1	Editor D	Editor Decision: Reconsider after major revisions (03 Dec 2015) by Christine Stumpp								
2	Comment	s to the Author:								
3	Dear authors,									
4										
5	the same	two referees reviewed the revised version of the manuscript. They state that still not								
6	all previo	us comments have been answered or implemented in the text adequately.								
7	Specifical	Specifically, it includes the following main issues:								
8 9 10 11 12 13	(i) (ii)	 posed research questions not fully answered in the manuscript a. We hope that the current version of the manuscript answers most of the questions. Still there will be some points that could not be answered with the current data. However, we discussed possibilities to answers those in the future. little comparison with other studies in discussion 								
14 15		a. We added references in the discussion section and discussed more detailed with regard to the objectives.								
16 17 18	(111)	too long introduction, a. We substantially shortened the introduction section to be more focused on the main objectives								
19 20 21	(iv)	method comparison not addressed properlya. We focused the discussion on the comparison. Potential limitations are also discussed.								
 22 23 24 25 26 27 	(v)	 reproducibility of results low because of high standard deviations, a. We agree that the standard deviations are high if they are compared to those from measurements directly from water samples. However, considering the analytical error that is made by soil water extractions (i.e. Königer et al., 2010) with < 0.8 ‰ and < 4 for ‰ for δ¹⁸O and δ²H respectively, the error that is made by the in-situ approach is lower. 								
28 29	(vi)	poorly written and unclear sections (English), a. we improved the English and rewrote the unclear sections.								
30 31 32	(vii)	typos. a. We corrected for typos and hope we found everything.								
33	In add	lition, the manuscript gets rather long and I strongly recommend focusing on the								
34	main	main objectives addressed. A very last time, I give you the chance to revise the								
35	manu	manuscript according to the recommendations. Please go carefully through the individual								

. .

good recommendations are fundamental for improving the quality of your manuscript and 37

reviewer comments; also have a look at the previous recommendations. Many of these

for meeting the standard requirements for publication in HESS. After resubmission, I will
 make a final decision.

3 Answer:

4 Dear Christine Stumpp,

5 We offer an excuse because the last review was not addressed properly and the answers to 6 the reviewers not adequately considered in the manuscript. We went again through both of 7 the two reviewer comments and think that the manuscript could be substantially improved 8 by including the recommendation of the two reviewers. We hope that the manuscript will 9 now meet the standard requirement to be published in HESS. Further we added a 10 document (Abramova, 1969) to the supplementary material that was for some reason not 11 available to the reviewers. This should of cause not be published with our manuscript.

We would appreciate to get the names of the reviewers if they agree. Then we would mention them in the Acknowledgements since their comments were a great support to improve the manuscript

15

16 We wish you a merry Christmas and a happy new year 2016.

In-situ unsaturated zone water stable isotope (2H and 18O) measurements in semi-arid environments: Potentials and limitations.

4

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- 14

1 Abstract

Stable isotopes (deuterium, ²H, and oxygen-18, ¹⁸O) of soil water were measured in the field
using liquid water isotope analyzer (tunable off-axis integrated cavity output spectroscope,
OA-ICOS, LGR) and commercially available soil gas probes (BGL-30, UMS, Munich) in the
semi-arid Cuvelai-Etosha Basin (CEB), Namibia.

6 Results support the applicability of an in-situ measurement system for the determination of 7 stable isotopes in soil pore water. High spatial and temporal resolution was achieved in the study area with reasonable accuracy and measurements were in agreement with laboratory-8 9 based cryogenic vacuum extraction and subsequent cavity ring down laser spectroscopic 10 isotope analysis (CRDS). After drift correction of the in-situ isotope data, precision for over 140 measurements taken during two consecutive field campaigns (June and November, 2014) 11 were 1.8 ‰ and 0.48 ‰ for δ^2 H and δ^{18} O, respectively. Mean accuracy using quality check 12 standards was 5 ‰ and 0.3 ‰ for δ^2 H and δ^{18} O, respectively. The isotope depth profiles are 13 14 used quantitatively to calculate a soil water balance. The contribution of transpiration to total evapotranspiration ranged between 72 % and 92 %. Short after a rain event the contribution of 15 transpiration was much lower with 35 % to 50 %. 16

17 Potential limitations of such an in-situ system are related to environmental conditions which 18 could be extended using a temperature controlled chamber for the laser spectrometer. Further, 19 the applicability of the system using previously oven dried soil material might be limited by 20 physicochemical soil properties (i.e. clay minerals). Furthermore the influence of soil respired 21 CO_2 to isotope values within the root zone could not be deduced from the data. 22

1 **1 Introduction**

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

17 In most unsaturated zone studies manual removal of soil samples and a subsequent extraction of soil water in the laboratory was necessary using either vacuum extraction (e.g., West et al., 18 19 2006; Koeniger et al., 2011; Orlowski et al., 2013), equilibration (e.g., Wassenaar et al., 20 2008), mechanical sqeezing, azeotropic distillation or centrifugation methods (e.g., Walker et 21 al., 1994; Kelln et al., 2001). These methods cause both disturbance to the integrity of the 22 natural soil system and possible evaporation during the sampling procedure. The latter is 23 especially important for dry soils. Hence, soil water extraction techniques are labor intensive 24 and expensive which is limiting the use of stable isotopes compared to the other state variables such as soil moisture or matrix potential measurements. Indeed, there are suction 25 26 cup installations which allow a removal of soil water non-destructively but they are not 27 applicable in (semi-) arid environments. This is especially true during the dry season where 28 vapor transport (i.e. evaporation) is the dominant driver for water fluxes in the unsaturated 29 zone but is much less studied than the liquid water component (Soderberg et al., 2012). In this 30 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. Volkmann and Weiler, (2014) developed custom built 9 poly-ethylene (PE) probes with an equilibration chamber allowing additional mixing of the 10 vapor to prevent condensation in the sample line. They further proposed a sophisticated 11 system with a CRDS device (Picarro L2120-i, CA, USA) calibrated with standards added to 12 previously oven dried substrate from their study site.

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

26

27 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 km² where the northern part (approx. 52,000 km²) belongs to Angola and the southern part to Namibia. This sedimentary basin is divided into four major sub-basins called Iishana, Niipele, Olushandja and Tsumeb and can be further separated into different drainage zones. Measurements were

conducted within the eastern sand zone close to the township of Elundu as indicated in Figure 1 2 1. The assignment of the catchment and its sub-basins is based on geography, population distribution and water infrastructure (Dragnich et al., 2004). The main shallow aquifer system 3 4 in the CEB is a multilayer aquifer system in the Andoni formation with a thickness of 6 to 80 5 m. The main groundwater flow is towards the Etosha pan with an average gradient of 0.2 % (Christelis and Struckmeier, 2001). Beside the shallow aquifer, recent studies identified an 6 7 area of 500 km² potentially containing fresh groundwater at a depth of 200 m namely the 8 Ohangwena II aquifer (Lindenmaier and Christelis, 2012; Lindenmaier et al., 2014). 9 Groundwater recharge mechanisms concerning both, the shallow and the deep aquifer are not 10 yet fully understood. The shallow aquifer system consists partly of freshwater lenses on 11 brackish to saline groundwater mostly in the Iishana region. Perched discontinuous aquifers 12 are found in the eastern part of the basin they develop on clay lenses in the subsurface and are 13 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 with 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.

20 The investigated site is forested, predominantly vegetated with *Combretum collinum*, Acacia erioloba and Baikiea plurijuga. The deep Kalahari sand can reach a depth of over 40 meters 21 and has high saturated hydraulic conductivity $(2304 - 2409 \text{ cm } \text{day}^{-1})$ determined with 22 double-ring infiltration experiments, high porosity (0.4) and low field capacity (~ 3.5 %). 23 24 Sampling and measurements were conducted during two field campaigns. The first field campaign was carried out between June 9th and 15th, 2014 and the second between November 25 15th and 22nd, 2014. To determine heterogeneity of infiltration and evaporation processes and 26 27 to evaluate an in-situ approach determining stable isotopes in soil water nine plots within an area of 9,000m² were investigated. During the first campaign soil gas probes were installed at 28 depths of 2, 5, 10, 15, 20, 25, 30, 40 and 50 cm. Two plots were established with different 29 vegetation characteristics such that one was vegetated with shrubs and the other was exposed 30 31 without any vegetation. During the second field campaign probes were installed at depths of 2, 5, 7.5, 10, 12.5, 15, 17.5, 20, 25, 30, 40, 50, 60, 70, 80, 90 and 100 cm to reach a maximum 32

resolution especially for the top layer. Soil moisture measurements were conducted with a time domain reflectrometry system (TDR, EasyTest, Poland) at the beginning of each measurements cycle with the same resolution. In addition to the in-situ measurements samples were collected in head space glass vials, crimp sealed to avoid evaporation and the soil water extracted in the laboratory. Samples were transported via aircraft to the laboratory of the Federal Institute of Geosciences and Natural Resources (BGR) in Hannover, Germany.

7 In the laboratory grain size analyses was conducted on 10 g soil material from the extracted 8 soil samples with the method proposed by Altuhafi et al. (2013). Soil water was extracted 9 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 10 11 instead of a water bath. The sample vials are entered into the hot aluminium block to evaporate the water sample. Each sample was evacuated at -3 mbar vacuum and extracted for 12 15 min. The extracted water samples were subsequently measured with a cavity ring-down 13 14 spectrometer (CRDS, model L2120-i, manufactured by Picarro Inc.). ¹⁸O/¹⁶O and ²H/¹H isotope ratios are normalized on the international δ - scale and expressed as parts per thousand: 15

16
$$\delta = \left[\left(\frac{R_{sample}}{R_{reference}} \right) - 1 \right]$$
 [1]

where R_{sample} (-) denotes the ${}^{18}O/{}^{16}O$ isotope ratio (respectively ${}^{2}H/{}^{1}H$) of a water sample and 17 R_{standard} (-) those of the Vienna Standard Mean Ocean Water (VSMOW) (Coplen, 2011). All 18 19 values where corrected for drift and memory applying the method proposed by van Geldern 20 and Barth, (2012). Accuracies for long-term quality check standards are better than 0.2 ‰ and 0.8 % for water samples, but an additional error for sandy soils needs to be considered which 21 can be better than 0.8 ‰ and 4 ‰ for δ^{18} O and δ^{2} H, respectively as suggested by Königer et 22 al. (2011). The standard deviation determined from replicate samples (three per extracted soil 23 24 sample) is used as an additional analytical error. Subscripts are used to distinguish between 25 either the in-situ (I) and the cryogenically (C) derived isotope values in the remaining text.

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 response to the requests of the laser

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

11 Four repetitive measurements at each depth were performed during the first campaign. During 12 the second campaign six consecutive measurements were performed at each depth. A 13 measurement cycle consists of three steps: i.) a flushing phase where the cavity is evacuated, 14 ii.) the sample intake opening a particular valve and iii.) the measurement of the sample. 15 Flushing introduces a vacuum of 0.1 torr or less. The sample intake is controlled by valves which are opened for 10 s for each measurement allowing a volumetric flow rate between 95 16 17 and 110 ml/min. The transported gas volume is measured with a flow rate control device (Analyt-MTC, 0-200 ml min⁻¹). The probe and the transport lines to the analyser have a 18 volume of approximately 40 ml. The lines are made of steel and are connected with 19 Swagelok[®] connectors. After six consecutive measurements at one depth, the sampled soil 20 volume is approximately 120 ml. Assuming that the soil volume around the 300 mm long 21 22 probe is sampled equally over the whole length, a diameter of 1cm around the probe will be 23 directly affected by the uptake of vapor via the probe. Hence the top layer is measured with reasonable accuracy for this particular setup. The measurement of a 1 m deep profile 24 25 considering 16 different depths with six repetitions and a resolution down to 2.5 cm for the 26 top 20 cm takes about 4.5 hours. The OA-ICOS device needs an additional warm up of about 27 two hours in order to get a 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 in distance from each other 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 is done using 200 g of previously oven dried (at 105 °C for at least 24 h) 1 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 4 Germany) from the laboratory of the University of Windhoek to the field site and were then 5 spiked directly in the field with a volume of 5 ml standard before the experiment at the day of measurement. Normalization to the international scale is done using one low standard 6 7 (HGLA) and one high standard (HMER). In addition one standard for drift correction (HDES) 8 and a quality check standard (HLAU) were used. The quality check standard is a water of 9 known isotopic composition that is treated as an unknown sample. The difference between 10 that known value and those measured expresses the accuracy of the measurement. All 11 standards were measured at the beginning of each experimental sequence; additionally HDES 12 and HLAU were measured at the end of each sequence. Isotope values of the used standards 13 are illustrated in Table 1. The standards were used only for two consecutive measurement 14 series and then new standards were prepared. Calibration standards were kept in flasks with a 15 diameter of 2 cm and a length of 50 cm. Soil gas probes were subsequently entered and the 16 flasks sealed to avoid evaporation.

