Technical note: Mobile, discrete in situ vapor sampling for measurements of matrix-bound water stable isotopes

Barbara Herbstritt[1], Benjamin Gralher[1,2], Stefan Seeger[1], Michael Rinderer[1,3], Markus Weiler[1]

[1] *Hydrology, Faculty of Environment and Natural Resources, University of Freiburg, Germany*

[2] *Groundwater Management, Technical University of Dresden, Germany*

[3] *now at: geo7 AG, Bern, Switzerland*

Abstract

Methodological advancements have been made in in situ observations of water stable isotopes that have provided valuable insights in ecohydrological processes. The continuous measurement capabilities of laser-based analyzers allow for high temporal resolutions and non-destructive, minimally invasive study designs of such in situ approaches. However, isotope analyzers are expensive, heavy, and require shelter and access to electrical power which impedes many in situ assays. Therefore, we developed a new, inexpensive technique to collect discrete water vapor samples in the field via diffusion-tight inflatable bags that can later be analysed in the lab. In a series of structured experiments, we tested different procedural settings, bag materials, and closure types for diffusion-tightness during storage as well as for practical handling during filling and extraction. To facilitate re-usage of sampling bags, we present a conditioning procedure using ambient air as primer. In order to validate our method, direct measurements through hydrophobic in situ probes were compared to repeated measurements of vapor sampled with our bags from the same source. Performing pertinent calibration procedures, accuracy was better than 0.4‰ for $\delta^{18}O$ and 1.9‰ for δ^2H after one day of storage. Our technique is particularly suitable in combination with minimal invasive water vapor sampling in situ probes that have already been employed for soils and tree xylem. It is an important step towards monitoring stable isotope distributions and also

1   time-series in soils and trees without the need to have field-access to an analyzer and therefore

2   a promising tool for many applications in eco-hydrology and meteorology.

3   **1 Introduction**

4   Analyses of stable isotope composition of hydrogen and oxygen (δ^2H and δ^{18}O) in soils and

5   plant water have proven to be powerful tools and are therefore widely employed in ecology,

6   hydrology, and related disciplines. Stable isotopes of pore water have been used to provide

7   insights into soil evaporation (Zimmermann et al., 1967; Allison, 1982; Allison et al., 1983;

8   Barnes and Allison, 1988; Walker et al., 1988) and groundwater recharge rates (Dincer et al.,

9   1974; Saxena, 1984; Darling and Bath, 1988). They were used in soil hydrology to study

10   unsaturated and saturated subsurface flow processes, mixing and residence times (Sklash and

11   Farvolden, 1979; Buttle and Sami, 1990; McDonnell, 1990; Stewart and McDonnell, 1991;

12   Gazis and Feng, 2004; Laudon et al., 2004; Garvelmann et al., 2012), and to quantify

13   evapotranspiration partitioning (Brunel et al., 1997; Hsieh et al., 1998a; Wang and Yakir,

14   2000; Yepez et al., 2005; Rothfuss et al., 2010). Applications of water stable isotopes in

15   ecology have allowed researchers to identify plant water sources (Dawson & Ehleringer,

16   1991), to describe water use patterns (Schwinning et al., 2002), and to determine competitive

17   interactions (Ehleringer et al., 1991, Meißner et al., 2012). In plant physiology, insights into

18   plant hydraulic architecture (Drake & Franks, 2003) were possible with isotope techniques,

19   root water uptake was quantified (Rothfuss & Javaux, 2017) as well as hydraulic lift

20   (Caldwell & Richards, 1989; Meunier et al., 2018).

21   Conventionally, measurements of pore water and tree xylem water isotope composition are

22   obtained through destructive sampling of soil cores or manual collection of sapwood and

23   subsequent water extraction for isotope ratio mass spectrometry (IRMS) analysis (Ehleringer

24   et al., 2000, West et al., 2006). IRMS instrumentation allows for high measurement precision

25   (Horita & Kendall, 2004), but is expensive and requires highly time-consuming and laborious

1   sample pre-treatment (Kerstel & Gianfrani, 2008). A less expensive and overall more

2   convenient approach relying on laser-based water stable isotope analyzers is the direct vapor

3   equilibration laser spectrometry (DVE-LS) where samples of soil matrix, rocks or plant tissue

4   are in equilibrium with a corresponding vapor phase (Wassenaar et al., 2008; Hendry et al.,

5   2015; Gralher et al., 2021).

6   Although promising, the disadvantage is still that destructive soil sampling or harvesting of

7   plant material generally prevents repeated samples from one place. Destructive sampling

8   restricts the number of samples that can be obtained over time and space. This makes high-

9   frequency or even continuous measurements difficult to sustain or simply infeasible. Number

10 and spatiotemporal scope of lab-scale experimental setups as well as environmental isotope

11 studies continued to expand, but were still limited by the available indirect observational

12 techniques (West et al., 2010).

13 The growing distribution of laser-based water stable isotope analyzers in recent years also

14 enabled minimal-invasive, direct, continuous, and simultaneous measurements of δ^2H and

15 δ^{18}O of water vapor. Only herewith, time series observations from the same point became

16 possible. Available isotope ratio infrared spectroscopy (IRIS) instruments allow for

17 measurements at a precision and accuracy comparable to that of IRMS (Berden et al., 2000;

18 Crosson, 2008; Kerstel and Gianfrani, 2008; Gupta et al., 2009). Importantly, laser-based

19 instruments are portable and therefore potentially field-deployable. Especially the small

20 measurement cavity size (35 mL) of wavelength-scanned cavity ring-down spectroscopy

21 (WS-CRDS) instruments makes them ideal for lab-scale experimental setups as well as for

22 small sensor designs. The spread of laser-based instruments has therefore stimulated recent

23 developments of a number of in situ methods for direct measurements of water stable isotopes

24 in various fields. Precipitation measurements were carried out via gas-permeable ePTFE

25 surgical tubings (Munksgaard et al., 2011). Soil column breakthrough curves (Herbstritt et al.,

1   2012) as well as analyses of precipitation and canopy throughfall in parallel were achieved via

2   small hydrophobic membrane contactors (Herbstritt et al., 2019). The isotopic composition of

3   pore water was analysed in lab-scale experiments via hydrophobic microporous tubings

4   (Rothfuss et al., 2013) as well as in natural soil profiles with custom-made hydrophobic

5   porous in situ water isotope probes (WIPs) (Volkmann and Weiler, 2014). Similar in situ

6   probes were also used in tree stems in labelling experiments to analyze the isotopic

7   composition of xylem sap (Volkmann et al., 2016a; Seeger and Weiler, 2021). The 'borehole

8   method' (Marshall et al., 2020) is an alternative way to obtain in situ samples of tree xylem

9   water vapor. Measurements of the isotopic composition of transpired water were conducted

