- <sup>1</sup> *In-situ* unsaturated zone water stable isotope (<sup>2</sup>H and <sup>18</sup>O)
- 2 measurements in semi-arid environments: A soil water
- 3 balance.
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## 1 Abstract

Stable isotopes (deuterium, <sup>2</sup>H, and oxygen-18, <sup>18</sup>O) of soil water were measured in the field 2 using a liquid water isotope analyzer (tunable off-axis integrated cavity output spectroscope, 3 4 OA-ICOS, LGR) and commercially available soil gas probes (BGL-30, UMS, Munich) in the 5 semi-arid Cuvelai-Etosha Basin (CEB), Namibia. Results support the applicability of an in-6 situ measurement system for the determination of stable isotopes in soil pore water. High 7 spatial and temporal resolution was achieved in the study area with reasonable accuracy and 8 measurements were in agreement with laboratory-based cryogenic vacuum extraction and 9 subsequent cavity ring down laser spectroscopic isotope analysis (CRDS, L2120-i, Picarro Inc.). After drift and span correction of the *in-situ* isotope data, precision for over 140 10 measurements taken during two consecutive field campaigns (June and November, 2014) 11 were 1.8 ‰ and 0.48 ‰ for  $\delta^2 H$  and  $\delta^{18} O$ , respectively. Mean measurement trueness is 12 determined using quality check standards and was 5 ‰ and 0.3 ‰ for  $\delta^2 H$  and  $\delta^{18} O$ , 13 14 respectively. The isotope depth profiles are used quantitatively to calculate a soil water 15 balance. The contribution of transpiration to total evapotranspiration ranged between 72 % and 92 %. Shortly after a rain event, the contribution of transpiration was much lower with 35 16 % to 50 %. Potential limitations of such an *in-situ* system are related to environmental 17 conditions which could be minimized by using a temperature controlled chamber for the laser 18 spectrometer. Further, the applicability of the system using previously oven dried soil material 19 might be limited by physicochemical soil properties (i.e. clay minerals). Uncertainty of the *in*-20 21 situ system is suggested to be reduced by improving the calibration procedure and further 22 studying fractionation effects influencing the isotope ratios in the soil water, especially at low 23 water contents. Furthermore, the influence of soil respired CO<sub>2</sub> to isotope values within the 24 root zone could not be deduced from the data.

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#### 1 **1 Introduction**

2 Water stable isotopes have been successfully used for decades as powerful proxies for the 3 description of water fluxes such as infiltration in humid (Saxena, 1987) or semi-arid regions (e.g., Dincer et al., 1974; Allison and Hughes, 1983), evapotranspiration (e.g., Barnes and 4 5 Allison, 1988, Wang et al., 2012; Dubbert et al., 2013; Skrzypek et al., 2015), plant root water uptake (e.g., Dawson and Ehleringer, 1991; Ehleringer and Dawson, 1992; Dawson, 1996; 6 7 Yang et al., 2010), hydraulic redistribution (Dawson, 1993; Caldwell et al., 1998), and in 8 catchment hydrology (e.g., Sklash and Farvolden, 1979; Richard and Shoemaker, 1986; 9 Tetzlaff et al., 2007; Kendall and McDonnell, 2012). Soil water stable isotopes provide 10 information on flow path ways and mixing within the unsaturated zone (e.g., Gazis and Feng, 2004; Stumpp and Maloszewski, 2010; Garvelmann et al., 2012; Mueller et al., 2014). Soil 11 12 water stable isotope studies were also used to reduce parameter uncertainty in unsaturated zone model approaches (Sprenger et al., 2014). Further work has been done to use soil water 13 14 stable isotopes for quantitative recharge estimations (e.g., Beyer et al., 2015) which are actively discussed in early and recent reviews (e.g., Allison et al., 1994; Scanlon et al., 2002, 15 16 Königer et al., 2015). But, the usefulness of evaporation profiles to determine recharge rates 17 remains debatable (Herczeg et al, 2011).

18 In most unsaturated zone studies, manual removal of soil samples and a subsequent extraction 19 of soil water in the laboratory was necessary using either vacuum extraction (e.g., West et al., 20 2006; Koeniger et al., 2011; Orlowski et al., 2013), equilibration (e.g., Wassenaar et al., 2008), mechanical squeezing, azeotropic distillation or centrifugation methods (e.g., Walker 21 22 et al., 1994; Kelln et al., 2001). These methods cause both disturbance to the integrity of the 23 natural soil system and possible evaporation during the sampling procedure. The latter is 24 especially important for dry soils. Hence, soil water extraction techniques are labor intensive and expensive which is limiting the use of stable isotopes compared to the other variables 25 26 such as soil moisture or matrix potential measurements. Indeed, there are suction cup 27 installations which allow a removal of soil water non-destructively but they are not applicable 28 in (semi-) arid environments. This is especially true during the dry season where vapor 29 transport (i.e. evaporation) is the dominant driver for water fluxes in the unsaturated zone but 30 is much less studied than the liquid water component (Soderberg et al., 2012). In this context, the determination of stable isotopes from sampling the vapor of the pore space appears useful. 31

Principles to sample soil air for the determination of stable isotopes were already indicated by 1 2 Allison et al., (1987) and Schack-Kirchner et al., (1993). An attempt to measure stable isotopes in a sandy loam using a liquid water analyzer (OA-ICOS, Los Gatos Research, DLT-3 100) is presented in a recent review by Soderberg et al., (2012). The first study monitoring 4 5 stable isotopes in-situ in unsaturated sandy soil water under laboratory conditions made use of poly-propylene (PP) membranes (Rothfuss et al., 2013). Measurements were performed with 6 7 a cavity-ring-down spectrometer (CRDS) (L1102-I, Picarro, CA, USA) calibrated with liquid 8 water injections using a vaporizer unit. More recently they presented a long-term application 9 of their in-situ system under laboratory conditions (Rothfuss et al., 2015). Volkmann and 10 Weiler (2014) developed custom built poly-ethylene (PE) probes with an equilibration 11 chamber allowing additional mixing of the vapor to prevent condensation in the sample line. 12 They further proposed a sophisticated system with a CRDS device (Picarro L2120-i, CA, 13 USA) calibrated with standards added to previously oven dried substrate from their study site.

14 In the present study in-situ usability of commercially available PP-membranes (BGL-30, 15 Umweltmesssysteme, Munich) using a liquid water analyzer (Los Gatos Research, DLT-100) for a determination of stable isotopes in soil pore water is demonstrated. The proposed system 16 17 is applied under harsh remote field conditions in a semi-arid environment in soil with moisture contents ranging from 0.3 to 6 %. In comparison to earlier in-situ studies this study 18 19 presents I.) An improved automatization with minimal technical modification of 20 commercially available parts. II.) We demonstrate that *in-situ* measurements are comparable 21 to data derived from cryogenic vacuum extractions. But also, that there are differences at the 22 transition to the atmosphere which will be discussed. Such a comparison seems to be useful 23 since the cryogenic soil water extraction allows a direct determination of the soil water isotopic composition. III.) Finally, derived isotope data is used quantitatively to determine the 24 25 soil water balance of a deep sandy unsaturated zone and for the partitioning of transpiration 26 and evaporation.