17 Soil water balance

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

23
$$R = \left[\frac{22}{\delta^2 H_{shift}}\right]^2$$
 [2]

 $24 \quad \text{ and for } \delta^{18}O$

25
$$R = \left[\frac{3}{\delta^2 O_{shift}}\right]^2$$
[3]

Assuming steady state soil evaporation is calculated from the isotope depth profiles using an analytical 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} [hPa], the tortuosity with τ =0.67 [-], the diffusitivity of water vapor in air $D^v = 24 * 10^{-6} [m^2 s^{-1}]$, the density of water ρ [$kg m^{-3}$], the porosity p and the soil water content $\theta_v [m^3 m^{-3}]$. 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} 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 δ is calculated from the fitted parameters z_{ef} , the isotope 11 value of the reservoir δ_{res} and the isotope ratio at the evaporating front δ_{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 grain 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 α calculated at 24 °C, the minimum r¹ and the maximum r² 16 grain size of the soil.

17 3 Results

18 Campaign 1

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

During the first campaign (June 15th, 2014) measurements were taken at two plots (E1.1, E1.2) at a distance of 25 meters on the same day. The measurement at E1.1 started at 09:30 and later at 16:00 at plot E1.2. Plot E1.1 was not vegetated and had a thin soil crust in the top first 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 to 0.7 % at 50 cm depth (Figure 3, center). The isotope depth profiles were of similar shape 2 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 shape of the isotope 6 depth profiles was different for δ^{18} O and δ^{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 very low water contents 15 16 (< 1 %), 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_{max} and 30 %_{min}; night ~20 °C_{min} and ~ 90 %_{max}). 21 Two rainfall events were recorded (November 12nd, 2014: 12 mm morning, November 13rd, 22 23 2014, 30 mm morning) at the climate station in Eenhana which is approximately 15 kilometers west of the experimental site. However, there is no isotope data available until 24 November 17th, 2014. Later during the campaign a small rain event (16 mm) could be 25 sampled for isotopes on November 17th, 2014 at 8:00 a.m. with -0.6 % and 3.0 % for δ^{18} O 26 and δ^2 H, respectively. A smaller event (4 mm) could be sampled at November 19th, 2014 with 27 isotope values of 3.6 ‰ and 28.8 ‰ for δ^{18} O and δ^{2} H. Both events are indicated in Figure 7 28 29 by a grey dot on the x-axis.

30 The plots that were sampled in November (rainy season) have higher water contents 31 compared to those of the first campaign. One non-vegetated plot of the second campaign

1 (E2.7, see Fig. 4 right hand side and Table 2) is used to compare the in-situ and the laboratory 2 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 3 enrichment of δ^{18} O is in the top layer declining exponentially with depth for both methods. 4 There is good agreement between $\delta^{18}O_I$ and $\delta^{18}O_C$ except for the depth at 30 cm and 50 cm. In 5 contrast, there are substantial differences between $\delta^2 H_I$ and $\delta^2 H_C$. Above 25 cm values of $\delta^2 H_C$ 6 are higher (-15.5 % to -22.6 %) than for $\delta^2 H_I$ (-25.0 % to -29.2 %), and vice versa lower 7 below 25 cm with -23.4 % to -15.2 % for $\delta^2 H_C$ and -11.6 % to -5.1 % for $\delta^2 H_I$, respectively. 8

9 There is a good agreement between in-situ and cryogenically obtained isotope measurements 10 for both isotope depth profiles of the first campaign between 15 and 50 cm (RMSE= 3.9 and 9.2 % for δ^{18} O and δ^{2} H, respectively). However, higher values were observed for the in-situ 11 approach at shallower depth (RMSE= 7.0 and 43.4 % for δ^{18} O and δ^{2} H, respectively). In 12 general, better agreement can be observed for δ^{18} O compared to δ^{2} H values. Both isotope 13 14 profiles of the first campaign derived from the cryogenic vacuum extraction show a maximum at 15 cm with an exponential decline down to depth. Values of the in-situ measurement show 15 this maximum at 10 cm, but only for $\delta^{18}O_{I}$. The profile of the second campaign does show 16 good agreement within the top 25 cm for $\delta^{18}O_I$ but for δ^2H only within the upper 10 cm. In 17 terms of accuracy for the set of these three profiles we obtain 6.86 % and 1.87 % for $\delta^2 H_I$ and 18 $\delta^{18}O_{I}$ respectively. 19

A compilation of the quality check standards for $\delta^2 H_{qc}$ and $\delta^{18}O_{qc}$ of the two campaigns is 20 21 shown in Table 2. The standard deviation of the repetitive measurements for each depth is a 22 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 5.2 ‰ $\delta^2 H$ 23 and 0.66 $\% \delta^{18}$ O, respectively. The mean precision of the repetitive measurements (σ_{rep}) is 24 two times better for $\delta^2 H_I$ than for the precision of the repetitive measurements (σ_{crv}) for values 25 26 derived with the cryogenic vacuum extraction $\delta^2 H_{C}$. Values of $\delta^{18}O_{ac}$ show a higher similarity (refer to Table 2). The measurement of the second profile E1.2 is less precise for $\delta^2 H_I$ but in 27 the same range as $\delta^2 H_c$. Similar precision as for profile E1.1 is found for the third profile E2.7 28 for both δ^2 H and δ^{18} O, respectively. 29

30

31 δ^{18} O vs δ^{2} H

In Figure 5 the δ^{18} O to δ^{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 non-6 vegetated plot and 3.1 ($R^2 = 0.96$) for the vegetated plot. In-situ measurements of the non-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 δ^2 H values. 9 10 Excluding the top 15 cm of the in-situ measurement the slope remains the same but R² 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 (σ_{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 (σ_{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 σ_{qc} and $\sigma_{rep.}$ However, the precision of δ^2 H is within the range of the mean accuracy of 5.1 ‰. The accuracy of δ^{18} O is much 22 higher with 0.11 ‰. There are two outliers (E2.8, E2.9) who were not considered for the 23 24 mean precision nor for the mean accuracy.

25 Mean values of each transect are shown to illustrate an averaged temporal characteristic with intermittent rainfall (Figure 6) for this particular area. The first transect is affected only from 26 27 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 affected by the 16 mm event (17th November, 2014) of which 28 29 isotope data is available and the 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 30 additional precipitation on the 19th Nov 2014 with an amount of 4 mm. Maximum infiltration 31 32 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 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 $\delta^{2}H$ 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

8 contrast, the standard deviation of δ^{18} O and δ^{2} H increases with decreasing soil water content.

9 Soil water balance

10 Precipitation (P) for the rainy season was measured with an amount of 660 mm. Recharge 11 estimated from soil water stable isotope data is less than 1 % of precipitation. It ranges between R = 4 – 5 mm y⁻¹ derived from $\delta^2 H_{shift}$ and $\delta^{18} O_{shift}$, respectively. The soil water 12 storage (S) is derived from the soil moisture depth profile and the evaporation front is 13 14 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_{ef} using the isotope depth 15 profiles. The mean of all results from E1.1 and E1.2 is $120 \pm 50 \text{ mm y}^{-1}$. Then, Recharge (R), 16 soil water storage (S) and soil evaporation (E) are subtracted from precipitation (P). The 17 remainder is potentially available for transpiration (T) with 510 \pm 50 mm y⁻¹. Runoff can be 18 19 neglected because it was not observed at the experimental site. Hence, the contribution of 20 transpiration to total evapotranspiration (E/T_{pot}) is 77 \pm 7 %. The potential contribution of 21 transpiration (E/T_{pot}) or root water uptake at the non-vegetated plot is between 76 and 92 %. At the site underneath the canopy and vegetated with shrubs E/T_{pot} is between 72 and 92 %. 22 Values of z_{ef} range between 110 and 290 mm which is in agreement with values derived from 23 a physical model proposed by Or et al., (2013). Considering two different ranges, one for 24

a physical model proposed by Or et al., (2013). Considering two different ranges, one for finer and one for coarser texture, 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⁻¹ and 161 - 201 mm y⁻¹ for r¹ and r², respectively.

After the rain events during the second field campaign the evapotranspiration pattern is dominated by soil evaporation. The evaporation front is still developing ($z_{ef} = 82 - 90$ mm)

1 and E/T_{pot} is much lower with 35 – 51 %. Applying this methodology to the different 2 transects, 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 δ^{18} O and δ^{2} H, respectively. This is a feasible precision if it is compared the precision of 7 isotope values from the cryogenic vacuum extraction method which are 0.8 ‰ and 3.5 ‰ for 8 9 δ^{18} O and δ^{2} H, respectively. It is still worse compared to the precision that can be achieved measuring stable isotopes directly from water samples (0.2 % and 0.8 % for δ^{18} O and δ^{2} H). 10 However, it needs to be considered that such laser spectrometers are in general mounted in a 11 12 temperature controlled laboratory. In this study, accuracy and precision of the presented in-13 situ system is mainly limited by the environmental conditions. If the laser spectrometer and 14 the autosampler would be operated within a temperature controlled environment, possibly, the 15 precision could be improved. However, this study could demonstrate that it is possible to 16 determine stable isotopes of soil water directly in the field with a similar or even better precision compared to destructive sampling and a subsequent soil water extraction in the 17 18 laboratory. This creates possibilities to investigate water vapor transport processes that are 19 difficult to measure with other techniques such as soil moisture or suction tension 20 measurements. Evaporation processes are physically well described (i.e. Or et al., 2013), but 21 their determination in the field remains very difficult. An approach to observe evaporation 22 was presented by Rothfuss et al. (2015) who could show the development of an isotope depth 23 profile in a drying soil column experiment with a similar in-situ approach as in the present 24 study. However, their experimental setup did not reflect conditions that can be found at our 25 study site, since much higher temperature and humidity gradients were observed between day 26 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 very low water holding capacity and very low abundance of silt and clay. The cryogenic vacuum extraction is capable to extract the entire 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 with the soil gas probe in a very coarse material atmospheric vapor or even vapor 7 from other parts of the soil can lead to a mixed sample. However, the extracted air volume is 8 very low and a divergence of isotope values is only visible within the top 15 cm of the dry 9 profiles (Figure 3, left and center). Evaporative enrichment is reflected in the deuterium excess (dex) and also in the so-called evaporation line (Craig and Gordon, 1965). Evaporative 10 11 enrichment could also be enhanced by the uptake of water vapor through the measurement 12 (Figures 5 and 6). The equilibrium condition prevailing between soil liquid and gas phases is 13 disturbed when water vapor is removed. Then the sampled water vapor can be depleted at 14 first. After some time, depending on the uptake rate and the soil water content, the initial 15 isotopic composition of the remaining soil water might enrich itself and isotope values in the sampled gas will become more enriched. This effect might be reflected in a reduced precision. 16 17 However, enrichment caused by the uptake of air through the measurement is not visible for deeper parts of profile E1.2 which is very dry as well. Hence, arguing with low water contents 18 19 would suggest to have enriched values for deeper parts of the vegetated profile. This is not 20 observed at the vegetated plot where soil water contents are below 1% throughout the whole 21 profile (Figure 3, center). Since the in-situ approach is based on the same principle as the 22 equilibration bag method its applicability on samples with low water content is supported by a 23 recent study of Hendry et al., (2015). They found that the accuracy of their equilibration 24 procedure could be improved by increasing the sample amount.