10   using leaf chambers (Wang et al., 2012; Dubbert et al., 2014) or whole-plant chambers
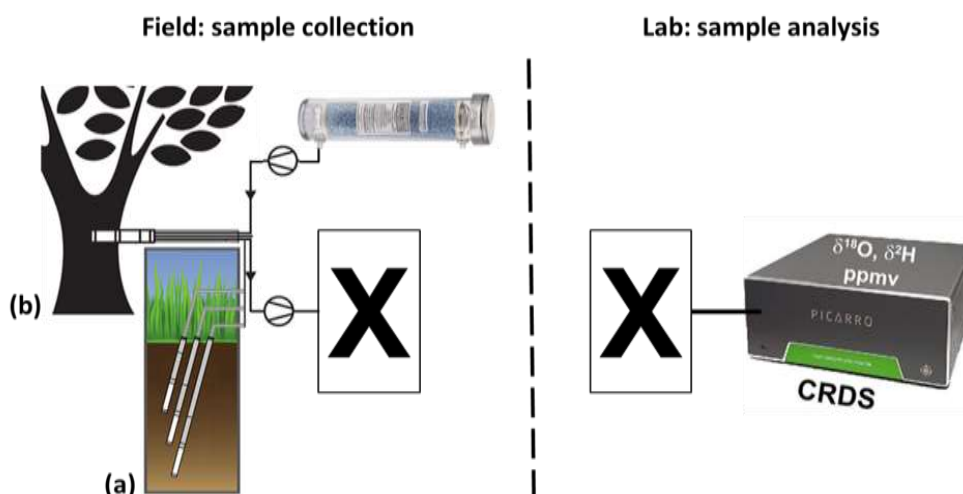
11   (Volkmann et al., 2016b).

12   The isotopic composition of the liquid water of interest in all these in situ studies was inferred

13   from sampling and measuring a corresponding vapor phase. Water vapor of interest was either

14   withdrawn directly e.g. from soil profiles, out of tree boreholes, or exchange and equilibration

15   with a carrier gas through different types of hydrophobic membranes were facilitated.

16   However, operating laser-based analyzers at the study site requires power-consuming, heavy

17   and expensive equipment to be brought to the field with the risk of damages and the

18   disadvantage of relative immobility. Consequently, rough or remote terrains as well as

19   spacious experimental designs, exceeding possible tubing lengths between in situ

20   measurements and the isotope analyzer are virtually excluded with this approach. First

21   attempts to overcome these obstacles by collecting discrete vapor samples under such

22   circumstances into glass bottles were recently presented. In both approaches, the sampled

23   vapor had to be diluted continuously during measurement, to compensate for negative

24   pressure when sucked into the analyzer by releasing e.g. dry air into the rigid, fragile

25   sampling flasks. The first approach (Havranek et al., 2020) can be seen as a proof of concept.

1   In a follow-up, Havranek et al. (2022) describe a field application of their setup which

2   requires considerable financial resources for the components in use, extensive technical

3   know-how for construction as well as substantial effort for field installation of a limited

4   number of flasks. Their recommended operation procedure requires long flushing times,

5   leading to filling times per flask of more than one hour, which strongly reduces the sample

6   throughput and thus the achievable temporal resolution. The second approach (Magh et al.,

7   2022) partly resolved these issues but still relies on specialty tools, lacks reproducibility due

8   to the small volume of sampled vapor and currently does not provide the data accuracy

9   needed for natural abundance isotope assays. Further, a sophisticated calculation procedure is

10   necessary for both approaches to remove the effects of the initial pulse of water vapor during

11   the start of the measurement phase, which clearly biases the obtained isotope data.

12   Therefore, the aim of this study is to develop a technique to collect discrete vapor samples in

13   the field for subsequent lab-based analyses, that overcomes the aforementioned problems

14   while still ensuring handiness as well as cost and time efficiency. For this purpose, we varied

15   the applied gas flowrate through established non-destructive in situ water isotope probes

16   (WIPs) to improve per-sample time consumption. We tested the diffusion-tightness and

17   inertness of various commercially available gas sampling bags as well as custom-made

18   inflatable containers comprising different materials and closing mechanisms. We identified

19   the best performing bags and coupled it with WIPs in order to collect and temporarily store

20   discrete vapor samples prior to lab-based isotope analyses. Also, we identified necessary

21   preparatory steps to optimize the reproduction of in situ data.

Figure 1. Schematic of projected vapor sampling via in situ (a) soil- and (b) xylem-water isotope probes (modified from Volkmann & Weiler, 2014 and Volkmann et al., 2016a). The left part describes the intended field setting while the right part describes the intended laboratory setting: sampled vapor is first filled into appropriate, to-be-identified containers (X) and later analyzed in the lab via CRDS.

2 Methodology

2.1 Effect of changing gas throughflow rates on the isotopic composition

In the first part of this study we tried to optimize sample filling times. For this purpose we investigated the effect of varying gas flowrates through the to-be-employed in situ water isotope probes (WIPs). Originally, the applied flow rates had been set to match analyzer demand which becomes obsolete for the collection of discrete vapor samples. In the case of discrete vapor sampling through WIPs into air-tight containers, different, arbitrary flowrates can be selected, which inversely affect the filling times of the containers. For repeated analysis of a single vapor sample we found a total gas sample volume of 0.5 - 1 L to be sufficient (Gralher et al., 2021). Further, we aimed at sampling times in the field of no more than 5 minutes per sample. Therefore, flow-rates of both dry air through the WIP and the corresponding gas sampling rate into the containers were increased stepwise up to

1   150 mL/min. We also tested the effects of omitting the dilution when increasing the

2   throughflow rates. In order to keep the gas flow inside the WIP balanced between the

3   inflowing carrier gas and the outflowing sampling gas and in doing so avoid over- or under-

4   pressure, the sampling rates had to match the throughflow rates. For these tests a WIP was

5   installed in an evaporation-shielded box filled with moist sand with a stable liquid water

6   isotopic composition and kept at a constant temperature of 20.8 °C. For precise isotope

7   measurements we used dry synthetic air ('zero air').

8   Precise flowrates of the synthetic air from the pressurized gas bottle into the WIP were

9   facilitated by a digital mass flow controller (PN 35828, Analyt MTC, Müllheim, Germany),

10   while sampling at the same flowrate was facilitated by a small air pump (PN LP27-12, Pollin

11   Electronic GmbH, Pförring, Germany) where the pumping rate can be controlled manually via

12   the applied voltage and controlled with a mass flow meter (PN 35808, Analyt MTC). The

13   fractions of sampling rates exceeding the analyzer demand of ~ 35 mL/min were vented to air

14   through an open split near the sample inlet port of the isotope analyzer (L2120- or L2130-*i*,

15   Picarro Inc., Santa Clara, CA, USA). The analyzer provided quasi-continuous (0.5 Hz)

16   readings of water vapor mixing ratio (in ppmv), oxygen and hydrogen isotope readings (in

17   ‰), and spectral parameters ('h2o_vy', 'organic_MeOHampl') which we also collected from

18   room air on every day of bag measurements. This setup allowed for facilitating the demanded

19   low and constant stream of gas to the analyzer while at the same time arbitrarily varying the

20   gas flow through the attached WIP.

21   **2.2 Material and closure type selection**

22   **2.2.1 Dry air inflation**

23   Rigid glass or steel bottles and cylinders conventionally used for gas sampling were excluded

24   in our approach, since constant flow through the WIPs was needed in our setup and under-

25   pressure at the analyzer during measurements has to be avoided. Commercially available

1   gasbags with large volumes (2.5 L, 10 L) are available with reusable gas valves in opposite to

2   bags with smaller volumes (0.5 L – 1 L), which come with septa or other degrading closures.

