describes the questionable range, and a z-
308 score > 5 representing an unacceptable range (Wassenaar et al., 2012; Orlowski et al., 2016a).

3. Results

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~~acceptable 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 duration

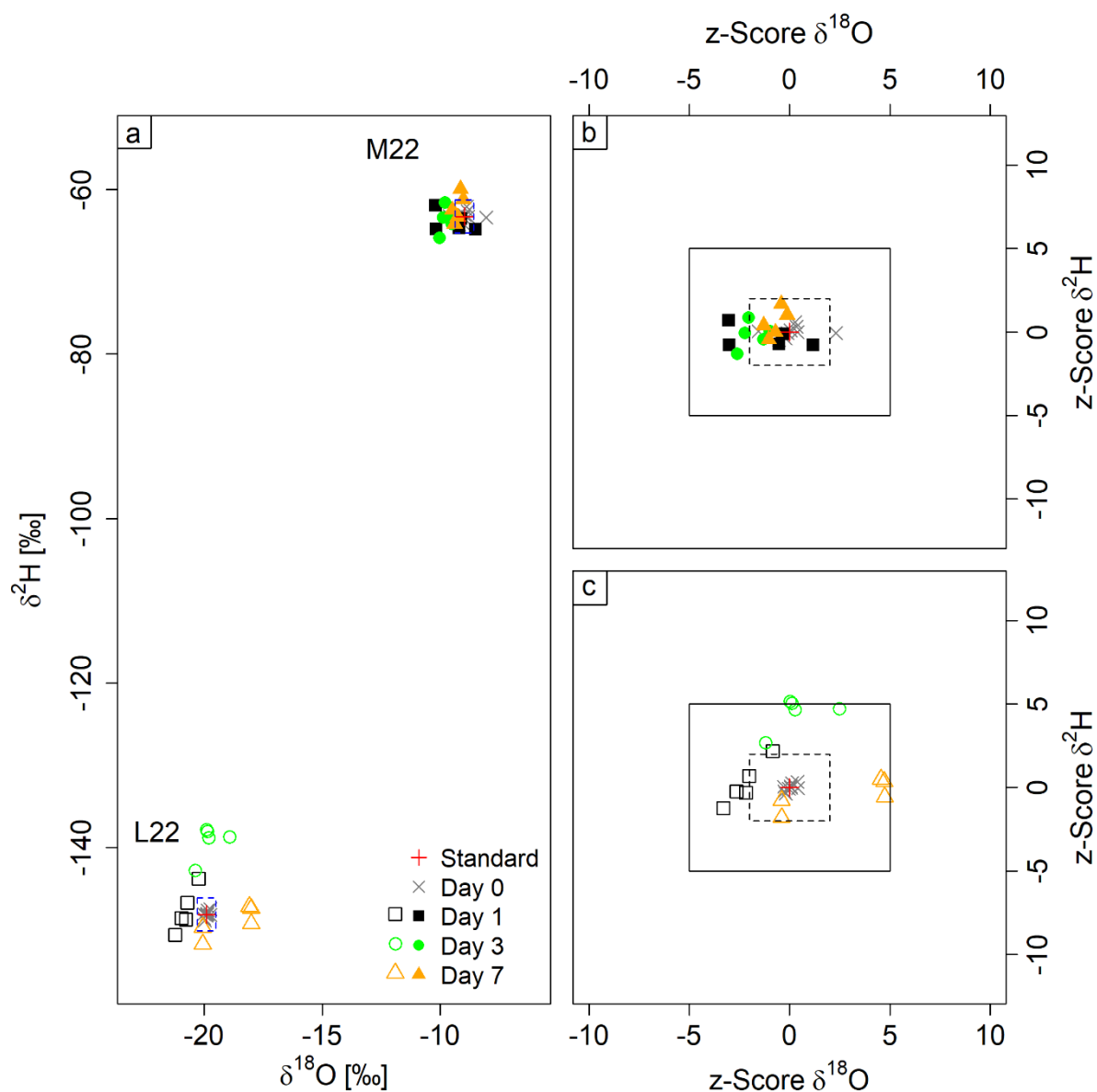



Figure 3: Dual isotope plots showing variation over several days of water-vapor storage in gas bags. The panel on the left shows results from both experiments (a) and those on the right show z-score plots for standard M22 (filled symbols, b) and L22 (open symbols, c). The black boxes describe the questionable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

317 Used laboratory standards, L22 and M22, spanned an isotopic ~~gradient~~range of – 9.0 to - 19.9

318 ‰ in $\delta^{18}O$ and - 63.3 to - 148.1 ‰ in δ^2H (Fig. 3a; filled symbols: M22, empty symbols: L22).