25 Beside this, it has to be noted that destructive sampling was conducted one day after the insitu measurements because it was assumed that the isotope profiles are in steady state (Barnes 26 27 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 28 29 attributed to kinetic processes, because vapor transport (i.e. evaporation) and hence isotopic 30 enrichment will more pronounced at shallow depths as described by Braud et al. (2009). 31 Natural temporal variability such as high temperature and humidity changes between day and night could be another possible explanation. During the day evaporation dries the top layer 32

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

10 Another possibility for a change in isotopic composition at shallow depths can be hydraulic 11 lift. In this case water from deeper soil layers with higher water potential can move through 12 the root system to soil layers with lower water potential (Dawson et al., 1993) The dense root 13 mat of fine roots observed in the upper part of the soil profile together with very low water 14 contents and the differences between the isotope depth profiles could be an indicator for this 15 process. However, the measurement of soil physical properties, stable isotopes of soil water 16 and xylem covering the diurnal cycle would be necessary to distinguish between either vapor 17 back diffusion or hydraulic redistribution.

18 Campaign 2

19 In contrast to depth profiles of the first campaign the rain influenced profile E2.7 doesn't 20 show such a divergence in the top layer as observed at E1.1 and E1.2. As shown in Figure 5 21 the deuterium excess indicates that precipitation water is dominating. Good agreement is 22 found in the top layer for both isotopologues. Mixing with atmospheric vapor might be negligible considering the high soil water contents. Destructive sampling was done directly 23 24 before the in-situ measurement started. It has to be noted that, in-situ measurements at 10 cm 25 depth were done 90 min after the destructive sampling was conducted. In-situ measurements 26 at 30 cm depth were conducted even 120 min later. Differences can be caused by the time lag 27 between destructive sampling and in-situ measurement, vapor transport processes induced by 28 temperature gradients or diffusion.

29 Considering that under the present "wet" conditions (but also if the soil moisture is around 30 wilting point) humidity of the pore space is close to saturation. Then temperature gradients 31 will cause a movement of vapor downward and upward depending on the temperature profile 1 (Abramova, 1969). Further, soil evaporation can be separated into direct evaporation from a 2 water saturated surface (stage I evaporation) and diffusion controlled vapor transport (stage II 3 evaporation) (Or et al., 2013). Therefore, observed differences between $\delta^2 H_I$ and $\delta^2 H_C$ for 4 profile E2.7 (Figure , right) might be attributed to the exchange between the evaporation 5 depleted vapor that was transported from the deeper part (30 cm to 50cm) to shallower depth 6 (12.5 cm and 25 cm) due to diffusion controlled evaporation (stage II).

$7 \qquad \delta^{18}O \ vs \ \delta^2 H$

8 Values for in-situ measurements and cryogenic extraction plot on evaporation lines which are 9 similar in slope (excluding the top 12.5 cm). The outliers in the top-right area and those above the LMWL of the δ^2 H vs. δ^{18} O plot (Fig. 5) are from the top 12.5 cm of the profiles. As 10 discussed earlier, diurnal temperature and humidity cycles could cause i.e. condensation in the 11 12 upper part of the soil profile, but also higher enrichment during the daytime compared to the 13 conditions during the night when the soil is colder than the vapor in the atmosphere. Further, 14 the interaction between soil water potential and water vapor, which might be driven by relative humidity (Wilson et al., 1997) but the effect to isotope fractionation, is not well 15 16 understood and will be a challenge to future research (Soderberg et al., 2012). The 17 investigation of such processes using in-situ approaches for stable isotope analysis seem to be 18 promising in this regard, since the composition of vapor can be measured in the field.

19 Spatio-temporal variability

20 The boundary conditions of the second field campaign caused a quite heterogeneous pattern regarding both the development of the moisture front and the isotope depth profiles. It can be 21 22 observed how the infiltrating water develops under evaporation with light intermitted rainfall events. This is reflected in both the shape of isotope depth profiles of the three transects and 23 24 the standard deviations within one transect (Figure 6). Other studies showed similar patterns 25 in the context of a numerical experiment (Singleton et al., 2004). The first transect (Figure 6, 26 Transect 1) has variable isotope values throughout the whole depth. The isotope depth profile 27 of transect one shows maxima and minima of isotope values which appear with a similar 28 shape as a profile in a humid climate. This kind of layering is commonly used in humid 29 regions to determine transit times of unsaturated zone water where precipitation has seasonal 30 different isotopic composition (Coplen et al., 2000; Lee et al., 2007). However, here it is 31 attributed to variations in rainfall composition and infiltration patterns on a much smaller time scale namely daily. Zimmermann et al., (1967) previously described that isotopically distinct 32

rain that is consecutively infiltrating into the soil will move 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) might correspond to certain rain events which would not emerge from the soil moisture measurements alone. These depleted zones are not visible in the other transects which are possibly overprinted by vapor transport processes and evaporation.

7 Short time after rains stop the top part of the evaporation profile (Transect 1) was 8 considerably displaced as theoretically described by Allison et al., (1984). Variations of 9 isotope values are attenuated with time by vapor phase redistribution (Transect 2) (Fontes et al., 1986) and an evaporation profile is begins to develop (Transect 3) (Rothfuss et al., 2015). 10 11 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 the presented in-12 13 situ measurements have great potential to visualize theoretically discussed processes with 14 feasible accuracy under natural field conditions.

15 Spatial variability of soil moisture is well known (Western et al., 2004). It can be expected 16 that also stable isotopes will distribute heterogeneous within the unsaturated zone. The relationship between mean soil moisture and $\delta^2 H$ does not allow a resilient conclusion 17 because of the low accuracy. However, it appears that it behaves different for $\delta^2 H$ and $\delta^{18}O$ 18 19 values compared to soil moisture. The differences might be related to vapor diffusion 20 processes or to biological processes. For instance, Dawson et al. (2002) discussed the isotopic 21 composition of different carbon and water pools. Soil respired (CO₂) will equilibrate with the 22 abundant soil water and might cause additional changes of the isotopic composition of the soil 23 pore water.

24 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 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 calculation 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 small 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).

8 **Potential limitations**

9 Water vapor mixing ratio dependencies (Wang et al., 2009; Sturm and Knohl, 2010; Rambo et 10 al., 2011; Aemisegger et al., 2012) are of minor importance in this study, because the water content was maintained within the density of approximately 2- 4*10¹⁶ molecules cm⁻³ 11 as 12 recommended by Los Gatos Research. It is assumed that small variations will be reflected in the standard deviation of the measurements. Additionally, inference through organic 13 14 contamination is neglected in this study. However, if necessary to account for inference recent 15 efforts include calibration strategies in this regard (Wu et al., 2014). Possible fractionation 16 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 $0.5 \text{ meg } 100\text{g}^{-1}$ and 17 total organic carbon (TOC) 0.22 %. 18

19 During the second field campaign information on long term precision and spatio-temporal 20 variability was investigated. Comparing the quality check standards of the two campaigns the precision within one series (σ_{rep}) of $\delta^2 H$ is one-third better than the long term accuracy. 21 However, the accuracy of δ^{18} O is three times greater than the mean precision (Table 2). This 22 23 can likely be improved by utilizing a more sophisticated technical setup e.g. temperature 24 controlled conditions. Another reason could be the difference in the physical properties of the probe pores such as the diffusivity of gas (Merlivat et al., 1979). Though there is no detailed 25 26 chemical data available it is unlikely that chemical properties are responsible, since the sandy soil has a very low CEC. More likely are biological processes that are introduced due to the 27 28 sudden availability of water. Nevertheless, there is no data (i.e CO₂ measurements) available 29 to support this assumption. Therefore, it would be beneficial to measure CO_2 concentration in 30 parallel. However, the precision appears to be sufficient to monitor processes of a diurnal time 31 scale and also comparable to other systems that were tested in the field, e.g., Volkmann and Weiler et al. (2014) with values of 2.6 ‰ and 0.38 ‰ for δ^{2} H and δ^{18} O, respectively. 32

Condensation within the sample system can lead to unreliable data. This can be either 1 2 prevented by heating the sample lines, flushing the sample lines with dry air or sufficient dilution of the sample. Thus, under conditions where the ambient temperature is significant 3 4 warmer then the soil temperature a simple valve controlled membrane inlet will be sufficient 5 for an indirect determination of isotopes in unsaturated zone or saturated zone water. During day time this is the case at the presented study site, but changes drastically overnight as 6 7 described. Dilution of the vapor concentration can be done by providing dry gas at the other 8 end of the available probes. In the case of pure diffusion sampling the maximum dilution rate 9 depends upon the absolute amount of water molecules in the vapor and is controlled by the 10 length of the probe, their diffusion properties, the flow velocity and the temperature at depth. 11 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 12 13 directly before the vapor enters the sample line (Volkmann and Weiler, 2014). This leads to 14 independence on flow velocity, probe length and membrane diffusion properties with regard to the water content of the sampled vapor. Under very dry conditions it might be useful to 15 16 increase the probe length, since the soil volume around the probe affected by the measurement 17 will be reduced.

18 A critical point is the long term application of membrane based methods. The pore space of 19 the probes can be altered over time which might increase the memory effect of the system. Further, the calibration of the in-situ methods of Volkmann and Weiler (2014) and Gaj et al. 20 21 (this study) used prior oven dried substrate for the calibration. This procedure assumes that all 22 water is evaporated during oven drying and only the added standard water will be measured 23 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 24 25 minerals is commonly removed under vacuum heating the sample to 200 to 300 °C for several 26 hours (VanDeVelde and Bowen, 2013). These adsorbed and interlayer water is bound on the 27 mineral surface and exchanges with atmospheric water vapor within hours (Savinand and 28 Epstein, 1970). Hence, for soils containing clay minerals a calibration procedure using 29 previosly oven dried soil materials might mislead. The presented direct comparison of the 30 cryogenic vacuum extraction with a membrane based in-situ measurement showed that this 31 calibration procedure is at least applicable for fine sand. However, it will probably lead to 32 insufficient data applying this calibration procedure to soil samples with finer texture, 33 especially if clay, silt and/or salt contents are high (Oerter et al., 2014).

1 5 Conclusion

2 The present study demonstrates that high resolution in-situ sampling of stable isotopes in the 3 unsaturated zone is feasible. In-situ measurements can be applied with minimal technical 4 effort for remote applications. They further show good agreement with values derived from 5 cryogenic soil water extractions. Differences between the two methods are predominantly 6 within the given accuracies of the methods. Divergence in the upper soil layer between in-situ 7 and destructive sampling suggest enhanced soil-atmosphere interactions, kinetic processes 8 due to high evaporation rates or hydraulic redistribution. Evaporation induced by the 9 measurement procedure might decrease the precision depending on the uptake rate and the 10 soil water content. However more important, to prevent the collection of insufficient data 11 applying an in situ approach one has to carefully consider the applied calibration procedure depending on the research question and the soil type. In addition, there is a trade-off between 12 technical effort, control setup, probe type, environmental conditions and costs. 13

Low humidity in relation to soil water potential and isotope fractionation needs further investigation. Long term accuracy within the presented campaigns is about two times lower for δ^2 H and three times for δ^{18} O than for the short term precision of each profile. This can possibly be improved by a better temperature control of the analyser or temperature compensated devices if available.

19 The presented and also other in-situ measurement approaches have great potential to 20 investigate transient processes within the unsaturated zone. This has not been possible to 21 study until field deployable laser spectrometer and in-situ techniques became available. The 22 determination of water stable isotopes in the unsaturated zone directly in the field allows 23 monitoring transient processes which would not be possible with destructive sampling 24 strategies. This creates new possibilities to the design of tracer experiments with water of 25 different isotopic composition as conservative tracer. However, this is limited by the 26 measurement frequency of the provided system which is now at least able to capture diurnal 27 processes with the presented vertical resolution. In addition, a much higher spatial resolution 28 can be achieved with much lower time consumption compared to conventional approaches. 29 The proposed technique offers the possibility to investigate unsolved questions regarding soil 30 atmosphere interactions such as water vapor intrusion and transport plus effects of diurnal 31 evaporation cycling on isotope depth profiles.

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

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

laboratory.