3   Hence, none of these combinations were suitable for our purposes, either due to their size or

4   due to the type of closure. Therefore, we tested three different inflatable bags of different

5   materials and reasonable sizes and combined them with different reclosable caps and valves

6   (Tab. 1). Specifically, we tested whether they were sufficiently reliable in terms of diffusion-

7   tightness and chemical inertness, also focusing on easy handling.

8   The different bag types were filled with pure N_2 (purity 99.996%) and analyzed immediately

9   thereafter with a CRDS isotope analyzer (L2130-*i*, Picarro Inc., Santa Clara, CA, USA). We

10   tested PE spoutbags (code 'PE-Sp', PN 1055) and single layer metalized spoutbags (code 'Al-

11   Sp', PN 1050, both available from Daklapack Europe, Oberhausen, Germany), of which we

12   replaced the original PE spout caps by caps with rubber septa. Filling and continuous vapor

13   isotope analyses were facilitated through these septa via an infusion needle (ID = 1 mm)

14   assembled to a 1/8" perfluoroalkoxy alkane (PFA) tube. We also tested two kinds of 3-layer

15   metalized zip bags with fill volumes of 1 L (PN: CB400-420BRZ, color: red) and 0.5 L (PN:

16   CB400-310GZ, color: gold, both available from Weber Packaging GmbH, Güglingen,

17   Germany). They were heat-sealed and equipped with silicone blots on the outside, which

18   served as septa after 2 days of drying (code 'Al3-Sil' for the 1 L bag, code 'Al3g-Sil' for the

19   0.5 L bag). The bags were filled and their content withdrawn for isotope analysis through the

20   silicone septa again via an infusion needle assembled to a 1/8" PFA tube.

21   To improve handiness and simplify filling and sample analysis when using the 3-layer

22   metalized bags, we tested two different types of valves as alternatives to our custom-made

23   silicone septa. We fixed small pneumatic brass couplings (PN KDG M5 NW2,7, Landefeld,

24   Kassel, Germany) on the 3-layer metalized 1 L zip bags (code 'Al3-PC'), which were then

25   heat-sealed. The respective plug connector (PN KSGI M5 NW2,7, Landefeld, Kassel,

1   Germany) was connected to a 1/8" PFA tube for filling and analysis. Also stainless steel

2   screw-lock gasbag valves with 6 mm hose fittings (PN 11701150, Linde, Pullach, Germany)

3   were mounted on 0.5 L and on 1 L 3-layer metalized zip bags (codes 'Al3s-GbV' and 'Al3-

4   GbV'). For increased leak-tightness we mounted an additional, custom-made rubber washer

5   between the valve and the inner wall of the bags which were then heat-sealed. For filling and

6   sample analysis the 6 mm hose fitting was adapted to a 1/8" PFA tube.

7   Table 1. Bag- and seal-type combinations and their properties tested for vapor sampling.

Code	Material	Bag style	Vol	Closure, cap or seal type	Inflation, filling, sampling via…
PE-Sp	PE	spoutbag	1 L	PE screw cap w/ rubber septum	Infusion needle and 1/8" PFA tube
Al-Sp	Al	spoutbag	1 L	PE screw cap w/ rubber septum	Infusion needle and 1/8" PFA tube
Al3g-Sil	Al 3ply gold	Zip bag	0.5 L	Silicone blot as septum	Infusion needle and 1/8" PFA tube
Al3-Sil	Al 3ply red	Zip bag	1 L	Silicone blot as septum	Infusion needle and 1/8" PFA tube
Al3-PC	Al 3ply red	Zip bag	1 L	Pneumatic brass coupling	Plug connector and 1/8" PFA tube
Al3-GbV	Al 3ply red	Zip bag	1 L	Stainless steel screw-lock valve	Hose fitting adapted to 1/8" PFA tube
Al3s-GbV	Al 3ply silver	Zip bag	0.5 L	Stainless steel screw-lock valve	Hose fitting adapted to 1/8" PFA tube

8

9   To detect gradual diffusive exchange of the bag content with ambient air or outgassing from

10   the employed material, 3 to 5 replicates of each bag/valve combination were flushed with N_2

11   and evacuated twice before they were again filled with pure N_2. They were then stored at

12   ambient temperature and repeatedly analyzed over the course of four weeks. Measurement

13   frequency was every two to three days during the first two weeks and one final time at the end

14   of the fourth week, unless a bag/valve combination was found unsatisfactory earlier.

15   **2.2.2 "Climate chamber" experiment**

16   To further test the vulnerability of projected discrete vapor samples regarding ambient

17   meteorological forcings we designed a small "climate chamber" which consisted of a plastic

18   box (inner dimensions 57 cm × 37 cm × 32 cm) covered by a plastic lid with all holes and slits

19   taped. We prepared six 'Al3s-GbV' bags filled with vapor from the same source (described in

20   detail in 2.3). Three bags were placed in the box straightforward while the other three were

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1   inserted in metal cans of the bags' size prior to placement in the box. Such metal cans are

2   normally used for the transport and storage of glass bottles containing liquid water sampled

3   for dissolved gases analysis. They are considered diffusion-tight when closed and sealed by

4   means of metal lids, rubber seal rings, and metal clasps as we did. Inside the box we also

5   placed an open bowl of water (ca. 350 mL) to quickly reach and then maintain a relative

6   humidity near 100% over the course of the test which lasted three weeks. The box was

7   deposited in the basement of our laboratory building to facilitate fairly stable temperature

8   conditions. Temperature (°C) and relative humidity (%) inside the box were recorded every

9   ten minutes with a CS215 probe connected to a CR200 logger (both from Campbell

10   Scientific, Logan, UT, USA). These data were then converted to water vapor mixing ratios

11   using Magnus' equation (Foken, 2008). Vapor concentration (ppmv) and isotope (δ^{18}O, δ^2H)

12   data from the vapor source used for filling the bags, from the inside of the box after 20 days,

13   and from the bags after 20 days of storage inside the box were collected with a Picarro 2120-*i*.

14   **2.3 Field application**

15   We tested the reliability of the projected sampling procedure first in a laboratory experiment

16   and later in the field using 'Al3-GbV' bags. For this purpose, four evaporation-shielded boxes

17   (V = 18 L) with moist sands with different water isotopic compositions were prepared and a

18   WIP in DDS mode (Volkmann & Weiler, 2014) was installed in each of the boxes to sample

19   their soil water vapor. We used a low-weight sampling setup that provided a constant air flow

20   of 150 mL/min with the small pumps described above (section 2.1). The incoming stream of

21   ambient air was dried by a 'Drierite' drying column (PN 26800, W. A. Hammond DRIERITE

22   Co. Ltd., Xenia, OH 45385, USA) and directed to the throughflow line of the WIP. The vapor

23   generated inside the WIP was withdrawn through the sampling line by a second small pump

24   with the same gas flow-rate. The stream of sampled vapor was directed to the isotope analyzer

25   (demanding 35 mL/min), using an open split for excess vapor (115 mL/min) near the

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1   analyzer's sample inlet port. Immediately after the direct measurement, the analyzer was

2   disconnected and the setup was used for directing the entire gas stream into the bags.