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## 28 2 Study Site and Methods

The study area is located in northern central Namibia and is part of the Cuvelai-Etosha-Basin (CEB). The whole surface water catchment has an extent of about 173,000 km<sup>2</sup> where the northern part (approx. 52,000 km<sup>2</sup>) belongs to Angola and the southern part to Namibia. This sedimentary basin is divided into four major sub-basins called Iishana, Niipele, Olushandja

1 and Tsumeb and can be further separated into different drainage zones. Measurements were 2 conducted within the eastern sand zone close to the township of Elundu as indicated in Figure 1. The assignment of the catchment and its sub-basins is based on geography, population 3 distribution and water infrastructure (Dragnich et al., 2004). The main shallow aquifer system 4 5 in the CEB is a multilayer aquifer system in the Andoni formation with a thickness of 6 to 80 m. The main groundwater flow is towards the Etosha pan with an average gradient of 0.2 % 6 7 (Christelis and Struckmeier, 2001). Beside the shallow aquifer, recent studies identified an 8 area of 500 km<sup>2</sup> potentially containing fresh groundwater at a depth of 200 m named the 9 Ohangwena II aquifer (Lindenmaier and Christelis, 2012; Lindenmaier et al., 2014). 10 Groundwater recharge mechanisms concerning both the shallow and the deep aquifer are not 11 yet fully understood. The shallow aquifer system consists partly of freshwater lenses on 12 brackish to saline groundwater mostly in the Iishana region. Perched discontinuous aquifers 13 are found in the eastern part of the basin that develop on clay lenses in the subsurface and are 14 managed through hand-dug wells.

The climate in the CEB is semi-arid with a rainy season lasting from November to April and a dry season from May to October. Annual average potential evaporation can reach up to 3,000 mm and decreases slightly from north to south (Mendelsohn et al., 2013). Annual average rainfall ranges between 250 and 600 mm, most of the rain is falling in January and February (Mendelsohn et al., 2013). The eastern part of the catchment receives more consistent rainfall whereas rain in the western part is less predictable.

21 The investigated site is forested, predominantly vegetated with Combretum collinum, Acacia 22 erioloba and Baikiea plurijuga. The deep Kalahari sand can reach a depth of over 40 meters and has high saturated hydraulic conductivity  $(2.3 - 2.4 \text{ m day}^{-1})$  determined with double-ring 23 24 infiltration experiments, high porosity (0.4) and low field capacity (~ 3.5 %). Sampling and measurements were conducted during two field campaigns. The first field campaign was 25 carried out between June 9<sup>th</sup> and 15<sup>th</sup>, 2014 and the second between November 15<sup>th</sup> and 22<sup>nd</sup>, 26 27 2014. To determine heterogeneity of infiltration and evaporation processes and to evaluate an in-situ approach determining stable isotopes in soil water nine plots within an area of 28 9,000 m<sup>2</sup> were investigated. During the first campaign soil gas probes were installed at depths 29 30 of 2, 5, 10, 15, 20, 25, 30, 40 and 50 cm. Two plots were established with different vegetation 31 characteristics such that one was vegetated with shrubs and the other was exposed without any vegetation. During the second field campaign probes were installed at depths of 2, 5, 7.5, 32

1 10, 12.5, 15, 17.5, 20, 25, 30, 40, 50, 60, 70, 80, 90 and 100 cm to reach a maximum 2 resolution especially for the top layer. Soil moisture measurements were conducted with a 3 time domain reflectrometry system (TDR, EasyTest, Poland) at the beginning of each 4 measurement cycle with the same resolution. In addition to the *in-situ* measurements samples 5 were collected in head space glass vials, crimp sealed to avoid evaporation and the soil water 6 extracted in the laboratory. Samples were transported via aircraft to the laboratory of the 7 Federal Institute of Geosciences and Natural Resources (BGR) in Hannover, Germany.

8 In the laboratory grain size analyses was conducted on 10 g of soil material from the extracted 9 soil samples with the method proposed by Altuhafi et al. (2013). Soil water was extracted 10 cryogenically using a slightly modified method of the cryogenic-vacuum extraction described by Koeniger et al., (2011). A custom built isolated aluminium block is heated to 105 °C 11 instead of a water bath. The sample vials are entered into the hot aluminium block to 12 13 evaporate the water sample. Each sample was evacuated at -3 mbar vacuum and extracted for 14 15 min. The extracted water samples were subsequently measured with a cavity ring-down spectrometer (CRDS, model L2120-i, manufactured by Picarro Inc.). <sup>18</sup>O/<sup>16</sup>O and <sup>2</sup>H/<sup>1</sup>H 15 isotope ratios are normalized on the international  $\delta$ - scale and expressed as parts per thousand: 16

17 
$$\delta = \left[ \left( \frac{R_{sample}}{R_{reference}} \right) - 1 \right]$$
 [1]

where  $R_{sample}$  (-) denotes the  ${}^{18}O/{}^{16}O$  isotope ratio (respectively  ${}^{2}H/{}^{1}H$ ) of a water sample and 18 R<sub>standard</sub> (-) those of the Vienna Standard Mean Ocean Water (VSMOW) (Coplen, 2011). All 19 20 values where corrected for drift and memory applying the method proposed by van Geldern and Barth (2012). Precision for long-term quality check standards are better than 0.2 ‰ and 21 22 0.8 % for water samples, but an additional error for sandy soils needs to be considered which can be better than 0.8 ‰ and 4 ‰ for  $\delta^{18}$ O and  $\delta^{2}$ H, respectively as suggested by Königer et 23 24 al. (2011). The standard deviation determined from replicate samples (three per extracted soil 25 sample) is used as an additional analytical error. Subscripts are used to distinguish between either the *in-situ* (I) and the cryogenically (C) derived isotope values in the remaining text. 26

For the determination of  $\delta^2 H_I$  and  $\delta^{18}O_I$ , commercially available soil gas probes (BGL-30, Umweltmesssysteme, Munich (UMS)) with a diameter of 9.4 mm and a length of 300 mm were connected to an integrated cavity off-axis liquid water isotope analyser (OA-ICOS, Los Gatos research, DLT100). This device does not measure continuously and it is mandatory to maintain the response from the laboratory autosampler, which is here done via the RS-232

interface of a Laptop computer and a computer code that responds to the requests of the laser 1 2 spectrometer (Figure 2). Each soil gas probe is separated from the main transport line with a valve (Clippard Minimatic, USA). The valves are switched by a high or low signal from the 3 data terminal ready (DTR) and request to send (RTS) pins of the modified USB-to-RS232 4 5 converter. A reduction of the electric tension output of the converter is necessary which is done using a resistor of 220  $\Omega$ . To secure the converter against inverse currents a common 6 7 diode is installed in reverse direction before the opto-isolater (ULN2303). The opto-isolater is 8 necessary to eliminate voltage spikes from the +12 V power supply. To avoid over heating of 9 the analyser during the day time by direct sun radiation, a gazebo was positioned above the 10 loading area of the pick-up truck where the analyser is mounted. Power was supplied to the 11 entire system using a common 230 V generator (Single Phase 2.5 kW, Petrol, Schultz).

12 Four repetitive measurements at each depth were performed during the first campaign. During 13 the second campaign six consecutive measurements were performed at each depth. A 14 measurement cycle consisted of three steps: i.) a flushing phase where the cavity is evacuated, 15 ii.) the sample intake opening a particular valve and iii.) the measurement of the sample. Flushing introduces a vacuum of 0.1 torr or less. The sample intake is controlled by valves 16 17 which are opened for 10 s for each measurement while allowing a volumetric flow rate between 95 and 110 ml/min. The transported gas volume is measured with a flow rate 18 measurement device (Analyt-MTC, 0-200 ml min<sup>-1</sup>). The probe and the transport lines to the 19 analyser have a volume of approximately 40 ml. The sample lines are made of steel and are 20 connected with Swagelok<sup>®</sup> connectors. After six consecutive measurements at one depth, the 21 22 sampled soil volume is approximately 120 ml. Assuming that the soil volume around the 300 23 mm long probe is sampled equally over the whole length, a diameter of 1cm around the probe will be directly affected by the uptake of vapor via the probe. Hence the top layer is measured 24 25 with reasonable resolution for this particular setup. The measurement of a 1 m deep profile considering 16 different depths with six repetitions and a resolution down to 2.5 cm for the 26 27 top 20 cm takes about 4.5 hours. The OA-ICOS device needs an additional warm up of about 28 two hours in order to obtain reasonable precision.