Abbreviation	Description	$\delta^2 H$ [‰] σ	δ ¹⁸ Ο [‰] σ
HMER	Hannover sea water	-3.1 ± 0.1	4 -0.4 ± 0.13
HDES	Hannover distilled water	-55.9 ± 0.1	9 -8.12 ± 0.14
HLAU	Hannover lauretaner water	$-64.6 \pm 0.$	$6 -9.73 \pm 0.10$
HGLA	Hannover glacier water	-152.1 ± 0.1	9 -20.27 ± 0.11

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

ID	Date	Init.Time	$\delta^2 H_{qc}$ [‰]	σ_{qc}	σ _{rep}	σ _{cry}	$\delta^{18}O_{qc}$ [‰]	σ_{qc}	σ _{rep}	σ _{cry}
E1.1	04.06.2014	09:30:00 I	B -60.09	± 5.13	1.4	3.7	-10.04 \pm	0.66	0.7	0.8
E1.2	04.06.2014	15:30:00	-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 I	-73.25	± 0.87	1.17		-10.38 \pm	0.34	0.45	
E2.2	16.11.2014	08:00:00 I	-69.83	± 0.99	1.26		-8.05 \pm	0.48	0.35	
E2.3	16.11.2014	13:30:00	-71.11	± 0.49	2.21		-10.29 ±	0.14	0.54	
E2.4	17.11.2014	11:00:00	-57.51	\pm 4.11	1.72		-8.45 \pm	0.14	0.28	
E2.5	18.11.2014	11:00:00	-64.82	± 1.86	1.52		-7.73 ±	0.34	0.28	
E2.6	19.11.2014	07:30:00 I	-75.62	± 1.84	2.49		-6.81 ±	0.81	0.5	
E2.7	19.11.2014	14:00:00 I	3 -79.35	± 1.27	1.93	3.5	-11.62 ±	0.36	0.45	0.45
E2.8	20.11.2014	11:30:00	-25.24	± 2.53	1.45		-3.68 \pm	0.25	0.24	
E2.9	21.11.2014	11:30:00	-23.00	\pm 17.17	1.74		-15.59 ±	4.17	0.37	
		_								
		X		2.15	1.86	3.57		0.36	0.46	0.62

1 Table 3: Soil evaporation (E) is derived from stable isotope depth profiles. The isotope value of the

- 2 reservoir δ_{res} , the evaporating front δ_{ef} and the effective depth z_{ef} are estimated from a exponential fit to
- 3 the isotope depth profiles. The Soil water storage (S) is calculated from the soil moisture depth profile.
- 4 Transpiration (T) is the remainder from annual precipitation (P=660 mm) after subtracting the Recharge
- 5 (R=4 and 5 mm for ²H and ¹⁸O, respectively), E and S. The partitioning between soil evaporation to
- 6 transpiration is calculated as the contribution of transpiration (E/T_{pot}) to evapotranspiration = E+T.

0										
	z _{ef} [mm]	δ _{res} [‰]	δ _{ef} [‰]	E [mm/y]		S [mm]	T [mm/y]		E/T _{pot} [%]	
Cryo				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

¹⁸O



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). δ^2 H is given in blue and δ^{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: δ^{18} O vs δ^{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: ¹⁸O (red), ²H (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 σ 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 (O) 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.

Anonymous Referee #1 Round_1 General comments

1 2 3

The study presents soil isotope depth profile data of a semi-arid region in Namibia measured in-situ via soil gas probes attached to an OA-ICOS. The manuscript is well written and structured as well as easy to read. The study is in the scope of the journal and I recommend the presented study for publication in HESS after revising the submitted manuscript based on the suggestions of the review process.

9 The introduction section is well written and the relevant processes and fundamentals of stable isotope 10 hydrology for this study are addressed. However, I suggest shorten the introduction since a lot of basic 11 information are given in extent.

The presented sampling approach and the methods used are well described. However, the data poses more questions than the authors can answer. The amount of samples taken from other water cycle components (e.g. rainfall, groundwater) is rather limited which makes it hard to interpret the measured

- components (e.g. rainfall, groundwater) is rather limited which makes it hard to interpret the measured soil isotope profile data on its own. More frequent rainfall isotope data would be helpful in this regard
- 16 to answer the following question: What is the driver of the isotopic composition in the presented soil 17 profiles?
- 18 Given the fact that rainfall and groundwater isotope data are very limited, a more detailed discussion
- 19 about the vegetation influence on soil water isotopes would be desired. It would further be desirable if
- 20 the authors could make better use of the spatio-temporal isotope variability rather than just presenting 21 depth profiles, which is nothing new.
- The authors show soil moisture data for each profile. Did they correlate soil moisture versus isotopic signatures to proof the minor impact on the development of the isotope soil profiles in their study area?
- 25 When comparing the new in-situ method to the widely used cryogenic vacuum extraction technique,
- differences especially for isotope data of the upper soil profile were measured which could not be satisfactorily explained. Could these differences in the top soil be attributed to method issues rather
- than to kinetic processes? Could the new in-situ method after all be limited in terms of low water
- contents (<5%) as the differences between the cryogenic vacuum extraction and the in-situ approach occurred within the very dry top 15 cm of the profiles (<2% soil moisture) and enriched isotope values
- 31 were likewise measured in the upper soil profile?
- For instance, Wassenaar et al. (2008) admitted a limitation of their method, which is likewise based on vapor equilibrium measurements in this regard (not suitable for water contents <5%). The authors addressed this issue in its own section but still, the question remains why almost inverse isotope results were obtained from cryogenic extraction and the in-situ approach (Fig. 4) and further isotope which extraction method (in-situ vs. cryogenic extraction) are more reliable in the end. Finally, the authors should include a small paragraph on future research directions in the study area or further applications of the in-situ approach.

39 40 **ANSWER**:

41 The driver of the isotopic composition in the soil can be either the infiltration of rain water, biological 42 processes such as hydraulic redistribution or vapor transport introduced by i.e. strong temperature.

- 42 processes such as hydraulic redistribution or vapor transport introduced by i.e. strong temperature, 43 humidity and matrix potential gradients. We agree that additional isotope data of rainfall would be 44 helpful. However, work in a remote region limits data availability as well as sampling time and weather 45 can be unpredictable.
- 46 We did not correlate soil moisture against the isotope data. This is a good point. We will include this 47 data and add a paragraph in the discussion section (see attached Fig. 1).
- However, the intention to show isotope depth profiles for each transect with their standard deviation for isotopes and soil moisture was to show the difference between the two. The variability within the isotope depth profiles shows a much more heterogeneous pattern than that of the soil moisture data.
- 50 Isotope depth profiles shows a much more neterogeneous pattern than that of the soil moisture data. 51 This might be related to vapor diffusion processes. Another possibility could be that biological
- 52 processes are relevant to isotope fractionation in the soil, such if bacteria, funghi or roots discriminate
- 53 between light or heavy isotopologues.
- 54

It is unlikely that the soil water content is the issue here. Because for the profile at the vegetated plot soil water contents are below 1% throughout the profile and not such enrichment can be observed. Values of ¹⁸O are even more depleted. However, relative humidity of the pore space could be the issue at that point which has to be considered in future studies, because we did not measure it in the soil.

The equilibration method of Wassenaar et al., (2008) applied to dry samples has the disadvantage that the headspace is filled with dry air. This causes a small amount of water to evaporate from the sample. This can cause enrichment of the reservoir and causes different isotope equilibrium between vapor and the sample. However, using the in-situ approach the present vapor is sampled directly and the reservoir especially in sandy soils will equilibrate very quickly. Another study of Hendry et al., 2015 could show that the equilibration bag method is applicable to dry samples if the sample amount is increased. In case of diffusive sampling the headspace will be the volume of air transported through the sampling line.

9 When to apply which method depends on the research question. It can be beneficial to compare 10 methods to account for different water pools or states of the soil water (i.e. vapor, liquid water).

11

12 We further added a small paragraph and discussed methodical possibilities, limitation and future 13 research directions in the final manuscript.

1415 Specific comments:

16 Reviewer 1:

- 17 Generally, the text should be checked for punctuation.
- 18 ANSWER:
- We rechecked the text for punctuation and typos.

21 Reviewer 1:

22 P6116 L17-25 and P6118 L1-16: shorten these sections

23 ANSWER:

As recommended we shortened the introduction section substantially.

2526 Reviewer 1:

27 P6120 L15: Volkmann and Weiler (2014) not (2013)

28 **ANSWER**:

29 We corrected the year.

3031 Reviewer 1:

2 P6122 L25: Consider deleting Equation (1), not necessarily needed

32 P6122 L25:33 ANSWER:

34 We prefer to keep the equation.

3536 Reviewer 1:

- 37 P6124 L7: How was the additional error for sandy soil extractions determined?
- 38 ANSWER:
- The additional error for sandy soils is determined from Königer et al., 2011. We added the citation.

41 Reviewer 1:

- 42 P6125 L1-3: Consider addressing this question in more detail in the discussion section:
- 43 Atmospheric boundary conditions varied drastically between day and night. How does
- 44 this affect the isotope results?

45 **ANSWER**:

46 We discussed that as follows:

47 "During the night, temperatures decrease and relative humidity increases. Low soil water contents and 48 a back diffusion of vapor into the upper part of the soil might cause condensation, affect isotope 49 values (Rothfuss et al., 2015) and can significantly increase soil water content (Henschel et al., 2008) 50 and might deplete isotope values of the remaining soil water within that upper layer. In a numerical 51 study it was already shown that diurnal variations of evaporation can be large depending on the

- 52 energy budget at the surface but the influence on isotope concentrations needs to be further
- investigated especially under field conditions (Braud et al., 2005). "
- 55 And Later

56 "Considering that, under the present "wet" conditions (but also if the soil is at wilting point or lower)

- 57 humidity of the pore space is close to saturation, then temperature gradients will cause a movement of
- 58 vapor downward and upward depending on the temperature profile (Abramova, 1969). Further, soil

- evaporation can be separated into direct evaporation from a water saturated surface (stage I 1 2 3 evaporation) and diffusion controlled vapor transport (stage II evaporation) (Or et al., 2013). Therefore, observed differences between $\delta^2 H_l$ and $\delta^2 H_c$ for profile E2.7 (Figure , right) might be attributed to the 4 5 exchange between the evaporation depleted vapor that was transported from the deeper part (30 cm to 50cm) to shallower depth (12.5 cm and 25 cm) due to diffusion controlled evaporation."

Reviewer 1:

- 6 7 8 9 P6126 L1: To which variations are you referring to (these?)?
- 10 ANSWER:
- 11 We changed "these" to: "temperature and humidity variations".

12 13 **Reviewer 1:**

14 P6126 L8-10: Include this rainfall isotope data in Fig. 4

15 ANSWER:

- 16 We included the available rainfall isotope data (indicated by grey dots).
- 17

18 Reviewer 1:

19 P6127 L21: With which method was deep soil water extracted and what does "deep" mean in terms of 20 depth? Could you give the standard deviation for the local groundwater and deep soil water values as 21 well?

22 ANSWER:

- 23 We added as recommended:
- "Additionally, mean values of local groundwater (σ^{18} O=0.91, σ^{2} H=4.27) and soil water down to a depth 24 25 of 4m with 10cm resolution are presented. The analytical error for sand soil water extractions can be 26 considered for the deep soil water profile (Fig. 2). " 27

28 Reviewer 1:

29 P6128 L13: Could you explain why the method seemed to be less accurate for 2H (mean accuracy of 30 5.1‰?

31 ANSWER:

32 In general the analytical error for ²H is higher as for ¹⁸O. (see Königer et al., 2011). In addition, 33 considering the adsorption spectrum ²H hast the smallest peak, therefore small changes can lead to 34 high uncertainties during the measurement. 35

36 **Reviewer 1:**

37 P6131 L20-21: Did the authors consider the fact that destructive soil sampling causes macro pores 38 with effects on the gas exchange and therewith on the isotopic composition. In the soil profile 39 measured in-situ after the destructive sampling?

40 ANSWER:

- 41 Considering the present soil texture is very unlikely that destructive sampling introduces macropores. 42 In addition, the probes penetrated 40 cm into the profile, though we expect almost undisturbed
- 43 conditions.
- 44
- 45

46 **Reviewer 1:**

47 P6133 L6-10: Present more recent studies as references.

48 ANSWER:

- 49 We added more recent studies to that paragraph.
- 50
- 51 Fig. 2: More detailed scheme would be helpful.