319 On average, the measured ~~values differed from known values by~~accuracy was -0.7 ± 0.6 ‰

320 $\delta^{18}O$ and -0.1 ± 2 ‰ δ^2H after 1 day, -0.3 ± 0.6 ‰ $\delta^{18}O$ and +4.3 ± 5.2 ‰ δ^2H after 3 days and,

321 +0.4 ± 1 ‰ $\delta^{18}O$ and +0.1 ± 2 ‰ δ^2H after 7 days of storage (Table S2/S3). Except for one

322 sample during the M22 experiment, the deviations from the true standard values ~~in~~for these

323 measurements were all ~~in the range of~~within ± 0.4 for $\delta^{18}O$ and 2 ‰ for δ^2H, and thus no bias

324 was associated with bag filling ~~of the bags~~.

325 The experiment using standard M22 resulted in an overall high accuracy for all measurements

326 of the three storage durations being – 0.5 ± 0.5 ‰ for $\delta^{18}O$ and 0 ± 1.6 ‰ for δ^2H. In addition,

327 no trend in isotopic signature could be observed over storage duration for either $\delta^{18}O$ or δ^2H.

328 Consequently, z-scores were either within the ~~accurate~~acceptable range or close to it, again with

329 no trend of decreasing accuracy over storage time.

330 The second storage test using L22, showed a lower accuracy due to lower precision for δ^2H,

331 being 2.8 ± 4.9 ‰, and – 0.1 ± 1.1 ‰ for $\delta^{18}O$ ~~and 2.8 ± 4.9 ‰.~~. However, no time trend was

332 observed. The decreased accuracy was mostly caused by the samples after ~~three~~3 days, as all

333 gas bags showed a significant enrichment (8.9 ± 2 ‰ δ^2H on average). The higher inaccuracy

334 after ~~three~~3 days of storage must be due to an error during the measurement, as accuracy

335 improved again after 7 days. The overall higher scatter (particularly for $\delta^{18}O$), which has a

336 different isotopic signature than the ambient air, led to initial concern over potential exchange

337 with ambient air. However, we do not think that is likely as the visible scatter already appeared

338 within ~~one~~1 day of storage, was not directed towards isotopic signatures of ambient air and did

339 not increase over time. The z-scores show ~~accurate~~acceptable values for δ^2H (except after 3

340 days) and more questionable values for $\delta^{18}O$. The average z-score was 0.3 ± 2.7 for $\delta^{18}O$ and

341 1.4 ± 2.5 for δ^2H.

3.2 Experiment II: Memory

343 In this experiment, the initial standard filled into the bags was L23, followed by cycles of filling

344 and emptying with standard H23. This standard sequence was reversed in the second part of the

345 experiment (initially H23, then cycles of L23). No clear memory effect was found in the first

346 part of the experiment (Fig. 4b), whereas a clear memory effect was observed after the first

347 filling (L1) of the second part of the experiment (Fig. 4c). However, this memory almost

348 disappeared ~~again~~ in the next repetition (L2).

As depicted in Fig. 4 (a and c), except for L1, almost all measurements fell within the target standard deviation for $\delta^{18}O$, while δ^2H values are more scattered. The same pattern can be seen for the z-scores (Fig. 4 b and c). ~~While almost all~~Three measurement points from L1 show unacceptable values, while the remaining z-scores ~~are in the accurate range~~show acceptable or ~~in the~~ questionable ~~range~~values at the threshold of ~~the accurate range, the values of L1 are clearly outside with values in the unacceptable~~acceptable range.