During the second field campaign three transects are measured consisting of three plots to characterize the spatio-temporal variability after two consecutive rain events. Each transect is 150 m apart as well as each profile within one transect. Transects consist of bare plots as well as vegetated plots (Table 2). However, lateral roots could be found at each plot.

Standard preparation was done using 200 g of previously oven dried (at 105 °C for at least 24 1 h) sandy substrate for each of the four standards (Table 2). The dried soil material has been 2 transported in aluminium bags (WEBA bags®, Weber Packaging GmbH, Güglingen, 3 Germany) from the laboratory of the University of Windhoek to the field site and were then 4 5 spiked directly in the field with a volume of 5 ml with water of known isotopic composition (Table 1) before the experiment commenced on the day of measurement. Normalization to the 6 7 international scale is done using one low standard (HGLA) and one high standard (HMER). 8 In addition, one standard for drift correction (HDES) and a quality check standard (HLAU) 9 were used. The quality check standard is a water of known isotopic composition that is treated 10 as an unknown sample. The difference between the known value of HLAU and the measured 11 isotope value of HLAU expresses the measurement trueness of the system (Barwick and Prichard, 2011). All standards were measured at the beginning of each experimental 12 13 sequence; additionally HDES and HLAU were measured at the end of each sequence. Isotope 14 values of the used standards are illustrated in Table 1. The standards were used only for two 15 consecutive measurement series and then new standards were prepared. Calibration standards 16 were kept in flasks with a diameter of 2 cm and a length of 50 cm, in which the soil gas 17 probes were stored and sealed to avoid evaporation.

### 18 Soil water balance

19 Recharge rates were determined in mm/y using a simple empirical relationship applied to the 20 data of the deep isotope depth profile (> 4 m). Therefore, the difference between the 21 deuterium excess of the LMWL and the intercept of the linear regression to isotope data of 22 deep soil water is defined as  $\delta^2 H_{shift}$ . This relationship is proposed by Allison et al., 1984 and 23 for  $\delta^2 H$  and  $\delta^{18}O$  given here as in Clark and Fritz, (1997):

$$24 \qquad R = \left[\frac{22}{\delta^2 H_{shift}}\right]^2$$
[2]

25 and

$$26 \qquad R = \left[\frac{3}{\delta^{18} O_{shift}}\right]^2 \tag{3}$$

Assuming steady state soil evaporation is calculated from the isotope depth profiles using ananalytical solution (Allison et al., 1984).

1 
$$E = (1 - h_a) N_{sat} \tau D_V \frac{(p - \theta_v)}{\rho z_{ef}}$$
[4]

Thus, evaporation can be determined providing the relative humidity  $h_a$  [-], the saturated water vapor pressure  $N_{sat}$  [*P*], the tortuosity with  $\tau$ =0.67 [-], the diffusitivity of water vapor in air  $D^v = 24 * 10^{-6}$  [*a*], the density of water  $\rho$  [*ML*<sup>-3</sup>], the porosity *p* [-] and the soil water content  $\theta_v$  [ $L^3L^{-3}$ ]. Calculations were conducted for a mean ambient temperature of 20 °C and 50 % relative air humidity and further with 27 °C and 60 % for Campaign 1 and Campaign 2, respectively. The depth of the evaporation front  $z_{ef}$  [L] can be determined by an exponential fit to the isotope depth profiles (Allison et al., 1985).

9 
$$\delta = \delta_{res} (\delta_{ef} - \delta_{res}) exp^{-z/z_{ef}}$$
[5]

10 The data of the isotope depth profile  $\delta$  is calculated from the fitted parameters  $z_{ef}$ , the isotope 11 value of the reservoir  $\delta_{res}$  and the isotope ratio at the evaporating front  $\delta_{ef}$ . This will give a 12 quantitative estimation of the soil water balance based on the presented isotope data. In 13 addition  $z_{ef}$  is determined from the grain size distribution as follows (Or et al., 2013):

14 
$$z_{ef} = \frac{2\alpha}{\rho g} \left( \frac{1}{r^1} - \frac{1}{r^2} \right)$$
 [6]

15 with the surface tension of water  $\alpha$  [*M T*<sup>-2</sup>] calculated at 24 °C, the gravity acceleration *g*, the 16 minimum r<sup>1</sup> [L] and the maximum r<sup>2</sup> [L] grain size of the soil.

## 17 3 Results

#### 18 Campaign 1

19 The first field campaign was conducted shortly after the rainy season (June 2014). No rain 20 occurred during that campaign. The texture (medium sand) was uniform throughout the depth 21 profile. No changes in texture were observed for the other investigated plots. Temperature and 22 humidity variability within the sampling period between daytime (~30 °C<sub>max</sub> and 15 %<sub>min</sub>) and 23 night (~ 9 °C<sub>min</sub> and ~ 90 %<sub>max</sub>) was high during the first campaign.

During the first campaign (June 15<sup>th</sup>, 2014) measurements were taken at two plots (E1.1, E1.2) at a distance of 25 meters apart on the same day. The measurement at E1.1 started at 09:30 and at 16:00 for plot E1.2. Plot E1.1 was not vegetated and had a thin soil crust in the top centimeter. Volumetric water content increased from 0.3 % at the top to 4.1 % at 50 cm depth (Figure 3, left). Plot E1.2 was vegetated, a dense root mat was visible in the upper 10

cm. In contrast to E1.1, water contents were much lower increasing from 0.3 % at the surface 1 2 to 0.7 % at 50 cm depth (Figure 3, center). The isotope depth profiles were of similar shape and magnitude for both profiles with a maximum at 10 cm and an exponential decline down 3 4 to the maximum depth. Due to low water contents in the upper 15 cm of the vegetated plot, 5 not enough water could be extracted with the cryogenic extraction method. However, at 10 cm depth the same pattern as for profile E1.1 could be observed. The shapes of the isotope 6 depth profiles were different for  $\delta^{18}$ O and  $\delta^{2}$ H within the upper 5 to 10 cm. For instance, the 7 maximum isotope values of  $\delta^2 H_c$  and  $\delta^{18}O_c$  were at 15 cm. In contrast, the maximum isotope 8 values of  $\delta^2 H_i$  and  $\delta^{18} O_i$  were at 10 cm. 9

10 As depicted in Figure 4, the deuterium excess for both profiles showed a maximum at 10 cm depth and exponentially declines down to 50 cm. At the vegetated plot, deuterium excess 11 12 values were positive within the top 7.5 cm. Comparing deuterium excess values of the 13 cryogenic extraction with those from the *in-situ* measurements, it could be found that they 14 agree well for the bare soil plot, but not at 10 cm and 15 cm depth. In contrast, all values measured in the field below 10 cm of the vegetated plot, which had low water contents (< 1 15 16 %), were shifted towards more positive values indicating less evaporative enrichment. In 17 comparison to the isotope depth profiles the deuterium excess depth profile has its minima at 18 10 cm for both methods excluding profile E2.7.