52 ANSWER:

- 53 The general scheme was that simple. However, more valves could be switched using additional 54
- wiring. The communication to the analyzer was maintained with a USB-to-RS232 interface. In this 55 particular case, we manipulated the USB-to-RS-232 converter in such a way that we could switch 12V
- 56 valves by providing high and low signals to the wires of the interface with a python command. We
- 57 thought that a detailed wiring diagram would be to technical and decided to show a simplified flow
- 58 diagram. However, the python code and more detailed information can be provided by the author. We
- 59 added a more detailed scheme and rewrote as follows:

"For the determination of $\delta^2 H_l$ and $\delta^{18} O_l$, commercially available soil gas probes (BGL-30, 1 2 3 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 4 research, DLT100). This device does not measure continuously and it is mandatory to maintain the 5 responds of the laboratory autosampler, which is here done via the RS-232 interface of a Laptop 6 computer and a computer code that responds to the requests of the laser spectrometer. Each soil gas 7 probe is separated from the main transport line with a valve (Clippard Minimatic, USA). The valves are 8 switched by a high or low signal from the data terminal ready (DTR) and request to send (RTS) pins of 9 the modified USB-to-RS232 converter. A reduction of the electric tension output of the converter is 10 necessary which is done using a resistor with 220 Ω . To secure the converter against inverse currents 11 a common diode is installed in reverse direction before the optocoppler (ULN2303). The optocoppler is 12 necessary to ensure the +12 V power supply. To avoid over heating of the analyser during day time by 13 direct sun radiation a gazebo was positioned above the loading area of the pick-up truck where the 14 analyser is mounted. Power supply of the entire system was maintained using a common 230 V 15 generator."

16 17

18 **Reviewer 1**:

19 Fig. 3: Redundant since texture was uniform throughout depth. The information given in the text is 20 sufficient.

- 21 ANSWER:
- 22 We will remove that figure in the final manuscript.

23 24 **Reviewer 1**:

- 25 Fig. 4: Enlarge this figure and include rainfall isotope data in the plot (if available)
- 26 **ANSWER:** We will enlarge the figure and add rainfall data if available.
- 27 28 **Reviewer 1:**
- 29 Fig. 7: Include rainfall isotope data (if available)
- 30 ANSWER:
- 31 The available rainfall isotope data is already included in this figure (grey dots at the top).



32

Figure 1: Mean soil moisture (Θ) of each depth plotted against the standard deviation $\sigma[\Theta]$ between each depth as well as standard deviation of $\sigma[\delta^{18}O]$ and $\sigma[\delta^{2}H]$.



 $\begin{array}{c}
1\\2\\3\\4\\5\\6\\7\\8\\9\\10\\11\\12\\13\\14\\15\\16\\17\\18\\19\\20\end{array}$

Figure 2: δ^{18} O vs δ^{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.

References

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11

- 12 Koeniger, P., Marshall, J. D., Link, T., and Mulch, A.: An inexpensive, fast, and reliable method for
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Anonymous Referee #2 Round 1

1 2 Received and published: 21 July 2015

- $\overline{3}$ In their manuscript entitled "In-situ unsaturated zone stable water isotope (2H and 18O) 4 measurements in semi-arid environments using tunable off-axis integrated cavity output 5 spectroscopy", Gaj and colleagues present a membrane-based method for sampling soil water vapor 6 for indirect determination of soil liquid water isotope com-
- 7 positions. This study follows from previous laboratory and field successful validation attempts and 8 resembles that of Volkmann and Weiler published in 2014 in HESS while having the distinct 9 advantage of using commercially-available soil gas probes instead of custom-built ones.
- 10 The manuscript is in general well written and easy to follow - approximations with the isotope slang 11 put aside. The experimental setup could use some detailing. This study is a relevant read falling within 12 the scientific scope of HESS and of great interest for the eco-/hydrological communities. I have
- 13 however some doubts as to the method
- 14 Employed to answer its central objective, i.e., the comparison between in-situ and destructive 15 methodologies. The discussion also remains too descriptive and qualitative.

16 17 Authors response:

18 Dear Referee2, we appreciate the revision of our manuscript and your comments that supported a 19 fruitful discussion on unsaturated zone isotope field and laboratory methods. Compared to other 20 studies we used a liquid water vapor analyzer. The advantage of this device is the short warm up 21 period; the disadvantage is a lack of temperature compensation. In addition, this device is not 22 measuring continuously which was an additional challenge for the setup compared to other studies 23 (Rothfuss et al., 2010; Volkmann & Weiler, (2014)).

24 The current principle behind the in-situ methods is the equilibration between water vapor and soil 25 water. It should be noted that beside commercially available soil gas probes and a different analyzer 26 applied in a remote area, another difference between previous validation attempts and the present 27 study is the comparison to a laboratory water extraction method. A comparison between the two 28 introduced methods appears to be reasonable because soil water will be extracted completely (at least 29 for sand). Additionally, fractionation between liquid water and water vapor can either be affected by 30 soil physical or chemical properties, as well as environmental conditions. Hence we, argue that multi-31 methodical validation attempts, from an isotope point of view, i.e. between equilibration and extraction 32 methods will become more important, for both field and laboratory experiments, especially for soils 33 with an increased content of silt and clay and in arid zone hydrology. Therewith, the central hypothesis 34 that both methods lead to the same result can be rejected, at least for the upper part of the soil as 35 discussed. Further research is needed to identify the driving processes in the upper part of the soil 36 column to improve soil water balance approaches in arid zone hydrology. 37

38 **GENERAL COMMENTS** 39

40 **Reviewer 2**

41 1/ As the authors state in their manuscript's introduction, on-line non-destructive isotopic methods 42 need to be compared with what constitutes the norm, i.e., cryogenic extraction of water and off-line 43 isotopic analysis. This comparison appears to be the central objective of the study. However the 44 experimental conditions under which the authors attempt validating their new method, i.e., field 45 conditions, cannot allow such a comparison.

46 Spatial heterogeneity of soil surface water content in the field is well known and observed. Why should 47 it be otherwise for stable isotopic compositions?

48 Dynamics of isotopic compositions in dry soil surface layers should also exist, especially where 49 day/night variations of atmospheric temperature/relative humidity are strong (which is the generally 50 case in semi-arid environments). In the Discussion the authors come also to the same conclusions to 51 explain the observed discrepancies, especially in the upper part of the soil profile. So why comparing 52 in the first place?

53

54 Logically, one should sample a representative volume of soil around the gas probe shortly after gas 55 uptake for a proper comparison, but mostly, one should do it under controlled conditions where at 56 least spatial heterogeneity is reduced. It is not clear to the reader which method is "right" and which 57 one is "wrong" here, or which method should be used "here" and which one "there".

ANSWER:

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We agree that a methodical comparison under field conditions has some uncertainties and has a different quality as a comparison under laboratory conditions. However, the comparison shows good agreement for most data points as shown in figure 4. Soil water is completely extracted from fine sand using the cryogenic vacuum extraction method. Though, it is a good benchmark for an indirect determination of soil water isotope composition using the in-situ measurement under field conditions. In the discussion we wrote:

10 "Further, the calibration of the in-situ methods of Volkmann and Weiler (2014) and Gaj et al. (this 11 study) used prior oven dried substrate for the calibration. This procedure assumes that all water is 12 evaporated during oven drying and only the added standard water will be measured afterwards. The 13 same assumption is made using the equilibration bag method if the standards are treated in the same 14 way as described. However, interlayer water or adsorbed water of clay minerals is commonly removed under vacuum heating the sample to 200 to 300 °C for several hours (VanDeVelde and Bowen, 2013). 15 16 These adsorbed and interlayer water is bound on the mineral surface and exchanges with 17 atmospheric water vapor within hours (Savinand and Epstein, 1970). Hence, for soils containing clay 18 minerals a calibration procedure using previosly oven dried soil materials might mislead. The 19 presented direct comparison of the cryogenic vacuum extraction with a membrane based in-situ 20 measurement showed that this calibration procedure is at least applicable for fine sand." 21

In our opinion it is straight forward to apply such a system directly in the field, rather than doing
 extensive laboratory testing.

25 A comparison under laboratory conditions as suggested by the reviewer won't give you information 26 about the robustness of your system under field conditions. If you do measurements in remote areas 27 which are only accessible with a four wheel drive vehicle it can be necessary to unmount your 28 analyzer each time you want to measure at a different spot. Hence you need to give the analyzer at 29 least 1 to 2 hours to warm up, for our particular setting (i.e. climate conditions, type of analyzer, etc...). 30 We agree that heterogeneity of soil surface water content .This is especially the case if the soil is 31 recently wetted or in an intermediate state of soil moisture. Both extremes the very dry and the very 32 wet state show lower variability. As you stated this is already well known and many research has been 33 done to account for the heterogeneity of soil moisture (i.e. Western et al., 2004). The driving 34 processes for soil moisture distribution and isotope distribution in soils can be different. For instance, 35 water vapor transport might cause a change in isotope composition due to evaporation and 36 condensation without introducing a net flux of moisture in the soil column. However, this will depend 37 on the considered time scale. Effects such as vapor transport and/or biological processes might 38 discriminate between isotopoloueges causing even more variability as only caused by soil physical 39 properties (Dawson et al. 2002).

40 A decision on whether one method is better than the other depend on the question to answer. 41 Therefore it might be recommendable to provide different approaches for the determination of soil 42 water isotopes (i.e. in-situ, cryogenic extraction or others) to account for different water pools and 43 states (i.e. vapor and water) and fractionation factors of soil water. The latter depends also on the 44 calibration procedure of an in-situ system. Finally there is no study applying an in-situ system in a 45 semi-arid remote area that we are aware of. In addition, nobody compared this methodology to an 46 extraction method to verify their applicability other than with another equilibration method, which would 47 logically lead to similar results. Multi methodical approaches will become more important if soils other 48 than with sandy texture are of interest. The limits and potentials with this regard will be discussed in 49 more detail in the final manuscript.

50

5152 Reviewer 2

53 2/ P6120L6: "Further unique is the type of automatization which allows a laboratory like operation".
 54 This is not true (see Volkmann and Weiler, 2014; Rothfuss et al., 2015). Furthermore, it is not clear
 55 how well the system works automatically as the announced "High spatial and temporal resolution"
 56 (P6116L5) in the Introduction is supported by 12 profiles "only".

57 58

ANSWER:

1 2 3 If the Laser spectrometer is able to measure in continuous mode (such as Picarro or the newer models of LGR) it is only necessary to control the air inlet using valves with any kind of control device 4 (see Volkmann and Weiler, 2014; Rothfuss et al., 2015). In contrast to previous studies we used an 5 OA-ICOS DLT-100 device of Los Gatos Research, which is a liquid water isotope analyzer. As you 6 know it is not possible to measure continuously with this device. The measurement cycle is explained 7 in our paper (6124L24-L29). If you want to measure several samples automatically you must maintain 8 9 the communication via the RS-232 interface. Otherwise you can only use the manual injection mode or the spectrometer will complain about a missing laboratory auto sampler. However with our 10 configuration a laptop, microcontroller or any other device having a serial connection and a python 11 shell can be connected to a laser spectrometer. Then it can be used as it would be run with liquid 12 injections. In addition the common correction templates can be used and each measurement can be 13 treated as it would be a liquid sample injected by an auto sampler. This for us means a laboratory like 14 operation. To our knowledge this was not done before and hence is rather unique.

15 From a technical point of view the reliability of the system depends upon each used component (i.e. 16 valves, computer, interface etc). The Bottleneck of the system in terms of maintenance are the membrane probes, air supply and standard container. The membrane pores might clock in fine 17 18 textured soils and need to be cleaned; the dry air supply is limited on the size of tank provided. It is 19 recommendable to refresh the standards in the containers at least every two days to avoid misleading 20 results. However, this will depend on the size of the container and the water content of the prepared 21 standard. 22

23 Reviewer 2

24 3/ P6127L5-16. Values for accuracy are really high, even after drift and span Corrections. To this 25 reviewer, it can only mean that these 6 repetitions exceed what the soil can offer water vapor at 26 thermodynamic equilibrium. Isotopic compositions would be ultimately impacted. Is there a trend from 27 repetition 1 to 6 for each measurement cycle, and depending on water content? With respect to this, 28 the authors should illustrate with an example of a measurement's cycle. 29

ANSWER:

30 31 The accuracy is determined using a quality check standard. The offset between the drift and span 32 corrected values and the known value will lead to the accuracy. . Though, it is a standard of known 33 isotopic composition that is treated as an unknown sample. (P6124 L14-17) The accuracy might be 34 affected by either drift that could not be corrected by the drift standard or device specific properties 35 affected by environmental conditions. The accuracy is not related to the repetitions at each depth and 36 hence does not reflect reservoir conditions!