3   Additionally, ambient vapor data were collected with the isotope analyzer. Replicates of

4   sampled vapor were filled in bags, which were then analyzed two hours later. Calibration was

5   facilitated using in situ and bag measurements of those samples displaying extreme δ^2H

6   values, treating these in situ values de facto as standards. Note that this led to the reproduction

7   of the intermediate in situ values rather than liquid water values referenced to the VSMOW-

8   SLAP scale (Craig, 1961). The derivation of liquid water values from vapor isotope

9   observations has been described in Volkmann & Weiler (2014).

10   **2.4 Reusability of sampling bags**

11   **2.4.1 Flushing attempts**

12   To test the reusability of the bags, we applied the following flushing procedure. 'Al3-GbV'

13   and 'Al3s-GbV' bags were filled with pure N_2, evacuated immediately thereafter with a

14   LABOPORT® diaphragm vacuum pump (N810.3 FT.18, KNF Neuberger GmbH,

15   Munzingen, Germany) and filled again with pure N_2. On the next day they were evacuated

16   again, filled with pure N_2 again and evacuated one final time. After these preparatory steps, 3-

17   5 bag replicates were used for sampling vapor from sources both isotopically different and

18   identical to the ones that had been sampled before with the respective bags. The setup used

19   for this purpose was identical to the one described in Section 2.3 except that different

20   diaphragm gas pumps (BOXER 22K, Boxer, Ottobeuren, Germany) were used. Vapor

21   concentration and isotope data of the bags were recorded with a Picarro L2120-*i* 1, 3, and 7

22   days after vapor sampling.

23   **2.4.2 Conditioning**

24   In order to further improve the reusability of the bags we tested two ways of conditioning

25   previously used sampling bags. The first way was by filling a batch of bags with dry synthetic

1   air, leave them filled for at least one day, analyze their vapor concentration and isotope

2   signature with a Picarro L2120-*i*, evacuate them, fill them again, and repeat this cycle several

3   times. The second way was identical except that moist, isotopically homogeneous air was

4   used for filling and priming. In both cases the absolute vapor concentrations and the standard

5   deviations (SD) of isotope readings from repeated batch measurements were considered as

6   predictor for conditioning efficiency. Efficiency was then scrutinized by using the so-

7   conditioned bags for collecting vapor samples from isotopically diverse sources (setup details

8   in 2.3) followed by repeated analyses over the course of up to seven days. Again, calibration

9   was facilitated using in situ and bag measurements of those samples displaying extreme

10   isotope values. We report precision and accuracy as quality measures of the calibration

11   process. The precision is the SD of calibrated isotope readings while the accuracy is the

12   deviation of the calibrated mean of repeated measurements from the respective target value.

13   **3 Results**

14   **3.1 Effect of changing gas throughflow rates on the isotopic composition**

15   With increasing flow-rates through the WIP, the vapor content originating from the source

16   water decreased in the sampling gas (Figure 2). At the same time, the isotopic composition for

17   both isotope ratios under investigation changed, indicating that no equilibrium between the

18   source water and the provided dry gas stream was established inside the WIP. Such kinetic

19   fractionation effects could be observed at all flow-rates. They were stronger for δ^{18}O than for

20   δ^2H. The induced decreasing vapor contents were strongly correlated with decreasing isotopic

21   signatures. In the case of the WIP operated in DDS mode with proportional dilution and

22   throughflow rates, vapor content ranged from 10325 to 14432 ppmv, while the concurrent

23   uncalibrated isotope readings were in a range of -18.92‰ to -30.99‰ in the case of δ^{18}O and

24   -136.85‰ to -143.41‰ in the case of δ^2H. The heaviest values of these ranges correspond to

1   the settings originally proposed by Volkmann & Weiler (2014). These changes correspond to

2   change rates of 0.241‰/(mL/min) for δ^{18}O and 0.131‰/(mL/min) for δ^2H. Similar

3   observations were made for the case when dilution was set to zero at higher flowrates. Here,

4   the vapor content ranged from 12256 to 20041 ppmv while the uncalibrated isotope readings

5   varied between -30.35‰ and -39.13‰ in the case of δ^{18}O and between -143.23‰ and -

6   146.95‰ in the case of δ^2H. Here, the changes correspond to change rates of

7   0.117‰/(mL/min) for δ^{18}O and 0.049‰/(mL/min) for δ^2H. Vapor was always sampled from

8   the same liquid water source which had an isotopic composition of -9.64‰ and -66.84‰ for

9   δ^{18}O and δ^2H, respectively, referenced to the VSMOW-SLAP scale (Craig, 1961). All

10 coefficients of determination (R²) between vapor content and isotope readings were greater

11 than 0.99. At the target flow-rate of 150 mL/min throughflow and 0 mL/min dilution vapor

12 content was close to 12,000 ppmv at 20.8 °C (Figure 2).

13
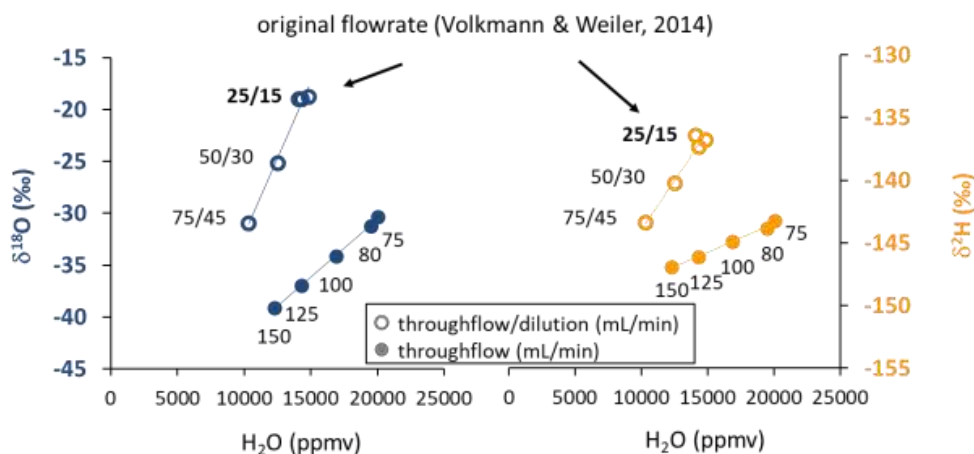
Figure 2. Scatterplot of water vapor isotopic composition (left: δ^{18}O, right: δ^2H) and vapor content obtained by varying gas throughflow rates with (open symbols) and without (closed symbols) dilution at a constant temperature. The numbers refer to the respective gasflow rates applied as throughflow/dilution or throughflow-only during the tests.

1 **3.2 Material and closure type selection**

2 **3.2.1 Dry air inflation**

3 **Diffusion-tightness and long-term storage effects.** During the test for diffusion-tightness

4 the water vapor content readings of the ambient air in the lab were in a range of 9000 – 18000

5 ppmv while inside the bags they were initially close to zero due to pure N_2 inflation. Over

6 time, these vapor pressure gradients were gradually levelled out with different rates. This is

7 qualitatively evident from the different slopes of the dashed lines (Fig. 3). PE spout-bags 'PE-

8 Sp' displayed the highest increase when after three days the vapor content had already

9 increased by ~7000 ppmv. Vapor content readings in the metalized spout-bags 'Al-Sp' were

10 ~4000 ppmv after three days. 3-layer metalized bags displayed the lowest vapor increase rate.