#### 19 Campaign 2

20 During the second campaign variations in temperature and humidity were much smaller compared to Campaign 1 (daytime ~35 °C<sub>max</sub> and 30 %RH<sub>min</sub>; night ~20 °C<sub>min</sub> and ~ 90 21 %RH<sub>max</sub>). Two rainfall events were recorded (November 12<sup>nd</sup>, 2014: 12 mm morning, 22 November 13<sup>rd</sup>, 2014, 30 mm morning) at the climate station in Eenhana which is 23 approximately 15 kilometers west of the experimental site. However, there was no isotope 24 data available until November 17<sup>th</sup>, 2014. Later on during the campaign, a small rain event 25 (16 mm) was sampled for isotopes on November 17<sup>th</sup>, 2014 at 8:00 a.m. with -0.6 ‰ and 3.0 26 ‰ for  $\delta^{18}$ O and  $\delta^{2}$ H, respectively. A smaller event (4 mm) was also sampled on November 27 19<sup>th</sup>, 2014 with isotope values of 3.6 ‰ and 28.8 ‰ for  $\delta^{18}$ O and  $\delta^{2}$ H, respectively. 28

The plots that were sampled in November (rainy season) have higher water contents compared to those of the first campaign. One non-vegetated plot of the second campaign (E2.7, see Fig. 4 right hand side and Table 2) is used to compare the *in-situ* and the laboratory results as an example with higher water contents. The water contents range between 4.4 % and 6.8 % with maximum values between 12.5 cm and 25 cm (Figure 3, right). Strongest enrichment of  $\delta^{18}$ O is in the top layer declining exponentially with depth for both methods. There is good agreement between  $\delta^{18}$ O<sub>I</sub> and  $\delta^{18}$ O<sub>C</sub> except for depths at 30 cm and 50 cm. In contrast, there are substantial differences between  $\delta^{2}$ H<sub>I</sub> and  $\delta^{2}$ H<sub>C</sub>. Above 25 cm values of  $\delta^{2}$ H<sub>C</sub> are higher (-15.5 ‰ to -22.6 ‰) than for  $\delta^{2}$ H<sub>I</sub> (-25.0 ‰ to -29.2 ‰), and vice versa lower below 25 cm with -23.4 ‰ to -15.2 ‰ for  $\delta^{2}$ H<sub>C</sub> and -11.6 ‰ to -5.1 ‰ for  $\delta^{2}$ H<sub>I</sub>, respectively.

7 The agreement between *in-situ* and cryogenically obtained isotope measurements is expressed 8 with the root mean square error (RMSE). There is a good agreement between *in-situ* and 9 cryogenically obtained isotope measurements for both isotope depth profiles of the first campaign between 15 and 50 cm (RMSE= 3.9 and 9.2 % for  $\delta^{18}$ O and  $\delta^{2}$ H, respectively). 10 However, higher values were observed for the *in-situ* approach at shallower depth (RMSE= 11 7.0 and 43.4 % for  $\delta^{18}$ O and  $\delta^{2}$ H, respectively). In general, better agreement can be observed 12 for  $\delta^{18}$ O compared to  $\delta^2$ H values. Both isotope profiles of the first campaign derived from the 13 cryogenic vacuum extraction show a maximum at 15 cm with an exponential decline down to 14 depth. Values of the *in-situ* measurement show this maximum at 10 cm, but only for  $\delta^{18}O_I$ . 15 The profile of the second campaign does show good agreement within the top 25 cm for  $\delta^{18}O_{I}$ 16 but for  $\delta^2 H$  only within the upper 10 cm. In terms of measurement trueness for the set of these 17 three profiles we obtain 6.86 ‰ and 1.87 ‰ for  $\delta^2 H_I$  and  $\delta^{18} O_I$  respectively. 18

A compilation of the quality check standards for  $\delta^2 H_{ac}$  and  $\delta^{18}O_{ac}$  of the two campaigns is 19 20 shown in Table 2. The standard deviation of the repetitive measurements for each depth is a 21 measure of measurement precision. After drift correction and normalisation of the isotope depth profile E1.1 the precision ( $\sigma_{qc})$  of the quality check standard (HLAU) was 5.1 ‰  $\delta^2 H$ 22 and 0.66 ‰  $\delta^{18}$ O, respectively. The mean precision of the repetitive measurements ( $\sigma_{rep}$ ) is 23 two times better for  $\delta^2 H_I$  than for the precision of the repetitive measurements ( $\sigma_{crv}$ ) for values 24 derived from the cryogenic vacuum extraction  $\delta^2 H_{C}$ . Values of  $\delta^{18}O_{qc}$  show higher similarity 25 26 (refer to Table 2). The measurement of the second profile E1.2 is less precise for  $\delta^2 H_I$  but in the same range as  $\delta^2 H_c$ . Similar precision as for profile E1.1 is found for the third profile E2.7 27 for both  $\delta^2 H$  and  $\delta^{18} O$ , respectively. 28

29

30  $\delta^{18}$ O vs  $\delta^{2}$ H

In Figure 5 the  $\delta^{18}$ O to  $\delta^{2}$ H relationship is shown. The LMWL is derived from historical data 1 2 collected in the CEB and has a slope of 7.3 ( $R^2 = 0.96$ ). Additionally, mean values of local 3 groundwater ( $\sigma^{18}O = 0.91$ ,  $\sigma^{2}H = 4.27$ ) and soil water down to a depth of 4 m with 10 cm 4 resolution are presented. Soil water from the first field campaign derived from the cryogenic 5 vacuum extraction plots along an evaporation line with a slope of 2.4 ( $R^2 = 0.79$ ) for the nonvegetated plot and 3.1 (R<sup>2</sup>= 0.96) for the vegetated plot. In-situ measurements of the non-6 7 vegetated plot have a slope of 3.9 ( $R^2 = 0.84$ ). Excluding the first 10 cm of the unvegetated 8 profile the slope is 2.9 ( $R^2 = 0.73$ ). Values of the vegetated site derived from the *in-situ* measurements have a slope of 3.0 (R=0.46) and are shifted towards more positive  $\delta^2$ H values. 9 Excluding the top 15 cm of the *in-situ* measurement the slope remains the same, but R<sup>2</sup> 10 11 increases to 0.9. Values from the second campaign show a much higher slope with 5.3 ( $R^2 =$ 0.75) for the *in-situ* measurement and 5.1 ( $R^2 = 0.96$ ) for the cryogenic vacuum extraction and 12 13 are plotting close to the LMWL.

#### 14 Spatio-temporal variability

15 Each profile of the second campaign is measured at 18 different depths and each depth with 16 six repetitions. After drift correction of the isotope data, the mean precision considering the quality check measurements ( $\sigma_{ac}$ ) for more than 140 measurement points is 2.15 % for  $\delta^2 H_I$ 17 and 0.36 % for  $\delta^{18}O_{I}$  (Table 2). Mean standard deviation of the repetitive measurements ( $\sigma_{rep}$ ) 18 of each depth is 1.86 ‰ for  $\delta^2 H_I$  and 0.46 ‰ for  $\delta^{18} O_I$ , respectively. As shown in Table 2, the 19 20 mean standard deviations of the repetitive measurements are similar to those derived from the 21 quality check standard. Differences are observed between  $\sigma_{qc}$  and  $\sigma_{rep.}$  However, the precision of  $\delta^2$ H is within the range of the mean measurement trueness of 5.4 ‰. The measurement 22 trueness of  $\delta^{18}$ O is much higher with 0.11 ‰. There are two outliers (E2.8, E2.9) who were 23 24 not considered for the mean precision.

25 Mean values of each transect are shown to illustrate an averaged temporal characteristic with intermittent rainfall (Figure 6) for this particular area, both rain events are indicated by a grey 26 27 dot on the x-axis. The first transect is affected only from the first set of rain events (E2.1 to E2.3) and was measured within two consecutive days. The next transect (E2.4 to E2.6) is 28 affected by the 16 mm event (17<sup>th</sup> November, 2014) of which isotope data is available and the 29 30 profiles were measured in a period of three days. Finally, the last three plots (E2.7 to E2.9) showed most evaporative enrichment and experienced only additional precipitation on the 19<sup>th</sup> 31 32 Nov 2014 with an amount of 4 mm. Maximum infiltration depth varied between 65 and 95 cm. Water content varied between 0.5 % and 9.5 %. Comparing the three transects it can be
observed that the variability of isotope depth profiles decreases from the first to the last
transect and an evaporation profile developed.