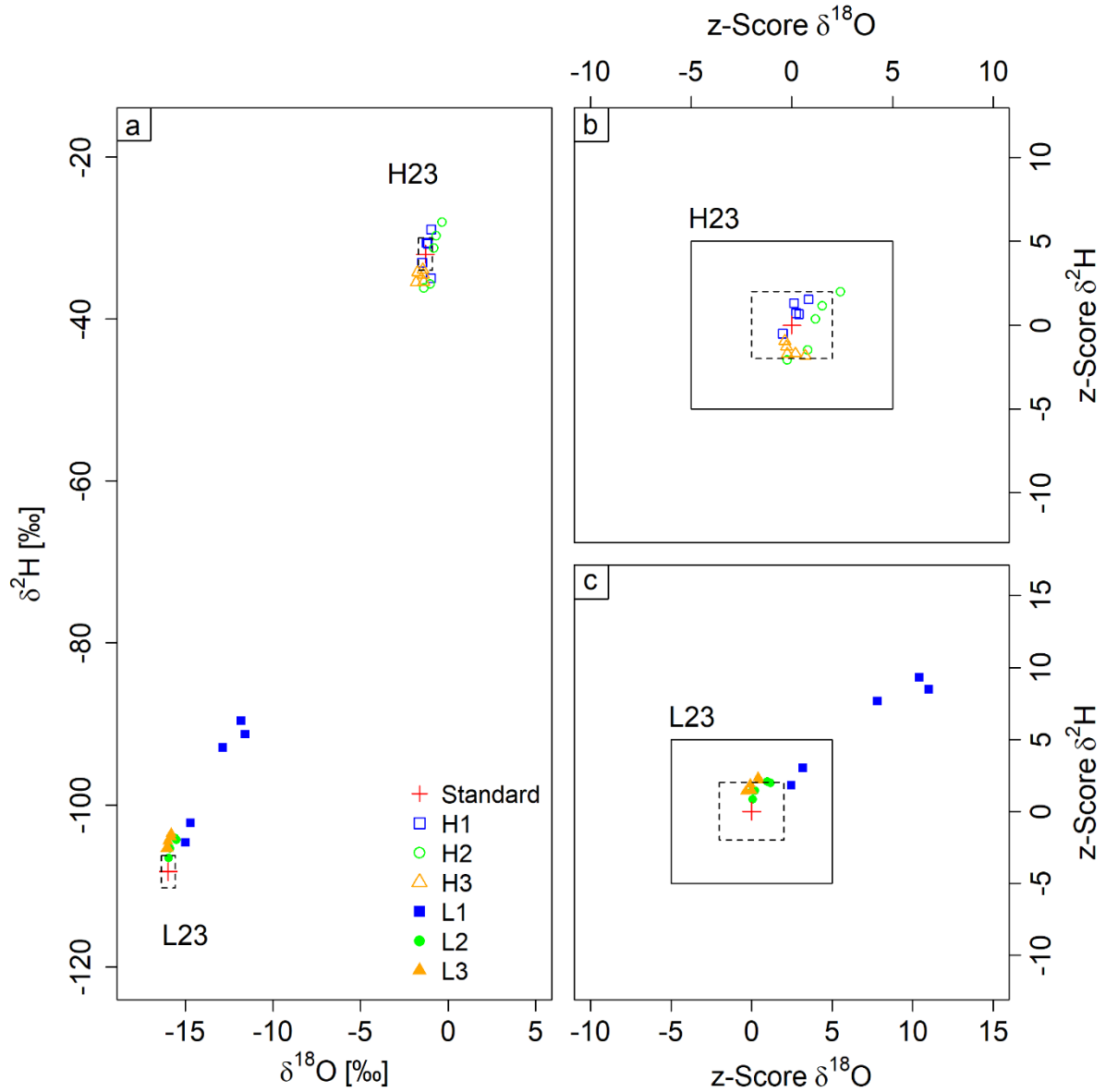



Figure 4: Memory experiment results with dual isotope plot for both experiments (a) and z-score plots for L23 to H23 (b) and H23 to L23 (c). The bags were filled first with standard H23, then repeatedly (1-3) with standard L23. The memory effect is evident only for measurement L1, the first to follow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