11 Design and thus air-tightness of these bags differed only with the type of septum or valves

12 used. The vapor content readings in the bag-types with the silicon blot ('Al3-Sil') were

13 ~1200 ppmv after four days.

14 Only for the better performing bag/valve combinations we extended the vapor content

15 measurements up to four weeks. After this period, mean vapor content readings in 'Al3-PC'

16 and 'Al3-GbV' bags were ~3000 ppmv and ~1450 ppmv, respectively. Mean vapor content

17 readings in 'Al3s-GbV' bags were ~420 ppmv after two weeks, which was the final value

18 possible for this bag type due to its smaller volume.

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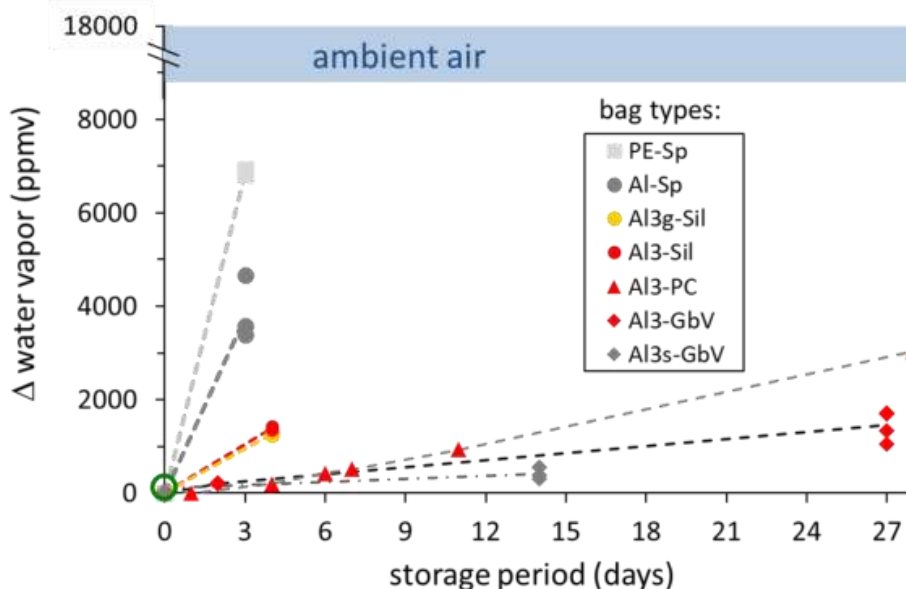
Figure 3. Time series of vapor content readings inside different bag types (closed symbols), initially

filled with pure N_2 (green open circle).

Spectral interference of outgassing material. In two bag types, deviations of the spectral

parameters from the pure N_2 signal were found, which were also correlated with the

respective isotope readings. The spectral line width variable indicative for gas composition

('h2o_vy') is 0.4309 ± 0.0015 ppm on our L2130-*i* analyzer for air containing oxygen at

atmospheric levels, while it is 0.4563 ± 0.0049 ppm for pure N_2. Vapor concentration of bag-

type 'Al3g-Sil' containing pure N_2, was below 2000 ppmv and should therefore plot at a

h2o_vy value of about 0.46 ppm like the bags 'Al3-Sil' (same material but different color),

but evolved towards 0.43 ppm. Simultaneously, apparent enrichment in heavy isotopes was

observed in 'Al3g-Sil' bags with an increase of around 80‰ in $\delta^{18}O$ and 150‰ in δ^2H,

compared to samples stored in 'Al3-Sil' bags.

In a commercially available 2.5L plastigas® bag (Linde) equipped with a gasbag valve (PN

11701150, Linde) (combination not featured in Fig. 3), we observed an apparent depletion in

1   δ^2H from -190‰ to -305‰ after 24h and to -360‰ after 72h. At the same time a spectral

2   variable recorded on our L2120-*i* analyzer, indicating potential contamination with organic

3   compounds ('organic_MeOHampl'), increased to 0.00760 ± 0.00014 after 24h and to 0.01005

4   ± 0.00012 after 72h. The initial value was 0.00095 ± 0.00026 which was also observed in

5   ambient air. We therefore excluded 'Al3g-Sil' and 2.5L plastigas® bags from further testing

6   due to the observed spectral interferences.

7   **3.2.2 "Climate chamber" experiment**
8   Temperature was quite stable inside the climate chamber as intended, ranging between 18.1°C

9   and 16.3°C. Relative humidity rose to > 97% within 6 hours and maintained on average at

10 99.5% throughout the remaining observation period, which translated to vapor mixing ratios

11 of 19972 ± 519 ppmv. Mean vapor contents from the source were 14365 ppmv during filling

12 and 12574 ppmv inside all bags after 20 days. Differences in mean vapor contents between

13 canned and un-canned bags were smaller than the respective variations within the two

14 batches. Isotope readings of all bags appeared to be enriched by 2.9‰ in δ^{18}O and 15.0‰ in

15 δ^2H relative to the source, again with negligible differences between the two batches (data

16 shown in supplement Fig. S1).

17 **3.3 Field application**
18 When comparing all isotope data of the direct in situ sampling from the sand boxes in the

19 field with the data from vapor sampled into the bags and measured 2 hours later, we found no

20 systematic bias towards congruent enrichment or depletion in heavy isotopes. Instead, all

21 isotope data of the bag measurements appeared to be shifted towards ambient air values by -

22 0.6 to +1.6‰ for δ^{18}O and +4 to -5‰ for δ^2H relative to their respective in situ measurements.

23 We used isotope readings of in situ and bag measurements from the samples displaying

24 extreme δ^2H values for calibration. Thereby, in situ values of the intermediate samples could

1   be reproduced with a precision of 0.15‰ and an accuracy of 0.8‰ for $\delta^{18}O$. The respective

2   numbers for δ^2H were 0.76‰ and 2.89‰ (Figure 4).
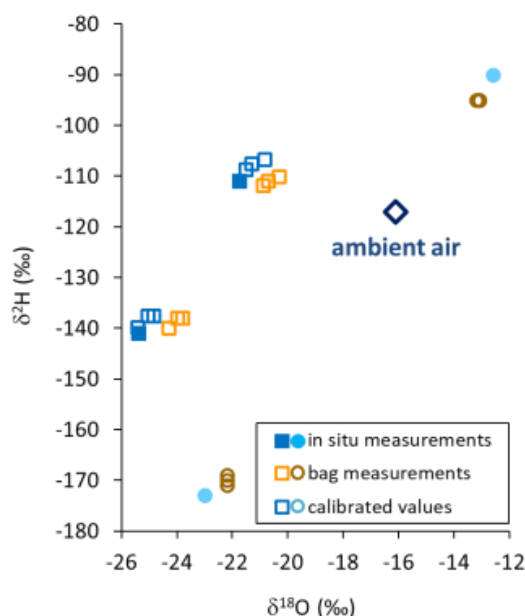
4   Figure 4. Isotope data from in situ measurements (filled symbols), raw bag measurements (orange and

5   brown open symbols), and calibrated in situ data calculated from bag measurements (blue and cyan

6   open symbols) using in situ (cyan closed symbols) and raw values (brown open symbols) of sources

7   displaying extreme δ^2H values. Ambient vapor at that day is displayed as a blue open diamond.