To account for spatial variability, mean values of soil moisture were calculated for each depth of the nine plots. Additionally, the standard deviation of each depth for soil moisture,  $\delta^{18}O$ and  $\delta^2H$  are calculated. Figure 7 shows mean soil moisture of each depth against the standard deviation of soil moisture and those of the two isotopes. Basically, high (> 4 %) and low (< 2 %) water content have lower variability of soil moisture compared to intermediate values. In contrast, the standard deviation of  $\delta^{18}O$  and  $\delta^2H$  increases with decreasing soil water content.

## 10 Soil water balance

11 Precipitation (P) for the rainy season was measured with an amount of 660 mm. Recharge estimated from soil water stable isotope data is less than 1 % of precipitation. It ranges 12 between R = 4 – 5 mm y<sup>-1</sup> derived from  $\delta^2 H_{shift}$  and  $\delta^{18} O_{shift}$ , respectively. The soil water 13 storage (S) is derived from the soil moisture depth profile and the evaporation front is 14 15 determined from the exponential fit to the water stable isotope depth profiles. Results are summarized in Table 3. Soil evaporation (E) is determined from z<sub>ef</sub> using the isotope depth 16 profiles. The mean of all results from E1.1 and E1.2 is  $120 \pm 50$  mm y<sup>-1</sup>. Then, recharge (R), 17 18 soil water storage (S) and soil evaporation (E) are subtracted from precipitation (P). The remainder is potentially available for transpiration (T) with 510  $\pm$ 50 mm y<sup>-1</sup>. Runoff can be 19 20 neglected because it was not observed at the experimental site. Hence, the contribution of 21 transpiration to total evapotranspiration (T/ET) is  $81 \pm 7$  %. The potential contribution of 22 transpiration (T/ET) or root water uptake at the non-vegetated plot is between 76 and 92 %. 23 At the site underneath the canopy and vegetated with shrubs (T/ET) is between 72 and 92 %.

Values of  $z_{ef}$  range between 110 and 290 mm which is in agreement with values derived from a physical model proposed by Or et al., (2013). Considering two different ranges, one for finer and one for coarser textures, we derive a depth  $z_{ef}$  of 210 mm and 118 mm for  $r^1 = 63$  -112 µm and  $r^2 = 630$  - 1120 µm, respectively. Using these values to calculated E for profiles from June 2014 we derive values between 67 - 79 mm y<sup>-1</sup> and 161 - 201 mm y<sup>-1</sup> for r<sup>1</sup> and r<sup>2</sup>, respectively.

30 After the rain events during the second field campaign the evapotranspiration pattern is 31 dominated by soil evaporation. The evaporation front is still developing ( $z_{ef} = 82 - 90$  mm) 1 and T/ET is much lower with 35 - 51 %. Applying this methodology to the different transects,

2 soil evaporation E decreases from 4 to below 1 mm  $d^{-1}$  (not shown).

# 3 4 Discussion

4 The potential to determine stable isotopes of soil water indirectly by measuring the vapor 5 from the pore space directly in the field could be demonstrated by using a liquid water 6 analyser. Results show that the precision of the *in-situ* approach is better than 0.8 ‰ and 2.5 % for  $\delta^{18}$ O and  $\delta^{2}$ H, respectively. This is a feasible precision if it is compared to the precision 7 of isotope values obtained from the cryogenic vacuum extraction method which are 0.8 ‰ 8 and 3.5 % for  $\delta^{18}$ O and  $\delta^{2}$ H, respectively. It is still worse compared to the precision that can 9 be achieved measuring stable isotopes directly from water samples (0.2 % and 0.8 % for  $\delta^{18}$ O 10 and  $\delta^2$ H). However, it needs to be considered that such laser spectrometers are in general 11 12 mounted in a temperature controlled laboratory. In this study, measurement trueness and 13 precision of the presented *in-situ* system is mainly limited by the environmental conditions. If 14 the laser spectrometer and the autosampler would be operated within a temperature controlled 15 environment, possibly, the precision could be improved. However, this study could demonstrate that it is possible to determine stable isotopes of soil water directly in the field 16 17 with a similar or even better precision compared to destructive sampling and a subsequent soil 18 water extraction in the laboratory. This creates possibilities to investigate water vapor 19 transport processes that are difficult to measure with other techniques such as soil moisture or 20 suction tension measurements. Evaporation processes are physically well described (i.e. Or et 21 al., 2013), but their determination in the field remains difficult. An approach to observe 22 evaporation was presented by Rothfuss et al. (2015) who could show the development of an 23 isotope depth profile in a drying soil column experiment with a similar *in-situ* approach as in 24 the present study. However, their experimental setup did not reflect conditions that can be 25 found at our study site, since much higher temperature and humidity gradients were observed 26 between day and night.

### 27 Campaign 1

Results of the first field campaign demonstrates good agreement of the isotope depth profiles between the cryogenic vacuum extraction method and the *in-situ* approach for deeper parts of the soil profile, but also a divergence in the top 15 cm. Differences could be a result of an incomplete soil water extraction, rayleigh fractionation caused by the uptake of air from the *in-situ* measurement, natural processes or natural heterogeneity. An incomplete extraction of water will result in depleted isotope values of the extracted soil water. However, this is unlikely for fine sand with low water holding capacity and low abundance of silt and clay. The cryogenic vacuum extraction is adequate to completely extract the water in sandy soils (Königer et al., 2011). Hence, the extracted soil water isotopic composition will reflect the "true" isotope values of the pore water.

6 Measuring soil water vapour or atmospheric vapour using the soil gas probe in a coarse 7 material can lead to a mixed sample. However, the extracted air volume is low and a 8 divergence of isotope values is only visible within the top 15 cm of the dry profiles (Figure 3, 9 left and center). Evaporative enrichment is reflected in the deuterium excess  $(d_{ex})$  and also in 10 the so-called evaporation line (Craig and Gordon, 1965). Evaporative enrichment could also 11 be enhanced by the uptake of water vapor through the measurement (Figures 5 and 6). The 12 equilibrium condition prevailing between soil liquid and gas phases is disturbed when water 13 vapor is removed, causing the sampled water vapor to be depleted at the first stage. After some time, depending on the uptake rate and the soil water content, the initial isotope values 14 15 of the remaining soil water may become higher; this will be reflected in the isotope values of the sampled gas and generally may be a cause of reduced precision. However, enrichment 16 17 caused by the uptake of air through the measurement is not visible for deeper parts of profile E1.2, which is dry as well. Hence, the argument that low water contents would advocate 18 19 showing higher isotope values for deeper parts of the vegetated profile would be consistent. 20 This is not observed at the vegetated plot where soil water contents are below 1% throughout 21 the whole profile (Figure 3, center). Since the *in-situ* approach is based on the same principle 22 as the equilibration bag method, its applicability on samples with low water content is 23 supported by a recent study of Hendry et al., (2015). They found that the measurement 24 accuracy of their equilibration procedure could be improved by increasing the sample amount 25 of low water content soils to increase the amount of water available for equilibration in the 26 bag.

It should be noted that destructive sampling was conducted one day after the *in-situ* measurements because it was assumed that the isotope profiles are in steady state (Barnes and Allison, 1988), and the experimental setup did not allow for simultaneous sampling. Therefore, the observed differences in the upper part of the soil profile might be rather attributed to kinetic processes, because vapor transport (i.e. evaporation) and hence isotopic enrichment will be more pronounced at shallow depths as described by Braud et al. (2009).