3.3 Experiment III: Memory test with storage

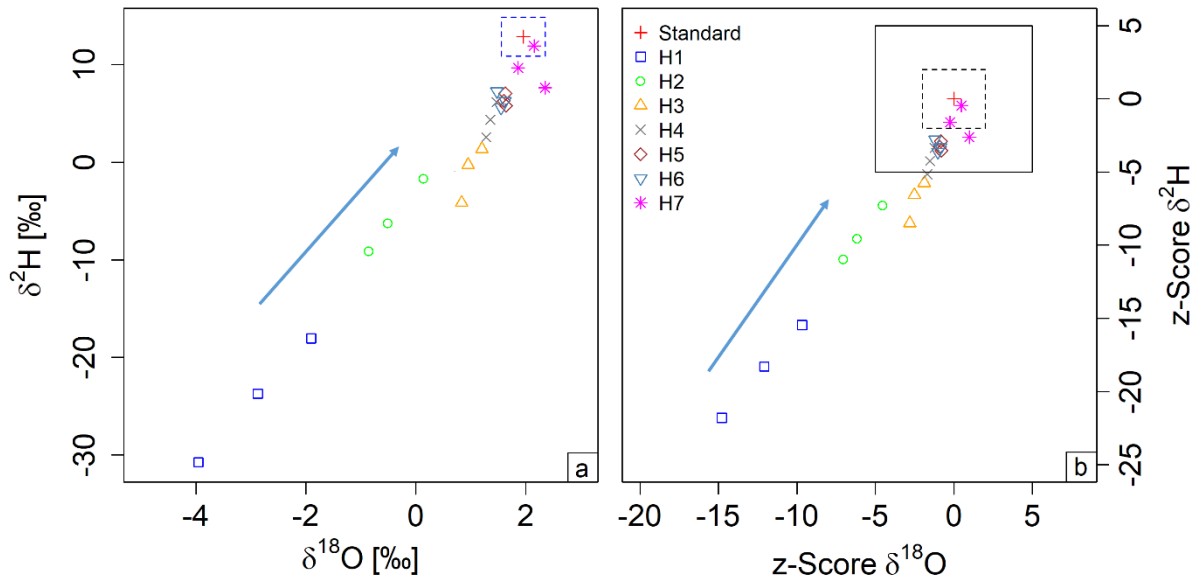



Figure 5: Memory test with storage experiment: dual isotope plot on the left (a) and z-score plot on the right (b). The red cross describes the target standard value. The blue dashed line (a) describes the defined standard deviation for measurements. The black box describes the questionable range while the dashed black box describes the accurate acceptable range, based on our classification of z-values (b) (Sec. 2.5). The arrow indicates the direction from strong to weak memory

No significant storage effect was observed over the one 1-day storage period, and there was no noticeable difference between the two repetitions (mean difference between days: 0.4 ± 0.4 ‰ δ^{18}O and 0.1 ± 1.9 ‰ δ^2H). However, when the water source was changed to HH22, there was a clear memory effect of a magnitude up to -4.9 ± 1 ‰ δ^{18}O in and -37 ± 6.4 in ‰ δ^2H (Fig. 5 and Tab. 2). After filling with the opposite standard, H22, the first measurements (H1) revealed a low accuracy due to low precision and trueness, which was improved by around 50% with each repetition until the average result of H7 was close to the target standard value. The z-scores followed a similar trend from H1 to H5, gradually decreasing. Although H1 and H2 showed unacceptable z-scores for δ^{18}O, and H3 fell within the questionable range, all subsequent measurements had z-scores within the accurate acceptable range. The δ^2H z-scores follow a similar trend to the z-scores for δ^{18}O, thus also indicating a clear memory effect. However, this effect persisted for more cycles in the case of δ^2H. The measurements H1 to H3 were in the unacceptable range, while the results for H4 to H6 were questionable.