8   **3.4 Reusability of sampling bags**

9   **3.4.1 Flushing attempts**

10   Generally, isotope data unanimously trended towards the values recorded previously from the

11   respective sample bags. These trends increased over time and changes were proportional to

12   the differences between current in situ and previous bag measurements on the individual bag

13   level. The trends were consistent for all tested bag types and appeared to be independent from

14   concurrent ambient air values for both isotope ratios investigated (data shown in supplement

15   Fig. S2).

1 **3.4.2 Conditioning**

2 The two different conditioning methods (dry and moist) applied to previously used sample

3 bags yielded contrary results. Conditioning with dry synthetic air caused vapor content

4 readings to decrease stepwise down to 324 ppmv (Figure 5a) while isotope signatures became

5 more enriched (isotope data shown in supplement Fig. S3). Their SDs generally decreased but

6 remained above 2.9‰ for $\delta^{18}O$ and 18.8‰ for δ^2H (Figure 5b). In contrast, conditioning with

7 moist air resulted in vapor content readings to decrease to 6740 ppmv, which was in the order

8 of the level of conditioning. Isotope signatures of so-primed bags clustered around the

9 conditioning values (data shown in supplement Fig. S4) with SDs decreasing to 0.05‰ for

10 $\delta^{18}O$ and 1.07‰ for δ^2H after 4 to 5 steps (Fig. 5b).
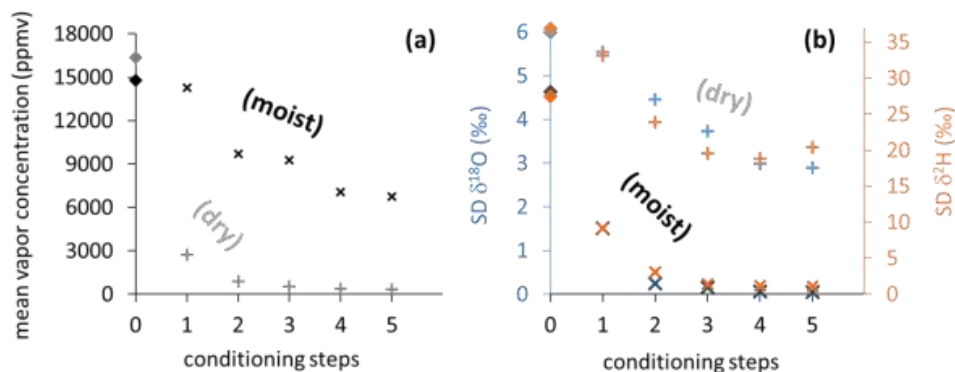

11
12

13 Figure 5. Vapor content readings (a) and SDs of isotope readings (b) from vapor sampling bags,
14 stepwise conditioned with dry synthetic air (light plus symbols) and moist air (dark cross symbols).
15 Light and dark diamond symbols on vertical axes represent mean values of pre-conditioning sample
16 measurements.

17 Re-using the conditioned bags for sampling vapor from isotopically diverse sources also

18 yielded contrasting results. SDs of isotope readings in bag replicates after dry conditioning

19 were larger than after moist conditioning. Repeated measurements generally resulted in a

20 decline of measurement precision and accuracy of mean isotope values (Fig. 6). Comparing in

1 situ values with bag measurements yielded no consistent picture in the case of dry

2 conditioning (Fig. 6a) whereas in the case of moist conditioning a bias towards the

3 conditioning values became evident which increased over time (Fig. 6b). Calibration for

4 reproduction of the intermediate in situ values worked better for moist- than for dry-

5 conditioned bags. This refers to the precision as well as to the accuracy (Tab. 2).
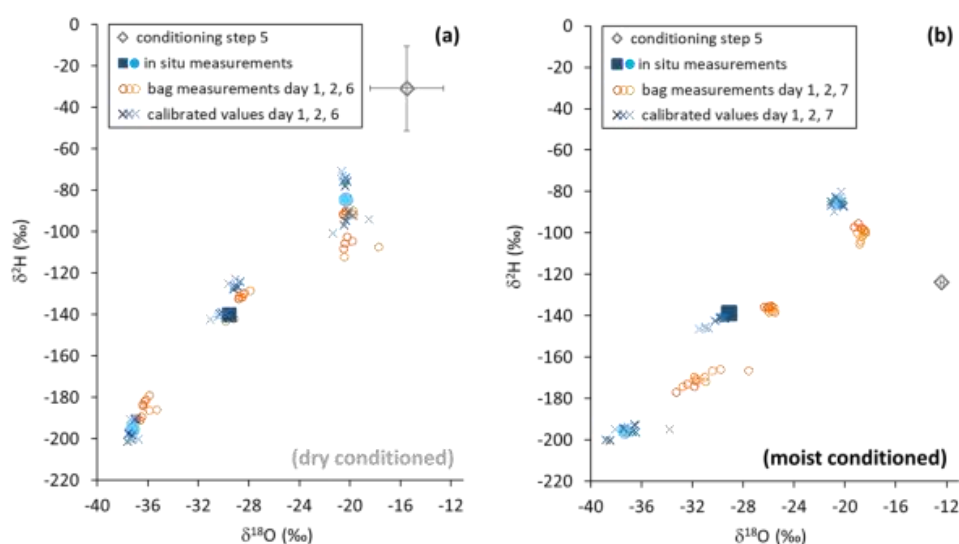
6

7 Figure 6. Isotope data from in situ measurements (filled symbols), gasbag measurements (open

8 circles), and in situ data calculated from gasbag measurements (asterisks) after conditioning with a dry

9 (a) and moist atmosphere (b). Pre-sampling levels are represented by gray diamonds. Note that error

10 bars (black) are smaller than the symbol in the case of moist conditioning (b).

11 Table 2. Conditioning effects on vapor stable isotope measurements from re-used sampling bags.

Day after sampling	Analysis iteration	Dry atmosphere conditioning				Moist atmosphere conditioning			
		$\delta^{18}O$ (‰)		δ^2H (‰)		$\delta^{18}O$ (‰)		δ^2H (‰)	
		precision	accuracy	precision	accuracy	precision	accuracy	precision	accuracy
1	1	0.58	-0.10	6.71	-7.16	0.25	0.41	0.41	1.93
2	2	0.70	-0.02	8.14	-7.89	0.30	0.70	0.75	2.59
6	3	0.87	0.51	10.36	-7.40				
7	3					0.30	1.91	0.40	7.18

12

1 **4 Discussion**

2 **Gas flow rate effects.** The goal of this study was to facilitate storage of in situ sampled vapor

3 without sensitive and costly analytical equipment in the field. The main applications we had

4 in mind were high frequent, minimally invasive in situ isotope measurements of water vapor

5 in soils and plant tissue as recently performed by e.g., Volkmann & Weiler (2014), Volkmann

6 et al. (2016a), Seeger & Weiler (2021), or Gessler et al. (2021). Their setups were based on

7 applying stable, yet low gasflow rates to their WIPs. These flowrates resulted in continuous

8 vapor samples assumed to be in isotopic equilibrium with the liquid water of interest. They

9 had been carefully adjusted to the employed analyzers' demands. However, in the intended

10 absence of an analyzer this necessity becomes obsolete. Therefore, we first tested the effect of

11 higher gasflow rates on the obtained vapor isotope signatures. We did so in order to facilitate

12 shorter filling times that would allow for higher filling frequencies of any containers of

13 sufficient volume (0.5 – 1 L) needed to collect and store vapor samples prior to lab-based

14 analyses.