37 In contrast, the analytical precision of each sample is determined from the standard deviation of 38 repetitive measurements. Hence, this value reflects the uncertainty related to the measurement cycle 39 and a potentially exploited reservoir (see table 2). These values are comparable to other in-situ 40 studies (see Volkmann & Weiler (2013)). Besides, the analytical error for soil water extraction in the 41 laboratory especially for very dry soils can be 3 and 5 times higher for 18O and 2H respectively (see 42 Königer et al., 2011). Hence the analytical error is better for the in-situ approach.

SPECIFIC COMMENTS

Reviewer 2

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P6116L17-20 The entire sentence should be rewritten:

- 1. "stable water isotopes" is an awkward expression one has the impression that isotopes of "stable water" are in question. Replace with "water stable isotopes".
- 2. "stable water isotopes (e.g. deuterium, 2H and oxygen-18, 18O)" should read: "hydrogen and oxygen stable isotopes in water (e.g., deuterium, 2H and oxygen-18, 18O)".
 - 3. "a linear relationship between 2H and 18O on a global scale" is not correct. Please replaced with "a linear relationship between water 2H and 18O isotopic compositions on a global scale"

Additionally, it is not clear to me what means "the areal input through precipitation which shows"

17 18 **ANSWER to 1-3**:

We substantially shortened the introduction section as recommended and removed also lines P6116L17-20.

21 22

23 Reviewer 2

P6117L3. "General isotopic composition". Be more precise, i.e., what does "general" mean here?
 ANSWER:

26 We removed P6117L3, because the introduction is much shorter more focused.

2728 Reviewer 2

- 29 P6118L10. Consider replacing "intensively" with "actively"
- 30 ANSWER:
- We changed *""intensively"* to *"actively"*

33 Reviewer 2

- 34 P6118L19. Consider replacing "intense" with "intensive"
- 35 ANSWER:
- 36 We changed *"intense"* to *"intensively"*

3738 Reviewer 2

P6119L13-15. "Measurements were performed with a cavity-ring-down spectrometer (CRDS) (L1102 I, Picarro, CA, USA) calibrated with liquid water injections using a vaporizer unit" This is not true; I
 think they used custom-built soil water vapor standards.

42 ANSWER:

- 43 (Volkmann and Weiler, 2014) used custom built soil water vapor standards. However the statement 44 you are referring to says: *"All standards were measured at 17,000 ppmv water vapor mixing ratio*
- 45 using the vaporizer unit of the analyzer and an autosampler" [P3749L40] (Rothfuss et al., 2013)

46 **Reviewer 2**

P6120L3. Regarding Objective 1. It is not clear to the reader why it is so important to measure waterstable isotopic profiles in semi-arid environments. Could you elaborate on this?

49 **ANSWER**:

- 50 We rearranged the introduction section and explained that destructive sampling: "[...] methods cause 51 both disturbance to the integrity of the natural soil system and possible evaporation during the 52 sampling procedure. The latter is especially important for dry soils. Hence, soil water extraction 53 techniques are labor intensive and expensive which is limiting the use of stable isotopes compared to 54 the other state variables such as soil moisture or matrix potential. Indeed, there are suction cup 55 installations which allow a removal of soil water non-destructively but they are not applicable in arid 56 environments. This is especially true during the dry season where vapor transport (i.e. evaporation) is 57 the dominant driver for water fluxes in the unsaturated zone. In this context, the determination of
- 58 stable isotope from sampling vapor of the pore space appears useful."

STUDY SITE AND METHODS

Reviewer 2

P6121L16-17. Consider replacing "between the 9 and 15 June 2014 and the second between 15 and 22 November 2014" with "between June 9th and 15th, 2014 and the second between November 15th and 22nd. 2014"

6 7 8 ANSWER: 9

We replaced with "between June 9th and 15th, 2014 and the second between November 15th and 22nd, 2014[°]

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13 **Reviewer 2**

14 P6122L3-12. Particule size determination is not further used in this study. I suggest not going into 15 details with the procedure. You might report the results in the text and not show Figure 3.

16 ANSWER:

17 We removed the figure and report the results in the text only.

18 19 **Reviewer 2**

20 P6122L22-24. Replace "Isotope values are expressed as parts per thousand in

21 Δ notation (e.g. 180 and 2H) and are normalized to the international scale using Eq. (1)"

 $\overline{22}$ with the following sentence:

23 "18O/16O and 2H/1H isotope ratios and reported on the

24 International "\delta" scale and expressed in parts per thousand"

25 ANSWER:

- 26 We replaced as recommended.
- 27 28

35

29 **Reviewer 2**

30 P6122L25. The factor "1000" is not part of the δ definition. (see IAEA technical reports and excellent 31 paper of Coplen, 2011). A δ value is still a ratio and expressed in ∞ for Commodity reasons only. ANSWER:

- 32 33
- We changed as recommended. 34

Reviewer 2

36 37 P6122L26 - P6123L3. This sentence is not clear: isotope ratios are reported on the

38 VSMOW scale solely, no? One has the impression that they are also compared to

39 those of SLAP. Consider rewriting the sentence: "where Rsample (-) denotes the isotope ratioto 40 VSMOW and SLAP, respectively" with: "where Rsample (-) denotes the 180/160 isotope ratio 41 (respectively 2H/1H) of a water sample and Rstandard (-) those of the Vienna Standard Mean Ocean 42 Water (VSMOW)". 43

44 ANSWER: We rewrote: "where Rsample (-) denotes the 180/160 isotope ratio (respectively 2H/1H) 45 of a water sample and Rstandard (-) those of the Vienna Standard Mean Ocean Water (VSMOW)".

46 47 **Reviewer 2**

48 P6123L5. Replace "by.van Geldern" with "by van Geldern"

49 **ANSWER:** We replaced "by.van Geldern" by "by van Geldern"

50 51 Reviewer 2

52 P6123L6-8. "Accuracies for long-term quality check standards are better than 0.2 and

53 0.8 ‰ for water samples, but an additional error for sandy soil extractions has to be

- 54 taken into account which is better than 0.8 and 4 ‰ for 18O and 2H, respectively". 55
 - 1. Can you define "quality check"
 - 2. How were the "additional errors for sandy soil extractions" determined??
- 56 57
- 58 ANSWER:

To 1.) We defined quality check as follows: "The quality check standard is a water of known isotopic composition that is treated as an unknown sample. The difference between that known value and those measured expresses the accuracy of the measurement."

To 2.) The additional error for sandy soils is determined as follows:

"An additional analytical error for soil water extractions is determined from the standard deviation between replicate samples."

8 9 **Reviewer 2**

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10 P6123L18-21. Unnecessary detail. Consider erasing.

11 **ANSWER**:

12 Since a more detailed scheme of the technical setup was desired by reviewer 2 it is explained as 13 follows (Figure 2):

14 "This device does not measure continuously and it is mandatory to maintain the responds of the 15 laboratory autosampler, which is here done via the RS-232 interface of a Laptop computer and a 16 computer code that responds to the requests of the laser spectrometer. Each soil gas probe is 17 separated from the main transport line with a valve (Clippard Minimatic, USA). The valves are 18 switched by a high or low signal from the data terminal ready (DTR) and request to send (RTS) pins of 19 the modified USB-to-RS232 converter. A reduction of the electric tension output of the converter is 20 necessary which is done using a resistor with 220 Ω . To secure the converter against inverse currents 21 a common diode is installed in reverse direction before the optocoppler (ULN2303). The optocoppler is 22 necessary to ensure the +12 V power supply."

23 24 **Reviewer 2**

25 P6124L2. "Swagelok®" instead of "Swagelok©". It goes as well for "WEBA bags"

26 **ANSWER**:

27 We corrected as recommended.

28 29 **Reviewer 2**

30 (P6124L11) (specify firm, city and country of origin, I couldn't find it on the web)

31 **ANSWER**:

32 We specified "(WEBA bags[®], Weber Packaging GmbH, Güglingen, Germany)."

3334 Reviewer 2

35 P6124L10-21. This is rather unclear. What are these standards? Soil water standards solutions? From 36 where to where were they "transported in WEBA bags". Please

36 where to where were they "transported in WEBA bags". Please

37 elaborate on this.

- 38 ANSWER:
- 39 We rewrote the sentences as follows:

40 "Standard preparation is done using 200 g of previously oven dried sandy substrate (at 105 °C for at 41 least 24 h) for each of the four standards (Table 2). The standards have been transported in 42 aluminium bags (WEBA bags[®], Weber Packaging GmbH, Güglingen, Germany) from the laboratory of 43 the University of Windhoek (UNAM) to the field site and were spiked directly in the field with a volume 44 of 5 ml standard before the experiment at the day of the measurement.

45 46 **RESULTS**

40 RESOLTS 47 Reviewer 2

- 48 General remark: I'd keep with paste sense.
- 49 **ANSWER**:
- 50 Thanks for this recommendation we will keep the sentences in past tense.
- 51

52 **Reviewer 2**

53 P6125L5. I suggest "June 15th, 2014" (goes for the rest of the manuscript)

54 **ANSWER**:

55 We rearranged all dates as recommended.

56 57 **Reviewer 2**

- 58 P6125L18-19. Replace "and are exponentially decline down to 50 cm" with "and exponentially decline
- 59 down to 50 cm"

ANSWER:

1 2 3

We replaced: "As depicted in Figure 5, the deuterium excess for both profiles shows a maximum at 10 cm depth and exponentially decline down to 50 cm."

4 5 Reviewer 2

6 7 P6125L19-20. I wonder what is the interest of calculating a deuterium excess value for soil water that is strongly impacted by evaporation? What gives the obtained value in that case?

8 ANSWER:

- 9 Under the assumption that the isotope depth profile is in steady state a comparison between the
- 10 deuterium excess of the two methods could indicate whether there is additional enrichment due to the
- 11 in-situ method or not.
- 12 We further described:

13 "For instance, the maximum isotope values of $\delta^2 H_c$ and δ^{18} Oc were at 15 cm. In contrast, the maximum isotope values of $\delta^2 H_i$ and $\delta^{18} O_i$ were at 10 cm." 14

15 And

16 "In comparison to the isotope depth profiles the deuterium excess depth profile has its minima at 10 17 cm for both methods excluding profile E2.7."

18 **Reviewer 2**

19 P6126L20.5 values cannot be "enriched/depleted" but are "higher/lower than"

20 ANSWER:

21 We changed:

22 "Above 25 cm values of $\delta^2 H_c$ are more enriched (-15.5 to -22.6 ‰) than for $\delta^2 H_l$ (-25.0 to -29.2 ‰), 23 and vice versa depleted below 25 cm with -23.4 to -15.2 % for $\delta^2 H_c$ and -11.6 to -5.1 % for $\delta^2 H_l$, 24 respectively." 25

То

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30 31 "Above 25 cm values of $\delta^2 H_{\rm C}$ are higher (-15.5 to -22.6 ‰) than for $\delta^2 H_{\rm I}$ (-25.0 to -29.2 ‰), and vice versa lower below 25 cm with -23.4 to -15.2 ‰ for $\delta^2 H_c$ and -11.6 to -5.1 ‰ for $\delta^2 H_h$ respectively."

Reviewer 2

32 33 P6126L24-27. Sentence could use some rearrangement, I suggest something like that: "There was a 34 good agreement between in-situ and cryogenically obtained isotope measurements for both isotope 35 depth profiles of the first campaign between 15 and 50 cm (RMSE= 3.9 and 9.2 ‰ for 18O and 2H, 36 resp.). However, higher values were observed in situ at shallower depth (RMSE= 7.0 and 43.4 % for 37 18O and 2H, resp.).'

38 ANSWER:

39 We changed as follows:

40 "There was a good agreement between in-situ and cryogenically obtained isotope measurements for 41 both isotope depth profiles of the first campaign between 15 and 50 cm (RMSE= 3.9 and 9.2 % for 42 δ^{18} O and δ^2 H, respectively). However, higher values were observed for the in-situ approach at shallower depth (RMSE= 7.0 and 43.4 % for δ^{18} O and δ^{2} H, respectively)." 43 44

45 **Reviewer 2**

- 46 P6128L16-18. Belongs to "STUDY SITE AND METHODS".
- 47 ANSWER: As recommend this paragraph was moved to "Study sites and methods"
- 48

49 **Reviewer 2**

- 50 P6128L17-P6129L2. It would have been even better to show all three profiles for each
- 51 transect instead of giving mean values and sd.