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

Repetition	Diff. δ^{18}O [‰]	Diff. δ^2H [‰]
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

3.4 Experiment IV: Field filling and bag reuse

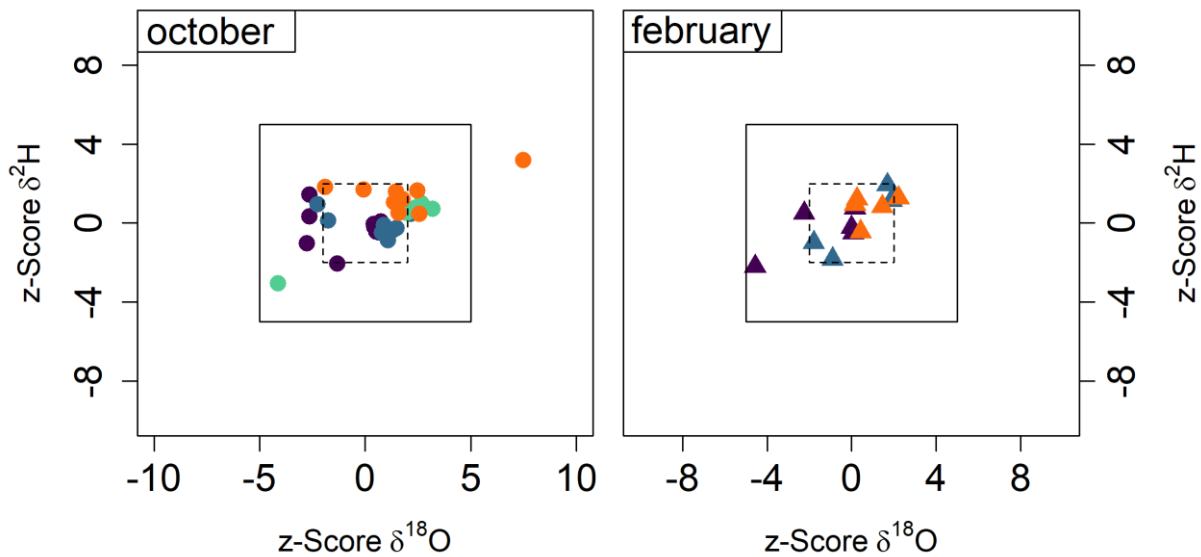



Figure 6: In October (left), in situ CRDS measurements were compared with bag measurements taken and measured directly after filling. In February (right), in situ CRDS measurements were compared with reused bags measured the next day in the laboratory (after 10 cycles of flushing with dry air).

To compare the measurements during the two campaigns and calculate the Zz-scores (Eq. 4), we considered the measured isotopic value 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