15 Although pure N_2 as a carrier gas would have been cheaper, we used synthetic air in order to

16 maintain a consistent nitrogen-to-oxygen mixing ratio. This helped to avoid gas matrix effects

17 previously demonstrated for CRDS instruments (Gralher et al., 2016). We found that gasflow

18 rates higher than the ones previously applied (Volkmann & Weiler, 2014; Volkmann et al.,

19 2016) immediately resulted in incomplete equilibrium between the liquid water under

20 investigation and the obtained vapor sample (Fig. 2). This became evident by decreasing,

21 below-saturation vapor contents as well as lighter isotope readings. On the other side, we

22 found that even the highest gasflow rates applied in this study (150 mL/min) still yielded

23 vapor concentrations (~12000 ppmv @ 21°C) that are high enough to be within the analyzer's

24 optimum measurement range and thus enable sufficiently precise isotope measurements for

25 resolving natural variations (URL1). At the same time, a dilution of the obtained vapor stream

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1   is obsolete under such settings as the low obtained vapor concentrations impose no risk of

2   condensation. Of course, field sites being sampled for vapor while enduring temperatures that

3   are much higher than the lab temperature might yield too high vapor concentrations. Then

4   even higher flow rates or the re-application of a dilution flow is necessary for compensation

5   to avoid condensation and thus un-correctable isotope fractionation. This implies that like for

6   other indirect, minimally invasive methods (Volkmann & Weiler, 2014; Magh et al., 2022)

7   knowledge about the temperature or maintenance of its consistency at the points of vapor

8   sampling is mandatory for interpreting the obtained isotope data. Cases where temperature

9   differs considerably among sampling sites and/or the site of calibration standard preparation

10 require additional correction schemes considering the temperature-dependencies of water-

11 vapor isotope fractionation. This could be facilitated either via mathematical approaches

12 based on the dependencies described e.g., by Majoube (1971) or via empirical approaches

13 derived from sets of calibration standards that were collected while intentionally being

14 subjected to different, controlled temperatures. Calibration standards can be prepared e.g., by

15 installing WIPs in evaporation-shielded, sand-filled boxes wetted with water of known

16 isotopic composition as detailed in Volkmann & Weiler (2014).

17 The changes in isotope readings and thus deviations from equilibrium were smaller for δ^2H

18 than for $\delta^{18}O$ in absolute numbers (10.1‰ vs. 20.21‰, respectively) and even more so in

19 relation to naturally occurring isotope variations, where changes usually exhibit an 8:1 ratio in

20 meteoric waters (= slope of the GMWL, Craig, 1961). Therefore, in situ isotope assays

21 relying on discrete vapor sampling for later analysis with a setup similar to the one foreseen

22 here, have to ensure precise control of the applied gasflow rates for samples and co-measured

23 standards in order to comply with the paramount Principle of Identical Treatment (Werner

24 and Brand, 2001). If the isotope ratio under investigation is optional, we recommend

25 interpreting hydrogen rather than oxygen isotope ratios given the lower susceptibility

1   regarding gas flow rate effects and thus a more favorable signal-to-noise ratio. In this context,

2   it is quite convenient that labeling studies are more cost-efficient when using deuterium as

3   tracer rather than oxygen-18 (Magh et al., 2022).

4   Flowrates through the probes, exceeding previously recommended settings (Volkmann &

5   Weiler, 2014) immediately resulted in changes of vapor concentration and isotope readings

6   (Fig. 2). We therefore argue that neither the previous recommended nor our newly selected

7   settings result in complete isotopic equilibrium. Hence, both settings require precise control of

8   flowrates as any uncertainty in flowrate settings translates to systematic errors in isotope

9   readings. These errors are considerably higher at lower flowrates and higher for $\delta^{18}O$ than for

10 δ^2H. Aiming at lower flowrates in order to reliably achieve equilibrium readings appears

11 impractical for two reasons. Firstly, the employed analyzer's gas flow demand defines the

12 minimum total gas flow. A workaround applying higher dilution flowrates would yield

13 varying vapor concentrations and thus vapor concentration effects as can be seen from the

14 different isotope readings observed for 75mL throughflow rate with or without dilution (Fig.

15 2) thus potentially introducing additional errors. And secondly, applying lower flow rates

16 contradicts the study aim of shorter filling times and thus higher sample collection

17 frequencies and achievable temporal resolution.

18 **Material and closure type selection.** Our purpose was to find an inexpensive, yet reliable

19 vapor sample container as an alternative to commercially available gasbags, which we found

20 to be insufficient for our purposes either due to their large size or due to their degrading

21 closure type. Therefore, we had inflated also other types of sample bags with pure, dry

22 nitrogen gas. We found that only those combining laminated aluminum (Al) foil bodies and

23 metal screw-lock valves yielded useful barriers against ambient vapor pressures (Fig. 3).

24 These bags are mass products, originally produced for storing food or cosmetics and are much

25 cheaper than existing diffusion-tight containers from specialized suppliers. All other tested

1   combinations of bag materials and locks failed to prevent intrusion of ambient air which is

2   crucial for the storage of vapor samples. This corresponds to the finding of a previous study

3   where Al-laminated bags also performed best in avoiding evaporation from soil samples

4   (Gralher et al., 2021). Although the number of water molecules of these samples were three

5   magnitudes higher than in our study we were not surprised to find Al-laminated bags again

6   ranking best in material suitability.

7   Interestingly, not only the material but also the color of the material coating the diffusive

8   barrier appeared to play a role. Clearly, different colors are a result of different chemical

9   complex formulas used in the production and dyeing process. Unfortunately, they seem to

10 come with different outgassing properties and spectral interference potentials regarding the

11 intended isotope analyses. This issue always needs to be checked in advance. The presence of

12 certain organic compounds in a given gas sample may flaw laser-based isotope readings

13 (Brand et al., 2009; Hendry et al., 2011), some of which can be identified by changes in the

14 spectral parameter readings of the CRDS isotope analyzer.