1 Natural temporal variability such as high temperature and humidity changes between day and 2 night could be another possible explanation. During the day evaporation dries the top layer due to vapor transport into the atmosphere. During the night, temperatures decrease and 3 relative humidity increases. Low soil water contents and a back diffusion of vapor into the 4 5 upper part of the soil can cause condensation or adsorption (Agam and Berliner, 2006), affect isotope values (Rothfuss et al., 2015) and can significantly increase soil water content 6 7 (Henschel et al., 2008). This might deplete isotope values of the remaining soil water within 8 that upper layer. In a numerical study it was already shown that diurnal variations of 9 evaporation can be large depending on the energy budget at the surface, but the influence on 10 isotope concentrations needs further investigation, especially under field conditions (Braud et 11 al., 2005).

12 Another possibility for a change in isotopic composition at shallow depths can be hydraulic 13 lift. In this case, water from deeper soil layers with higher water potential can move through 14 the root system to soil layers with lower water potential (Dawson et al., 1993) The dense root 15 mat of fine roots observed in the upper part of the soil profile, together with low water contents and the differences between the isotope depth profiles, could be an indicator for this 16 17 process. However, the measurement of soil physical properties, stable isotopes of soil water 18 and xylem covering the diurnal cycle would be necessary to distinguish between vapour back 19 diffusion or hydraulic redistribution.

## 20 Campaign 2

21 In contrast to depth profiles of the first campaign the rain influenced profile E2.7 doesn't 22 show such a divergence in the top layer as observed at E1.1 and E1.2. As shown in Figure 5, 23 the deuterium excess indicates that precipitation water is dominating. Good agreement is 24 found in the top layer for both isotopologues. Mixing with atmospheric vapor might be 25 negligible considering the high soil water contents. Destructive sampling was done directly 26 before the *in-situ* measurement started. It has to be noted that, *in-situ* measurements at 10 cm 27 depth were done 90 min after the destructive sampling was conducted, while in-situ 28 measurements at 30 cm depth were conducted even 120 min later. Differences can be caused 29 by the time lag between destructive sampling and *in-situ* measurements, vapor transport 30 processes induced by temperature gradients, or diffusion.

Considering that under the present "wet" conditions (but also if the soil moisture is around 1 2 wilting point), humidity of the pore space is close to saturation. Temperature gradients will 3 cause movement of vapor downward or upward depending on the temperature profiles 4 (Abramova, 1969). Further, soil evaporation can be separated into direct evaporation from a 5 water saturated surface (stage I evaporation) and diffusion controlled vapor transport (stage II evaporation) (Or et al., 2013). Therefore, observed differences between  $\delta^2 H_I$  and  $\delta^2 H_C$  for 6 7 profile E2.7 (Figure 3, right) might be attributed to the exchange between the evaporation 8 depleted vapor that was transported from the deeper zone (30 cm to 50cm) to shallower 9 depths (12.5 cm and 25 cm) due to diffusion controlled evaporation (stage II).

# 10 $\delta^{18}$ O vs $\delta^{2}$ H

11 Values for *in-situ* measurements and cryogenic extraction plot on evaporation lines which are 12 similar in slope (excluding the top 12.5 cm). The outliers in the top-right area and those above the LMWL of the  $\delta^2 H$  vs.  $\delta^{18} O$  plot (Fig. 5) are from the top 12.5 cm of the profiles. As 13 14 discussed earlier, diurnal temperature and humidity cycles could cause condensation in the upper part of the soil profile, but also higher enrichment during the daytime as compared to 15 16 the conditions during the night when the soil is colder than atmospheric vapour. Further, the 17 interaction between soil water potential and water vapor, which might be driven by relative 18 humidity (Wilson et al., 1997) but the effect to isotope fractionation, but is not well 19 understood and will be a challenge to future research (Soderberg et al., 2012). The 20 investigation of such processes using *in-situ* approaches for stable isotope analysis seem to be promising in this regard, since the composition of vapor can be measured in the field. 21

#### 22 Spatio-temporal variability

23 The boundary conditions of the second field campaign caused quite a heterogeneous pattern regarding both the development of the moisture front and the isotope depth profiles. 24 25 Observations were made depicting how the infiltrating water developed under evaporation with light intermittent rainfall events. This is reflected in both the shape of isotope depth 26 27 profiles of the three transects and the standard deviations within one transect (Figure 6). Other 28 studies showed similar patterns in the context of a numerical experiment (Singleton et al., 2004). The first transect (Figure 6, Transect 1) has variable isotope values throughout the 29 whole depth. The isotope depth profile of transect one shows maxima and minima of isotope 30 values which appear to reflect a similar profile from a humid climate. This kind of layering is 31 32 commonly used in humid regions to determine transit times of unsaturated zone water where

precipitation has seasonality to its isotopic composition (Coplen et al., 2000; Lee et al., 2007). 1 2 However, here, it is attributed to variations in rainfall composition and infiltration patterns on a much smaller time scale, generally daily. Zimmermann et al., (1967) previously described 3 that isotopically distinct rain that is consecutively infiltrating into the soil will move 4 5 downward distinguishable by a boundary between older rainwater below and younger water above. Hence, the most depleted values found at 20 cm and 50 cm (Figure 6, Transect 1) 6 7 might correspond to certain rain events which would not emerge from the soil moisture 8 measurements alone. These depleted zones are not visible in the other transects which are 9 possibly overprinted by vapor transport processes and evaporation.

10 In the short time period after a precipitation event, the top part of the evaporation profile 11 (Transect 1) was considerably displaced as theoretically described by Allison et al., (1984). 12 Variations of isotope values are attenuated with time by vapor phase redistribution (Transect 13 2) (Fontes et al., 1986) and an evaporation profile begins to develop (Transect 3) (Rothfuss et 14 al., 2015). Further, it can be observed that infiltrating water of small intermittent events compresses the isotope profile (Barnes and Allison, 1988; Singleton et al., 2004). Therefore, 15 16 the presented *in-situ* measurements have great potential to visualize theoretically discussed 17 processes with feasible measurement trueness under natural field conditions.

18 Spatial variability of soil moisture is well known (Western et al., 2004). It can be expected 19 that stable isotopes will also distribute heterogeneously within the unsaturated zone. The relationship between mean soil moisture and  $\delta^2 H$  does not allow a resilient conclusion 20 because of low measurement trueness in this study. However, it appears that it behaves 21 differently for  $\delta^2$ H and  $\delta^{18}$ O values when compared to soil moisture. The differences might be 22 related to vapor diffusion processes or to biological processes. For instance, Dawson et al. 23 24 (2002) discussed the isotopic composition of different carbon and water pools. Soil respired 25  $(CO_2)$  will equilibrate with the abundant soil water and might cause additional changes to the isotopic composition of the soil pore water. 26

### 27 Soil Water Balance

The soil water balance is calculated from isotope depth profiles. The presented results are in agreement with other isotope based partitioning studies. Those studies suggest a contribution of transpiration of more than 70 % to the total evapotranspiration flux as Sutanto et al. (2014) discussed in a recent review. In addition, the findings from the first field campaign showed that the development of the evaporation profiles appeared to be independent of leaf / vegetation cover. Based on the data and calculations of this study, it seems that soil cover
 might be of minor importance for long term soil evaporation quantities.

Differences between the two sites of the first field campaign are minimal regarding the shape of the isotope depth profiles. In addition, the evaporating front and the calculated evaporation rates using equation 4 and equation 5 are similar for both sites. Because of the litter layer and the shaded nature of plot E1.2 it could be expected that less evaporation takes place and hence less enrichment and a lower deuterium excess would appear for the *in-situ* measurement (Figure 4). However, this is not visible and suggests humidity to be the main driver for isotopic enrichment as demonstrated in a numerical study by Braud et al. (2005).