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

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

3.5 Experiment V: Observation over a full cultivation period

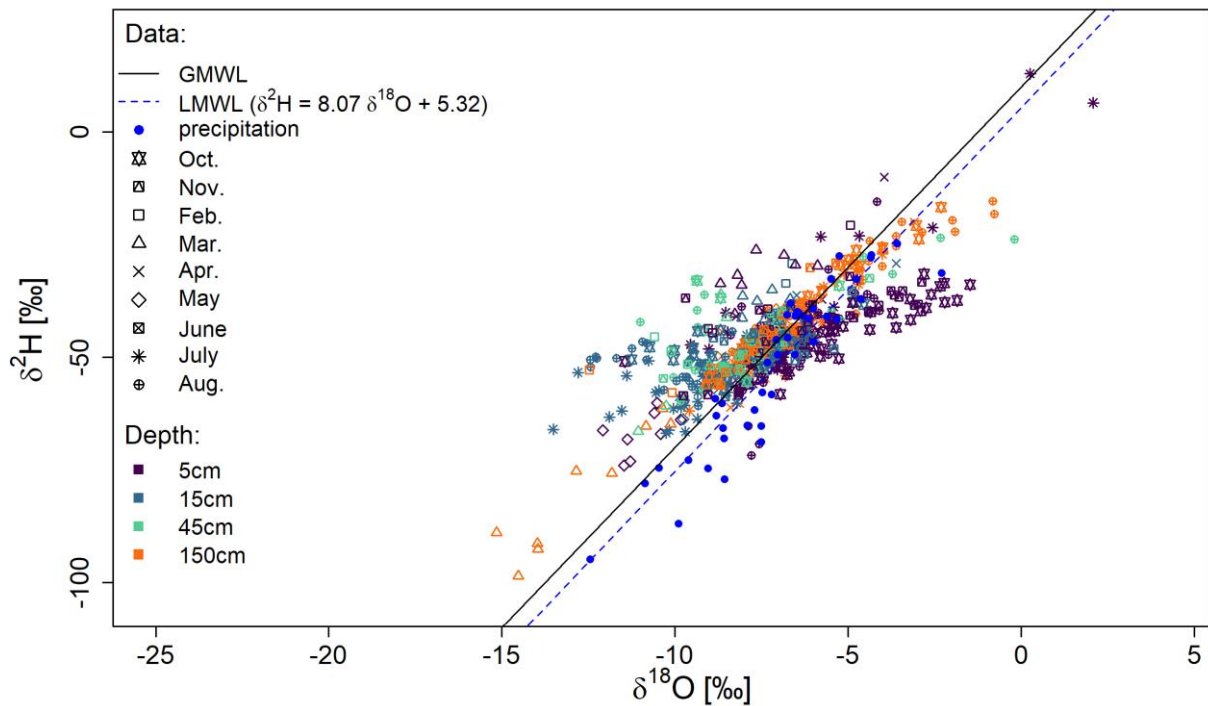



Figure 7: The dual isotope plot shows all 603 measurements taken during the cultivation period, including the Global Meteoric Water Line (GMWL; black line), the Local Meteoric Water Line (LMWL; blue dashed line) and the bag method measurements at 5, 15, 45 and 150 cm depth (purple, blue, green and yellow) during 9 different ~~month~~months.

Measurements of soil water isotope profiles over the full season (Fig. 7) revealed a wide range of isotopic signatures with 2.1 ‰ to -15.2 ‰ for $\delta^{18}O$ and 12.9 ‰ to -98.5 ‰ for δ^2H. 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 is nearly parallel to the Global Meteoric Water Line (GMWL). In general, the measurements show isotopic signatures similar to precipitation immediately after rain events and a trend toward evaporative enrichment during droughts (see Fig. S1, supplement), but with distinct differences between months (e.g., Mar. vs. Oct., at the 5 cm depth). Overall, our findings from the field trial suggest a good agreement with the LMWL and are plausible in terms of seasonal variability.

4. Discussion

4.1 Comparison to previous developments to store and measure water vapor

In general, it is difficult to compare the 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, our results for reused bag samples stored up to 24 hours are generally comparable in accuracy to previous studies of water vapor storage. For example, the Soil Water Isotope Storage System (SWISS) introduced by Havranek et al. (2020) showed a ~~high accuracy~~higher precision during a 30-day storage period in a laboratory experiment ($\pm$ 0.5 ‰ $\delta^{18}O$ and $\pm$ 2.4 ‰ δ^2H). This result was followed by several experiments, which showed an actual precision of 0.9 ‰ and 3.7‰ for $\delta^{18}O$ and δ^2H in field applications 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~~1 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 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 volume of the glass vials.

A recent paper compared different types of affordable food storage bags for water vapor sampling using standardized water with different isotopic signatures (Herbstritt et al~~.;~~., 2023). These authors conducted rigorous tests of diffusion tightness and inertness of various bag types. They 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, isotopically homogeneous air sample where the goal was not to eliminate the memory effect, but to make it predictable and remove it. After ~~one~~1 storage day, the accuracy was 0.25 $\pm$ 0.41‰ and 0.41 $\pm$ 1.93 ‰ for $\delta^{18}O$ and δ^2H. 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.

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 simplified gas transfers and may reduce leakage ~~and simplify gas transfers both in the lab and in the field~~. Third, we have suggested a means by which multiple flushes of the bags with dry air may eliminate, or at least minimize, the memory effect. ~~Fourth~~Aside from the differences, we ~~have~~likewise 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 flushes to remove. This time-dependent process does not seem to require slow flushing to reverse the memory effect (Expt. IV). 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 δ^2H 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~~10 flushes with dry air (Fig. S2). As expected, results were unaffected for both $\delta^{18}O$ and δ^2H directly after bag filling. While ~~storing~~storage did not influence the $\delta^{18}O$ signature, a clear but consistent effect was visible after ~~one~~1 day regarding δ^2H, which, contrary to the results of Herbstritt et al. (2023), did not increase over ~~three~~3 days storage. Since this effect was stable and we know the previous sample signature, this effect may be correctable ~~like~~as in the moist conditioning approach described by Herbstritt et al. (2023) or erasable by increasing the number of flushes. Concluding, our results suggest comparable accuracy to other methods for 24 hours, but the accuracy of long-term storage and high isotopic differences for consecutive samples should be further tested.