52 ANSWER:

53 It would have been possible to show all profiles, but the interpretation of all profiles would fill another 54 entire paper. What the authors intended to illustrate with this compilation was that the variability 55 between soil moisture and isotope depth profiles behave different. Thus, this graphic shows that 56 temporal variability of the isotope depth profiles decreases over the hole profile. However the 57 variability of soil moisture remains guite similar. This could mean that apart from the low changes in 58 water content, the isotopic composition changes over the hole depth due to vapor transport.

DISCUSSION

Reviewer 2

6 7

8

P6129L4-15. This is filled with much too general statements, e.g.,

- 1. which advantages, what improvements and with respect to what? 2
- 2. by "..transport of water vapor... not yet fully understood", do you mean evaporation? I'd say this is well understood from a theoretical point of view i.e., implemented in physical models only very difficult measuring.

9 ANSWER:

10 To 1.) and 2.) We tried to improve that section and rewrote as follows:

11 "The potential to determine stable isotopes of soil water indirectly by measuring the vapour from the pore space directly in the field could be demonstrated by using a liquid water analyser. Results show 12 that the precision of the in-situ approach is better than 0.8 % and 2.5 % for δ^{18} O and δ^{2} H, 13 respectively. This is a feasible precision if it is compared to the precision of the cryogenic vacuum 14 extraction method with 0.8 ‰ and 3.5 ‰ for δ^{18} of and δ^{2} H, respectively. It is still much worse 15 16 compared to the precision that can be reached measuring stable isotopes directly from water samples (0.2 ‰ and 0.8 ‰ for δ ¹⁸O and δ ²H). However it needs to be considered that such laser 17 18 spectrometers are in general mounted in a temperature controlled laboratory. In This study, Accuracy 19 and precision of the presented in-situ system is mainly limited by the environmental conditions. If the 20 laser spectrometer and the autosampler would have been kept within a temperature controlled 21 environment, possibly, the precision could be improved. However, this study could demonstrate that it 22 is possible to determine stable isotopes of soil water directly in the field with a similar or even better 23 precision compared with destructive sampling and a subsequent soil water extraction in the laboratory. 24 This creates possibilities to investigate water vapor transport processes within the unsaturated zone 25 and also those between the atmosphere. Evaporation processes are physically well described (i.e. Or 26 et al., 2013), but their determination is very difficult. An approach to observe evaporation was 27 presented by Rothfuss et al. (2015) who could show the development of an isotope depth profile in a 28 column experiment with a similar in-situ approach. They further discussed that back-diffusion of vapor 29 from the atmosphere into the soil column altered the top part of the isotope profile. However their 30 experimental setup did not reflect conditions that can be found at our study site, since much higher 31 temperature and humidity gradients occur between day and night."

32 Reviewer 2

P6129L23-24. What about natural soils with high salt and/or clay contents and their consequence to possible fractionation of soil water isotopes as point out by Oerter et al., 2014? This could lead to possible deviation between extracted and in-situ results.

36 **ANSWER**:

We agree that these effects are relevant and under conditions of high salt/clay content would need consideration. The presented location / soil consists of sand and the clay fraction is < 0.1 % also salinity is of minor importance. Therefore we added the following in the discussion:

40 "Possible fractionation due to high salt concentrations or chemical reactions as observed by Oerter et
41 al. (2014) are negligible, because the cation exchange capacity (CEC) of the sand was 0.5 meq/100g
42 and total organic carbon (TOC) 0.22 %."

44 **Reviewer 2**

P6130L10-17. A much better indicator for the extent of kinetic effects during evaporation of soil water is the so-called evaporation line (Craig et Gordon, 1965) rather than the deuterium excess. In addition, if removing of water vapor would disrupt the thermodynamic conditions prevailing between soil liquid and gas phases, the sampled water vapor would not be enriched but to the contrary depleted at first. It

- 49 would be only after some time depending on the uptake rate and initial water content that you would
- 50 measure isotope values in the sampled gas higher than the initial (equilibrium) values because the soil
- 51 liquid water parallel enriches itself with stable isotopes.

52 **ANSWER**:

- 53 This is really a very good explanation and could be another reason for the "high" standard deviation. 54 Highly appreciated comment we will consider this in the discussion as follows:
- 55 "Evaporative enrichment is reflected in the deuterium excess (d_{ex}) and also in the so-called
- 56 evaporation line (Craig and Gordon, 1965). This kind of enrichment could be enhanced by the uptake
- 57 of water vapor through the measurement (Figures 5 and 6). The equilibrium condition prevailing
- 58 between soil liquid and gas phases is disturbed when water vapor is removed. Then the sampled 59 water vapor can be depleted at first. After some time, depending on the uptake rate and the soil water

content, the initial isotopic composition of the remaining soil water might enrich itself and isotope values in the sampled gas higher will become more enriched."

Reviewer 2

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P6130L17-26 and P6131L23-24. I think these are the right explanations: differences between in situ and destructive methods stem from the natural spatio-temporal dynamics of water isotopic compositions and the fact that these measurements were not made simultaneously and for comparable soil volumes.

. 8 9 10 ANSWER:

11 We agree that spatial variability can cause differences between the two methods, however, destructive 12 samples were taken right next to the position were the in-situ measurements were done. The 13 agreement in the lower part of the profiles indicate that spatial variability might be low here. In 14 contrast, the differences in the upper part might be attributed to temporal variability. This might be 15 interesting to investigate in future in-situ studies since the determination via soil moisture 16 measurements might be difficult considering the low water contents. The measurement of the suction 17 tension could give more insights about the quantities, but not about the origin. Beside the intrusion of 18 atmospheric vapor hydraulic redistribution could also cause variation of the isotopic composition. 19

20 **Reviewer 2**

21 P6131L8-15. This comment seems a bit off-topic here. In addition, you do not have for instance 22 measured water potential profiles or capture the dynamics of xylem water isotope composition to 23 support you assumptions. Consider removing.

24 **ANSWER:** We removed as recommended. 25

26 27 **Reviewer 2**

28 P6131L24-25.δ 2HI values are "higher" than δ2HC

29 ANSWER:

30 We changed as recommended "more enriched" to "higher"

31 32 **Reviewer 2**

33 P6131L25-28. How can you say that evaporation takes place so deep in the soil? There is a good 34 chance that after the rain event, even under low water content the soil evaporates from the surface 35 only. For this you should know the residual water content for the sandy soil.

36 ANSWER:

37 We agree that evaporation takes place from the surface. However it might be also possible that 38 diffusion or vapor transport induced by temperature gradients alters the isotope profile also over 39 depth.

40 "Considering that, under the present "wet" conditions (but also if the soil is at wilting point or lower) 41 humidity of the pore space is close to saturation, then temperature gradients will cause a movement of 42 vapor downward and upward depending on the temperature profile (Abramova, 1969). Further, soil 43 evaporation can be separated into direct evaporation from a water saturated surface (stage I 44 evaporation) and diffusion controlled vapor transport (stage II evaporation) (Or et al., 2013)."

45 46 **Reviewer 2**

47 P6131L29- P6132L3. This is not very clear, nor is the reference accessible.

48 ANSWER:

- 49 We tried to clarify as in P6131L25-28 and added another more recent publication as reference. 50 Further we added the publication that was not accessible to the supplementary material.
- 51

52 Reviewer 2

53 P6132L4-10. Not only kinetic effect plays a role, but also the intrusion of atmosphere water vapor in 54 the upper soil layers as recently published by Rothfuss et al. this year in HESSD. I would avoid only 55 saying that "things are not yet fully understood" (this goes for almost everything no?)

56 ANSWER:

57 It is true that many things are not yet fully understood. However we try to avoid such expression if 58 inappropriate and restructured the paragraph:

"As discussed earlier, kinetic effects and diurnal variations in evaporation or condensation due to temperature gradients, the interaction between soil water potential, relative humidity and isotope fractionation is an additional challenge for future research (Soderberg et al., 2012 and Wilson et al., 1997). The investigation of such processes using in-situ approaches for stable isotope analysis seems to be promising with this regard, since the composition of vapor can be measured directly."

Reviewer 2

9 P6132L18-19. or maybe also due to the chemical properties of the porous material?

10 ANSWER:

11 We added: "Though there is no detailed chemical data available it is unlikely that chemical properties 12 are responsible, since the sandy soil has a very low CEC. More likely are biological processes that are 13 introduced due to the sudden availability of water. Nevertheless, there is no data (i.e CO_2 14 measurements) available to support this assumption."

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17 **Reviewer 2**

18 P6133L14-15. Allison et al. ("1983" and not "1984") analytical equation could not predict such a 19 "displacement" as this study's experimental conditions met neither isotopic steady state and 20 isothermal conditions.

21 ANSWER:

22 We are referring to the following publication were the evaporation process is described: 23

Allison G.B., Barnes, C. J., Hughes M.W., and Leaney, F. W.: Effect of climate and vegetation on oxygen-18 and deuterium profiles in soils, Int. Symp. Iso. Hydrol. Water Resour. Dev.), 105-123, 1984.

28 29

CONCLUSION

30 **Reviewer 2** 31

P6134L2-3. What constituted a possibility (evaporation is induced during sampling) is now a certitude? 32 ANSWER:

33 We changed as follows:

34 "Evaporation induced by the measurement procedure might decrease the precision depending on the 35 uptake rate and the soil water content."

36 37 **Reviewer 2**

38 P6134L19-20. This very last sentence is somewhat unappropriate and does not fit with the rest of the 39 conclusion (or the manuscript for that matter)

- 40 ANSWER:
- 41 We removed that sentence as recommended.

42 43

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46 TABLES

47 **Reviewer 2**

48 Table 2: The introduction of the "1000" factor in the definition of δ leads to curious labels such as 49 "10³*δ 180". Replace simply with "δ180 (‰". This goes for the Figures as well.

- 50 ANSWER:
- 51 We removed the factor "1000" from the equation and followed the recommendation of Coplen, (2011).
- 52 The use of " δ 180 % notation in column headings and axes should be therefore i.e. "10^3* δ 180".
- 53
- 54 FIGURES
- 55 **Reviewer 2**
- 56 Figure 2
- 57 I would have liked a scheme/picture of the prepared standards
- 58 ANSWER:
- 59 Unfortunately we missed to take pictures of the prepared standards.

Reviewer 2

1 2 3 Figures 5

Definition for "GWML", and the different subscripts are missing from the caption.

4 5 ANSWER: 6 7

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We rewrote the caption as follows:

"Figure 4: δ^{18} O vs δ^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."

12 13 **References:** 14

15 Coplen, T. B.: Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio 16 measurement results, Rapid Commun. Mass Spectrom., 25 (17), 2538-2560, doi:10.1002/rcm.5129, 17 2011. 18

19 Dawson, T. E., Mambelli, S., Plamboeck, A. H., Templer, P. H., and TU, K. P.: Stable Isotopes in Plant 20 Ecology, Annu. Rev. Ecol. Syst., 33 (1), 507-559, doi:10.1146/annurev.ecolsys.33.020602.095451, 21 2002. $\overline{22}$

23 Rothfuss, Y., Vereecken, H., and Brüggemann, N.: Monitoring water stable isotopic composition in 24 soils using gas-permeable tubing and infrared laser absorption spectroscopy, Water Resour. Res., 49 25 (6), 3747-3755, doi:10.1002/wrcr.20311, 2013. 26

27 Volkmann, T. and Weiler, M.: Continual in-situ monitoring of pore water stable isotopes, Hydrol. Earth 28 Syst. Sci. (18), 1819–1833, doi:10.5194/hess-18-1819-2014, 2013. Wassenaar, L. I., Hendry, M. J., 29 Chostner V.L., and Lis G.P.: High Resolution Pore Water 2H and 18O Measurements by 30 H2O(liquid)H2O(vapor) Equilibration Laser Spectroscopy, Environmental Science and Technology 31 (42), 9262–9267, 2008. 32

33 Western, Andrew W.; Zhou, Sen-Lin; Grayson, Rodger B.; McMahon, Thomas A.;Blöschl, Günter; 34 Wilson, David J. (2004): Spatial correlation of soil moisture in small catchments and its relationship to 35 dominant spatial Hydrological processes. Journal ofHydrology 286 (1-4), S. 113-134. DOI: 36 10.1016/j.jhydrol.2003.09.014

Reviewer 1: Round 2

1 2 3 The presented revised manuscript still does not answer most of the posed research questions. The newly included hypotheses are poorly written and it is questionable how testable they really are. The 4 discussion section could be backed up with additional references that are indeed comparable with the 5 presented results in terms of climatic settings or soil types (e. g. is reference Volkmann and Weiler, 6 7 2014 suitable here?!).