## 10 **Potential limitations**

11 Water vapor mixing ratio dependencies (Wang et al., 2009; Sturm and Knohl, 2010; Rambo et al., 2011; Aemisegger et al., 2012) are of minor importance in this study, because the water 12 content was maintained within the density of approximately 2-  $4*10^{16}$  molecules cm<sup>-3</sup> 13 as recommended by Los Gatos Research. It is assumed that small variations will be reflected in 14 15 the standard deviation of the measurements. Additionally, inference through organic 16 contamination is neglected in this study. However, if necessary to account for inference recent efforts include calibration strategies in this regard (Wu et al., 2014). Possible fractionation 17 18 due to high salt concentrations or chemical reactions as observed by Oerter et al. (2014) are negligible, because the cation exchange capacity (CEC) of the sand was 0.5 meq 100g<sup>-1</sup> and 19 total organic carbon (TOC) 0.22 %. 20

21 During the second field campaign, information on long term precision and spatio-temporal variability was investigated. Comparing the quality check standards of the two campaigns the 22 precision within one series ( $\sigma_{rep}$ ) of  $\delta^2 H$  is one-third better than the long term measurement 23 trueness. However, the measurement trueness of  $\delta^{18}$ O is three times greater than the mean 24 25 precision (Table 2). This can likely be improved by utilizing a more sophisticated technical setup e.g. temperature controlled conditions. Another reason could be the difference in the 26 27 physical properties of the probe pores such as the diffusivity of gas (Merlivat et al., 1979). 28 Though there is no detailed chemical data available it is unlikely that chemical properties are 29 responsible, since the sandy soil has a low CEC. More likely are biological processes that are 30 introduced due to the sudden availability of water, such as enhanced soil respiration (Dawson 31 et al., 2002). Nevertheless, there is no data (i.e CO<sub>2</sub> measurements) available to support this assumption. Therefore, it would be beneficial to measure CO<sub>2</sub> concentration in parallel. 32

However, the precision appears to be sufficient to monitor processes of a diurnal time scale and also comparable to other systems that were tested in the field, e.g., Volkmann and Weiler et al. (2014) demonstrating precision values of 2.6 ‰ and 0.38 ‰ for  $\delta^{2}$ H and  $\delta^{18}$ O, respectively.

5 Condensation within the sample system can lead to unreliable data. This can be either prevented by heating the sample lines, flushing the sample lines with dry air or sufficient 6 7 dilution of the sample. Thus, under conditions where the ambient temperature is significant 8 warmer then the soil temperature a simple valve controlled membrane inlet will be sufficient 9 for an indirect determination of isotopes in unsaturated zone or saturated zone water. During 10 the day time this is the case at the presented study site, but changes drastically overnight as 11 described. Dilution of the vapor concentration can be done by providing dry gas at the other 12 end of the available probes. In the case of pure diffusion sampling the maximum dilution rate 13 depends upon the absolute amount of water molecules in the vapor and is controlled by the 14 length of the probe, their diffusion properties, the flow velocity and the temperature at depth. 15 The flow velocity can be different depending on the laser spectrometer that is used. Adding a mixing chamber at the head of the probe has the distinct advantage of additional mixing 16 17 directly before the vapor enters the sample line (Volkmann and Weiler, 2014). This leads to 18 independence on flow velocity, probe length and membrane diffusion properties with regard 19 to the water content of the sampled vapor. Under dry conditions it might be useful to increase 20 the probe length, since the soil volume around the probe affected by the measurement will be 21 reduced.

22 A critical point is the long term application of membrane based methods. The pore space of 23 the probes can be altered over time which might increase the memory effect of the system. 24 Further, the calibration of the *in-situ* methods of Volkmann and Weiler (2014) and Gaj et al. 25 (this study) used prior oven dried substrate for calibration. This procedure assumes that all 26 water is evaporated during oven drying and only the added standard water will be measured 27 afterwards. The same assumption is made using the equilibration bag method if the standards are treated in the same way as described. However, interlayer water or adsorbed water of clay 28 minerals is commonly removed under vacuum heating the sample to 200 to 300 °C for several 29 30 hours (VanDeVelde and Bowen, 2013). The adsorbed and interlayer water is bound on the 31 mineral surface and exchanges with atmospheric water vapor within hours (Savinand and Epstein, 1970). Hence, for soils containing clay minerals a calibration procedure using 32

previosly oven dried soil materials might mislead. The presented direct comparison of the cryogenic vacuum extraction with a membrane based *in-situ* measurement showed that this calibration procedure is at least applicable for fine sand. However, it will probably lead to insufficient data applying this calibration procedure to soil samples with finer texture, especially if clay, silt and/or salt contents are high (Oerter et al., 2014).

## 6 **5 Conclusion**

7 The present study demonstrates that high resolution *in-situ* sampling of stable isotopes in the 8 unsaturated zone is feasible. Long term measurement trueness within the presented campaigns is about two times lower for  $\delta^2 H$  and three times for  $\delta^{18} O$  than for the short term precision of 9 each profile. This can possibly be improved by a better temperature control of the analyser or 10 11 temperature compensated devices if available. In-situ measurements can be applied with 12 minimal technical effort for remote applications. They further show good agreement with 13 values derived from cryogenic soil water extractions. Differences between the two methods 14 are predominantly within the given accuracies of the methods. Divergence in the upper soil 15 layer between *in-situ* and destructive sampling suggest enhanced soil-atmosphere interactions, 16 kinetic processes due to high evaporation rates or hydraulic redistribution. Evaporation 17 induced by the measurement procedure might decrease the precision depending on the uptake 18 rate and the soil water content. Low humidity in relation to soil water potential and isotope 19 fractionation needs further investigation. However more importantly, to prevent the collection 20 of insufficient data when applying an in situ approach, one has to carefully consider the 21 applied calibration procedure depending on the research question and the soil type. In 22 addition, there is a trade-off between technical effort, control setup, probe type, environmental 23 conditions and costs. The presented and also other *in-situ* measurement approaches have great 24 potential to investigate transient processes within the unsaturated zone. This has not been 25 possible to study until field deployable laser spectrometers and *in-situ* techniques became available. The determination of water stable isotopes in the unsaturated zone directly in the 26 27 field allows monitoring transient processes which would not be possible with destructive 28 sampling strategies. This creates new possibilities to the design of tracer experiments with 29 water of a labeled isotopic composition as conservative tracer. However, this is limited by the 30 measurement frequency of the provided system which is now at least able to capture diurnal 31 processes with the presented vertical resolution. In addition, a much higher spatial resolution 32 can be achieved with much lower time consumption compared to conventional approaches.

- 1 The proposed technique offers the possibility to investigate unsolved questions regarding soil
- 2 atmosphere interactions such as water vapor intrusion and transport plus effects of diurnal
- 3 evaporation cycling on isotope depth profiles.
- 4

# 1 Acknowledgements

2 This work was partly funded by the German Federal Ministry for Education and Research (BMBF) within the SASSCAL project (South African Science and Service Center for Climate 3 4 Change, Agriculture and Landuse) under contract number 01LG1201L. We wish to thank our colleagues Martin Quinger (BGR), Christoph Lohe (BGR), Shoopi Ugulu, and Wilhelm 5 6 Nuumbembe from University of Namibia, Windhoek, Namibia. Laboratory work was 7 supported by Jürgen Rausch and Lisa Brückner which is highly acknowledged. Also 8 appreciated is the technical support of Axel Lamparter, Marc Brockmann, Erik Lund and 9 Salome Krüger as well as Chris Gabrielli and Dyan Pratt for English proof reading. Finally, 10 we wish to acknowledge the fruitful discussion with the two anonymous reviewers, which 11 substantially improved the manuscript.