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 can change significantly as evaporated soil vapor is depleted in heavy isotopes, leaving the remaining soil water enriched in ^{18}O and ^2H (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~~smaller slope compared to the LMWL in the upper soil layer (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. In contrast, there are only slight trends in evaporative enrichment at lower depths (compare e.g. Sprenger et al., 2016).

4.2 Limitations, future perspective and cost classification

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~~ gas-permeable ~~tubes~~membranes 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~~As highlighted above, 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. For example, while the storage experiment I results for δ^2H were mostly accurate, we observed higher uncertainty for $\delta^{18}O$. Here, the light standard proved to be slightly more difficult to handle than the medium standard, while maintaining similar accuracy. At first glance, this decrease in accuracy seems to be similar for experiment II (higher uncertainty of light compared to heavy standard). In this experiment, a memory effect was expected given that the previous sample was not removed between standard fillings. However, when the initial standard was stored only briefly (minutes) before refilling with the opposite standard, as planned in experiment II, no clear memory effect was observed. The three measurements yielding unacceptable values were accidentally stored longer (45 min between filling and measurement, see blue squares in Fig. 4), providing valuable insight into a memory effect dependent on storage duration of the initial standard. Nevertheless, further studies should focus on whether samples with isotopically lighter signatures or isotopic signatures outside of the range tested in this study vary in accuracy when sampled and analyzed with the bag method. Based on our observations in experiment II, experiment III deliberately combined memory with storage resulting in a clear memory effect in the direction of the initial standard after 1 day of storage for bags that were not subjected to a flushing procedure (such as described in Herbstritt et al., 2024) before changing from one to the other standard. The observed number of refills required in this experiment with the standard H22 after an initial fill with L22 to eliminate this effect was used to guide our bag preparation strategy for bag reuse in the following experiment

IV. Unlike experiments I and II, this experiment tested only the direction from light to heavy isotopes. Given the remaining uncertainty from experiments I and II concerning our light standard performance, this should be revisited in future studies to test whether or not the combined effect of memory and storage is stable over the desired isotope range. Finally, our reuse experiment (IV) showed similar results to experiment I. Here, we proved that a preconditioning of 10 dry air flushes between two bag sampling campaigns worked for differences of up to 20 ‰ in δ^2H for consecutive samples, while a much higher difference of 76.2 ‰ revealed a memory effect of about 12 ‰ after 1 and 3 days of storage for δ^2H but not for $\delta^{18}O$ (experiment S2). These results clearly show that the method provided good results for our isotopic range in the field, but that further tests are required for experiments with a larger range of isotope signatures particularly when considering use of this method for labelling experiments. However, it should be noted that bags have never been tested for reuse with such high isotopic differences, and some increase in uncertainty is to be expected due to the small but present water transmission through the material. Considering this, the glass container used in other methods may be superior for longer storage times, although e.g. Magh et al. (2022) also recommended their method for storage times less than 3 days.

The cost ~~for~~of the ~~commercially available~~commercial gas bags we used was relatively low~~. To classify the costs per sample container~~ compared to the total cost of a typical field campaign. In perspective, the SWISS-System was clearly more expensive when considering costs per container, 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 samples were stored up to 24h, they were flushed multiple times between uses, they are reused for a relatively narrow range of isotopic signatures (in the case of δ^2H) e.g. reusing the same bags for the same sample probes, and that standards are taken through the whole sample collection, transport, and analysis process. Following the ~~described~~ conditions described, 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~~the reliability of soil membranes combined with gas bags for in situ soil water vapor sampling and subsequent water stable isotope analyses ~~was a reliable,~~, provided the analysis occurs within 24h. The method is cost-~~effective,~~efficient 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. ~~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, for larger differences in isotopic signatures, the bags need to be handled differently, which needs to be further investigated (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 δ^2H ~~[‰], which allows a wide applicability.~~[‰] for storage up to 24h. The possibility to ~~take~~collect and store samples easily and without permanent power supply extends the usability of water stable isotope measurements in the field.

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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