15 In the "climate chamber" experiment, we actually sampled vapor in order to test how its

16 concentration would change when the container is subjected to extreme moisture conditions

17 over a longer time period. Unexpectedly, we found that vapor concentrations slightly

18 decreased over time (Fig. S1). This clearly contradicted the applied vapor concentration

19 gradient relative to ambient conditions. Further, the extent of decrease was not affected by the

20 canning of some of the containers as typically proposed for sampling water for dissolved gas

21 analyses. Therefore, we argue that not only were the employed containers sufficiently

22 diffusion-tight against ambient meteorological forcings but also a fraction of the sampled

23 vapor must have been absorbed by the inside coating of the containers (which had been

24 repeatedly flushed with a dry atmosphere prior to vapor sampling). We can only speculate

25 that mixing with previously absorbed vapor led to the observed, fairly uniform enrichment in

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1   heavy isotopes for both, δ^{18}O and δ^2H. Presumably, the increase in vapor concentration inside

2   Al-laminated bags following pure nitrogen gas inflation in the first part of the material tests

3   (Fig. 3) was mainly due to release of previously absorbed vapor rather than via diffusive

4   intrusion from ambient.

5   **Field application.** This "conditioning" effect from previous filling or exposures would also

6   explain why isotope data from the field-derived samples unanimously appeared to shift

7   towards ambient air in dual-isotope space (Fig. 4). This was likely because all bags used for

8   this part of our study had been freshly prepared. In doing so, during valve installation they

9   had all been exposed to the same ambient air (in the lab) with a homogenous vapor isotopic

10   composition. Apparently, that air was isotopically quite similar to the one recorded during the

11   filling of the field samples. The proportional, systematic shift of isotope values allowed for a

12   robust calibration scheme to be applied. This scheme used in situ and bag measurements of

13   those samples displaying extreme δ^2H values. It reproduced the intermediate in situ isotope

14   values representative for sampling of the bags with a precision sufficient for resolving

15   naturally occurring variations of meteoric waters. The observed discrepancies between in situ

16   and bag measurements indicate that the Principle of Identical Treatment needs to be followed

17   also in terms of ambient vapor isotopic composition when preparing a batch of sample bags

18   for the collection of unknown samples as well as co-measured standards. Additionally, we

19   recommend using bags of identical size and inflating them to the same volume in order to

20   maintain a uniform ratio of sample volume to internal wall area.

21   **Reusability of sampling bags.** Initially, we had used dry air or pure nitrogen gas in an

22   attempt to erase the signal of previous fillings and thus avoid carryover effects when reusing

23   the sampling bags. However, this procedure did not produce the desired outcome. Repeated

24   measurements from identically filled bags still displayed a clear isotope pattern of the

25   previous fillings (Fig. S2). The range of this pattern must be associated with the measurement

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1   uncertainty if the latest filling had been an unknown sample and would thus prevent resolving

2   natural isotope variations. It was established before the first measurement after five days and

3   then seemed to persist.

4   Therefore, we tried to find a different, easy-to-implement flushing or conditioning routine that

5   would repeatedly enable precise vapor isotope measurements using our sampling bags. For

6   this purpose, we systematically compared the impact of dry to moist conditioning on the

7   measurement precision and accuracy of vapor from isotopically diverse sources. From

8   experience, we knew that room air vapor isotope signatures are usually quite persistent on

9   shorter timescales as necessary for filling batches of sampling bags using high-flowrate

10   devices such as vacuum pumps. Using this unlimited resource, we were able to establish a

11   conditioning routine that is easy to reproduce and enables the precise reproduction of in situ

12   isotope values following impertinent calibration schemes (Tab. 2). In this context, the low SD

13   of isotope readings from moist-conditioned bags proved to be a far better predictor of

14   conditioning efficiency than the low vapor concentration of dry-conditioned bags. We

15   therefore recommend conditioning entire batches of sample bags simultaneously with a moist,

16   isotopically homogeneous atmosphere prior to each isotope sampling campaign.

17   Further, we emphasize that for any given vapor sample an isotopic shift must be expected

18   between collection and subsequent, lab-based analysis. This shift became apparent e.g.,

19   during field application (Fig. 4) and the conditioning procedure (Fig. 6). It is characteristic

20   and implicit to our method. However, it is proportional relative to the priming signal.

21   Herewith, it becomes manageable through co-measuring calibration standards, prepared in

22   identically pre-treated bags.

23   Our conditioning routine was performed manually and its efficiency checked after every

24   conditioning iteration. However, we are confident that it can be easily automated for future

25   applications and its efficiency eventually assumed reliably without measurements as a matter

1   of experience. Further, it seems that for the SD being a meaningful parameter for conditioning

2   efficiency, the conditioning time steps need to match the projected sample storage time. This

3   also calls for automating the conditioning procedure.

4   We believe that the otherness of our method holds several advantages relative to previous

5   approaches for the collection and analysis of discrete vapor samples. In contrast to Havranek

6   et al. (2020, 2022), the non-automation allows for maximum temporal flexibility regarding

7   experimental designs. The spatial distribution of sampling sites is not limited by connectivity

8   to a central sampling system and associated tubing lengths. As all employed components are

9   small and light-weight, they can easily be deployed even in terrains that are rather difficult to

10   access. In contrast to Magh et al. (2022), the achieved precision and accuracy (Tab. 2) allow

11   for the resolution of even fine-scaled environmental isotope variations. Practically, our

12   method does not require any tools, not to mention specialty tools during handling or

13   refurbishing of crimp-sealed glass bottles and the lack of consumables such as septa makes it

14   cost-efficient. The combination of the screw-lock mechanism and a sufficiently large sample

15   volume is forgiving as it allows for multiple measurements from one sample bag. Also,

16   flushing and re-filling are possible without wearing of the closing mechanism. Using

17   evacuated, inflatable containers renders any in-field flushing obsolete thus reducing sampling

18   time and increasing feasible temporal resolution. Further, it eliminates the risk of breaking

19   glass during transport and handling. Finally, our method does not require additional gas

20   sources during analysis and allows for directly interpretable measurement readings without

21   the need to identify the relevant isotope data section via derivation of the vapor concentration

22   readings.

23   **5 Conclusions**

24   We present a new method for the collection of discrete water vapor samples in the field and

25   subsequent storage and isotope analysis in the lab. After systematic material testing, we

1   identified the optimum combination of inflatable bag and closure type that guarantees air-

2   tightness and avoids sample contamination by material outgassing. Our custom-made method

3   uses off-the-shelf components only and is easy to use, cost-efficient, sustainable and allows

4   for multiple measurements. Further, it allows for direct interpretation of the obtained isotope

5   results. The achieved precision and accuracy are not only suitable for labelling experiments

6   but also sufficient for resolving natural variations of water stable isotope signatures.

7   Preparation and co-measurement of calibration standards are indispensable for our approach

8   in order to correct for the implicit shift of the obtained isotope signal, induced by the

9   mandatory conditioning procedure. We are convinced that the conditioning procedure can be

10   automated, which would further reduce the per-sample workload when re-using sampling

11   bags. The presented approach allows for collecting vapor samples from soil matrix and plant

12   tissues in remote settings without an isotope analyzer in the field. The method therefore

13   widens the applicability of minimally invasive in situ approaches of matrix-bound water

14   stable isotope observations. We are therefore confident that our method will open new

15   observatory paths and thus contribute to novel insights in hydrology, soil science, plant

16   physiology and related disciplines.

Author contribution

18   BH, SS, MR and MW designed the first part of the experiments, BH and SS carried them out.

19   BH and BG designed the second part of the experiments, carried them out. BH, BG and MW

20   analysed and interpreted the data. BH and BG prepared the manuscript with contributions

21   from all co-authors.

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