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1

Table 1: Standards used for normalization, drift correction, quality check. The standards are used for

2 both, the measurements with the *in-situ* approach in the field and for the extracted soil water in the

3 laboratory.

Abbreviation	Description	$\delta^2 H$ [‰] $\sigma$	δ <sup>18</sup> Ο [‰] σ
HMER	Hannover sea water	$-3.1 \pm 0.4$	$-0.4 \pm 0.13$
HDES	Hannover distilled water	$-55.9 \pm 0.9$	$-8.12 \pm 0.14$
HLAU	Hannover lauretaner water	$-64.6 \pm 0.6$	$-9.73 \pm 0.10$
HGLA	Hannover glacier water	$-152.1 \pm 0.9$	$-20.27 \pm 0.11$

4

5 Table 2: Values for HLAU (qc) with the corresponding standard deviation of their repetitive 6 measurements ( $\sigma_{qc}$ ), the mean standard deviation of the repetitive measurements of each measurement 7 point ( $\sigma_{rep}$ ) and the corresponding values of the cryogenic vacuum extraction ( $\sigma_{cry}$ ) from the campaigns 8 June / November 2014. Bare plots (B) and vegetated plots (V) were measured.

ID	Date	Init.Time		$\delta^2 H_{qc}$ [‰]	$\sigma_{q}$	σrep	σ <sub>cry</sub>	$\delta^{18}O_{qc}$ [‰]	σ <sub>qc</sub>	σ <sub>rep</sub>	σ <sub>cry</sub>
E1.1	04.06.2014	09:30:00	В	-60.09	± 5.13	1.4	3.7	-10.04 ±	0.66	0.7	0.8
E1.2	04.06.2014	15:30:00	V	-74.96	± 2.83	3	3.5	-13.16 ±	0.01	0.6	0.6
		$\overline{X}$			± 3.98	2.2	3.6	±	0.34	0.65	0.70
E2.1	15.11.2014	10:50:00	В	-73.25	$\pm 0.87$	1.17		-10.38 ±	0.34	0.45	
E2.2	16.11.2014	08:00:00	В	-69.83	± 0.99	1.26		$-8.05 \pm$	0.48	0.35	
E2.3	16.11.2014	13:30:00	V	-71.11	± 0.49	2.21		-10.29 ±	0.14	0.54	
E2.4	17.11.2014	11:00:00	V	-57.51	± 4.11	1.72		$-8.45$ $\pm$	0.14	0.28	
E2.5	18.11.2014	11:00:00	V	-64.82	± 1.86	1.52		-7.73 ±	0.34	0.28	
E2.6	19.11.2014	07:30:00	В	-75.62	± 1.84	2.49		-6.81 ±	0.81	0.5	
E2.7	19.11.2014	14:00:00	В	-79.35	± 1.27	1.93	3.5	-11.62 ±	0.36	0.45	0.45
E2.8	20.11.2014	11:30:00	V	-25.24	± 2.53	1.45		$-3.68 \pm$	0.25	0.24	
E2.9	21.11.2014	11:30:00	V	-23.00	± 17.1	7 1.74		-15.59 ±	4.17	0.37	
		_									
		X			2.15	1.86	3.57		0.36	0.46	0.62

9

1Table 3: Soil evaporation (E) is derived from stable isotope depth profiles. The isotope value of the2reservoir  $\delta_{res}$ , the evaporating front  $\delta_{ef}$  and the effective depth  $z_{ef}$  are estimated from a exponential fit to3the isotope depth profiles. The Soil water storage (S) is calculated from the soil moisture depth profile.4Transpiration (T) is the remainder from annual precipitation (P=660 mm) after subtracting the Recharge5(R=4 and 5 mm for <sup>2</sup>H and <sup>18</sup>O, respectively), E and S. The partitioning between soil evaporation to6transpiration is calculated as the contribution of transpiration (T/ET) to evapotranspiration (ET) for a7range of soil moisture conditions  $\Theta$ .

	z <sub>ef</sub> [mm]	δ <sub>res</sub> [‰]	δ <sub>ef</sub> [‰]	E [mm/y]		S [mm]	T [mm/y]		T/ET [%]	
Cryo				Θ:1%	Θ:7%		Θ:1%	Θ:7%	Θ:1%	Θ:7%
bare	155	-8.2	31.4	147	125	40	468	490	76	80
vegetated	127	-5.2	32.5	179	151	9.5	467	495	72	77
Wet	79	-4.8	5.4	349	295	122	184	238	35	45
In-situ										
bare	115	-6.4	46	197	167	40	418	448	68	73
vegetated	139	-7.4	34.6	164	139	9.5	482	507	75	78
Wet	86	-5.8	5.9	321	271	122	212	262	40	49
${}^{2}\mathbf{H}$										
Cryo										
bare	388	-84.1	21.8	59	49	40	557	567	90	92
vegetated	364	-62.9	8.5	62	53	9.5	585	594	90	92
Wet	90	-26	28.7	307	259	122	227	275	43	51
In-situ										
bare	225	-65	49	101	86	40	515	530	84	86
vegetated	174	-42	69	131	111	9.5	516	536	80	83
Wet	82	-32.8	27	336	285	122	198	249	37	47

<sup>18</sup>O



2 Figure 1: The study area is located in the northern part of the Cuvelai-Etosha-Basin (CEB),

3 which is subdivided by the political border between Angola and Namibia (left). Sampling was

4 conducted in Elundu located in the center of the CEB (center, right).



2

3 Figure 2: Gas transport (right) is controlled by an automated electronic control (left). The PC

4 mimics the behavior of a laboratory autosampler communicating with the analyser via an USBto

5 Serial adapter. High and low signals from the data set ready pin can be used to switch valves

6 using an optocoppler (ULN2303). Vapor is transported via the transport line from the soil gas

7 probe to the ICOS device. The flow is measured with a mass flow controller (MFC).





Figure 3: Depths profiles of the field campaign in June 2014 (E1.1, E1.2) and the field campaign in November 2014 (E2.7) are shown. Compared are isotope depth profiles extracted with the cryogenic vacuum extraction (dashed, triangles) and measured *in-situ* (straight, dots).  $\delta^2$ H is given in blue and  $\delta^{18}$ O is given in red. Soil moisture is illustrated on the right of each plot (black). Standard deviation for each plot and each method is indicated by error bars in the legend of the plot.

9



- 11 Figure 4: Deuterium excess for the profiles E01.1, E01.2 sampled in June 2014 and E02.7
- 12 sampled in November 2014. Compared are values from the cryogenic vacuum extraction
- 13 (triangles) and the *in-situ* measurements (circles).





Figure 5:  $\delta^{18}$ O vs  $\delta^{2}$ H plot of the profiles E01.1, E01.2, E02.7. Further shown is the local meteoric water line (LMWL) for the northern part of Namibia as well as the global meteoric water line (GMWL). A mean value of shallow groundwater is plotted and additionally soil water of a depth profile down to a depth of 4 m.



Figure 6: <sup>18</sup>O (red), <sup>2</sup>H (blue) and soil moisture (black) depth profiles. Shown are mean values for three transects consisting of three single profiles derived from *in-situ* measurements. Mean standard deviation  $\sigma$  of all quality check standards (qc) are shown in the legend. Rainfall isotope values are indicated on the x-axes in grey.



Figure 7: Mean soil moisture ( $\Theta$ ) for each depth plotted against the standard deviation of soil moisture  $\sigma[\Theta]$  between each depth as well as standard deviation of  $\sigma[\delta^{18}O]$  and  $\sigma[\delta^{2}H]$ , repsectively.