8 Answer: We appreciate that the reviewer read the manuscript a second time and we excuse for the 9 rather fast and raw responds to the suggestions. We included more references in the discussion 10 section to support our observations. However, with regard to an in-situ field application for the 11 determination of stable isotopes of soil water, to our knowledge, the present study is the first that 12 attempted to measure in such a climate setting successfully. Therefore it will be crucial to find a 13 comparable study. 14

15 **Reviewer 1:**

16 Unfortunately, the authors did not decide to follow the suggestions on shortening parts of the rather 17 fundamental introduction section. Thus, some of the given information seemed to be redundant. 18

19 **Answer:** We substantially shortened the introduction section as recommended.

20 "Stable isotopes of water have been successfully used for decades as powerful proxies for the 21 description of water fluxes such as infiltration in humid (Saxena, 1987) or semi arid regions (Dincer et 22 al., 1974; Allison and Hughes, 1983), evapotranspiration (Barnes and Allison, 1988, Skrzypek et al., 23 2015), plant root water uptake (Dawson and Ehleringer, 1991; Ehleringer and Dawson, 1992; Dawson, 24 1996; Yang et al., 2010), hydraulic redistribution (Dawson, 1993; Caldwell et al., 1998), and in 25 catchment hydrology (e.g., Sklash and Farvolden, 1979; Richard and Shoemaker, 1986; Tetzlaff et al., 2007; Kendall and McDonnell, 2012). Water stable isotopes provide information on flow paths way and 26 27 mixing within the unsaturated zone (Gazis and Feng, 2004; Stumpp and Maloszewski, 2010; 28 Garvelmann et al., 2012; Mueller et al., 2014). Soil water stable isotope studies were also used to 29 reduce parameter uncertainty in unsaturated zone model approaches (Sprenger et al., 2014). Further 30 work has been done to use stable isotopes for quantitative recharge estimations which are actively 31 discussed in early and recent reviews (e.g., Allison et al., 1994; Scanlon et al., 2002). But the usefulness of evaporation profiles to determine recharge remains debatable (Herczeg et al, 2011).

32 33 In all unsaturated zone studies manual removal of soil samples and a subsequent extraction of soil 34 water in the laboratory was necessary using either vacuum extraction (e.g., West et al., 2006; 35 Koeniger et al., 2011; Orlowski et al., 2013), equilibration (e.g., Wassenaar et al., 2008), mechanical 36 sqeezing, azeotropic distillation or centrifugation methods (e.g., Walker et al., 1994; Kelln et al., 2001). 37 These methods cause both disturbance to the integrity of the natural soil system and possible 38 evaporation during the sampling procedure. The latter is especially important for dry soils. Hence, soil 39 water extraction techniques are labor intensive and expensive which is limiting the use of stable 40 isotopes compared to the other state variables such as soil moisture or matrix potential. Indeed, there 41 are suction cup installations which allow a removal of soil water non-destructively but they are not 42 applicable in arid environments. This is especially true during the dry season where vapor transport 43 (i.e. evaporation) is the dominant driver for water fluxes in the unsaturated zone. In this context, the 44 determination of stable isotope from sampling the vapor of the pore space appears useful.

45 Principles to sample soil air for the determination of stable isotopes were already indicated by Allison 46 et al., (1987) and Schack-Kirchner et al., (1993). An attempt to measure stable isotopes in a sandy 47 loam using a liquid water analyzer (OA-ICOS, Los Gatos Research, DLT-100) is presented in a recent 48 review by Soderberg et al., (2012). The first study monitoring stable isotopes in-situ in unsaturated 49 sandy soil water under laboratory conditions made use of poly-propylene (PP) membranes (Rothfuss 50 et al., 2013). Measurements were performed with a cavity-ring-down spectrometer (CRDS) (L1102-I, 51 Picarro, CA, USA) calibrated with liquid water injections using a vaporizer unit. Volkmann and Weiler, 52 (2014) developed custom built poly-ethylene (PE) probes with an equilibration chamber allowing 53 additional mixing of the vapor to prevent condensation in the sample line. They further proposed a 54 sophisticated system with a CRDS device (Picarro L2120-i, CA, USA) calibrated with standards 55 prepared on previously oven dried local substrate.

56 In the present study in-situ usability of commercially available PP-membranes (BGL-30, 57 Umweltmesssysteme, Munich) using a liquid water analyzer (Los Gatos Research, DLT-100) for a 58 determination of stable isotopes in soil pore water is demonstrated. The proposed system is applied 59 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 presents I.) an improved automatization with minimal technical modification of commercially available parts. II.) We demonstrate that in-situ measurements are comparable to data derived from cryogenic vacuum extractions. But also that, differences exist at the transition to the atmosphere. Such a comparison seems to be useful since a cryogenic extraction is a direct determination of the soil water isotopic composition. III.) Finally, derived isotope data is used quantitatively to determine a soil water balance of a thick sandy unsaturated zone and to separate soil evaporation from transpiration."

Reviewer 1:

Further, they did not satisfactorily address the issue on if the presented in-situ results are comparable
 with destructively sampled and cryogenically extracted soil water isotope values and how oven-drying
 (i.e temperatures) may affect the isotope results.

13 14 **Answer:**

9

15 We hope that the following changes satisfactorily address the issue on comparability between the two 16 methods and why we think that natural processes (i.e variability is observed here):

17 "Results of the first field campaign demonstrates good agreement of the isotope depth profiles 18 between the cryogenic vacuum extraction method and the in-situ approach for deeper parts of the soil 19 profile, but also a divergence in the top 15 cm. Differences could be a result of an incomplete soil 20 water extraction, rayleigh fractionation caused by the uptake of air from the in-situ measurement, 21 natural processes or 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 very low matrix potential and very low abundance of silt and clay. The cryogenic vacuum extraction does extract the entire water in sandy soils (Königer et al., 26 2011). Hence, the extracted soil water isotopic composition will reflect the "true" isotope values of the 27 pore water.

29 Measuring with the soil gas probe in a very coarse material atmospheric vapor or even vapor from 30 other parts of the soil can lead to a mixed sample. However, the extracted air volume is very low and a 31 divergence of isotope values is only visible within the top 15 cm of the dry profiles (Figure 3, left and 32 33 center). Evaporative enrichment is reflected in the deuterium excess (d_{ex}) and also in the so-called evaporation line (Craig and Gordon, 1965). Evaporative enrichment could also be enhanced by the 34 uptake of water vapor through the measurement (Figures 5 and 6). The equilibrium condition 35 prevailing between soil liquid and gas phases is disturbed when water vapor is removed. Then the 36 sampled water vapor can be depleted at first. After some time, depending on the uptake rate and the 37 soil water content, the initial isotopic composition of the remaining soil water might enrich itself and 38 isotope values in the sampled gas will become more enriched. This effect might be reflected in 39 reduced precision. However, enrichment caused by the uptake of air through the measurement is not 40 visible for deeper parts of profile E1.2 which is very dry as well. Hence, arguing with low water 41 contents would suggest to have enriched values for deeper parts of the vegetated profile. This is not 42 observed at the vegetated plot where soil water contents are below 1% throughout the whole profile. 43 Since the in-situ approach is based on the same principle as the equilibration bag method its 44 applicability on samples with low water content is supported by a recent study of Hendry et al., (2015). 45 They found that the accuracy of their equilibration procedure could be improved by increasing the 46 sample amount."

47 And further

48 "Further, the calibration of the in-situ methods of Volkmann and Weiler (2014) and Gaj et al. (this 49 study) used prior oven dried substrate for the calibration. This procedure assumes that all water is 50 evaporated during oven drying and only the added standard water will be measured afterwards. The 51 same assumption is made using the equilibration bag method if the standards are treated in the same 52 way as described. However, Interlayer water or adsorbed water of clay minerals is commonly removed 53 under vacuum heating the sample to 200 to 300 °C for several hours (VanDeVelde and Bowen, 2013). 54 These adsorbed and interlayer water is bound on the mineral surface and exchanges with 55 atmospheric water vapor within hours (Savinand and Epstein, 1970). Hence, for soils containing clay 56 minerals a calibration procedure using previosly oven dried soil materials might mislead. The 57 presented direct comparison of the cryogenic vacuum extraction with a membrane based in-situ 58 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 and/or salt contents are high (Oerter et al., 2014)."

Reviewer 1:

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The new paragraph on the soil water balance estimation seemed to be a rather old approach; however, it adds some more details on the development of the isotope soil profiles.

6 7 **Answer:** It is an old approach, but the interesting observation here is that the effective length z ef . 8 9 which is calculated from the isotope depth profile can also be calculated using a more recent calculation presented in Or et al., 2013.

10 11 Reviewer 1:

12 The new section which describes the in-situ sampling setup is not very well written and most of the 13 sentenctes are somewhat unclear.

14 **Answer:** We tried to clarify as follows:

"For the determination of $\delta^2 H_l$ and $\delta^{18} O_l$, commercially available soil gas probes (BGL-30, 15 16 Umweltmesssysteme, Munich (UMS)) with a diameter of 9.4 mm and a length of 300 mm were 17 connected to an integrated cavity off-axis liquid water isotope analyser (OA-ICOS, Los Gatos 18 research, DLT100). This device does not measure continuously and it is mandatory to maintain the 19 responds of the laboratory autosampler, which is here done via the RS-232 interface of a Laptop 20 computer and a computer code that responds to the requests of the laser spectrometer. Each soil gas 21 probe is separated from the main transport line with a valve (Clippard Minimatic, USA). The valves are 22 switched by a high or low signal from the data terminal ready (DTR) and request to send (RTS) pins of 23 the modified USB-to-RS232 converter. A reduction of the electric tension output of the converter is 24 necessary which is done using a resistor with 220 Ω . To secure the converter against inverse currents 25 a common diode is installed in reverse direction before the optocoppler (ULN2303). The optocoppler is 26 necessary to ensure the +12 V power supply. To avoid over heating of the analyser during day time by 27 direct sun radiation a gazebo was positioned above the loading area of the pick-up truck where the 28 analyser is mounted. Power supply of the entire system was maintained using a common 230 V 29 generator. "

- 30 The same is true for the new paragraph on p.20.
- 31 Answer:
- 32 We rearranged and rewrote the paragraph. 33

34 "Potential Limitations

35 Water vapor mixing ratio dependencies (Sturm and Knohl, 2010; Aemisegger et al., 2012) are of minor 36 importance in this study, because the water content was maintained within the density of 37 approximately 2- 4*10¹⁶ molecules cm⁻³ as recommended by Los Gatos Research. However, it is 38 assumed that small variations will be reflected in the standard deviation of the measurements. 39 Additionally, inference through organic contamination is neglected in this study. However, if necessary 40 to account for inference recent efforts include calibration strategies in this regard (Wu et al., 2014). 41 Possible fractionation due to high salt concentrations or chemical reactions as observed by Oerter et 42 al. (2014) are negligible, because the cation exchange capacity of the sand was 0.5 meg/100g and 43 total organic carbon (TOC) 0.22 %.

44 During the second field campaign information on long term precision and spatio-temporal variability 45 was investigated. Comparing the quality check standards of the two campaigns the precision within one series (σ_{rep}) of $\delta^2 H$ is one-third better than the long term accuracy. However, the accuracy of $\delta^{18} O$ 46 47 is three times greater than the mean precision (Table 2). This can likely be improved by utilizing a 48 more sophisticated technical setup e.g. temperature controlled conditions, standard preparation and 49 frequent cleaning of the probes. Another reason could be the difference in the physical properties of 50 the probe pores such as the diffusitivity of gas (Merlivat et al., 1979). Though there is no chemical data 51 available it is unlikely that chemical properties are responsible, since the sandy soil has a very low 52 CEC. Mote likely are biological processes that are introduced due to the sudden availability of water. 53 Nevertheless, there is no data (i.e CO_2 measurements) available to support this assumption. However, 54 the precision appears to be sufficient to monitor processes of a diurnal time scale and also 55 comparable to other systems that were tested in the field, e.g., Volkmann and Weiler et al. (2014) with values of 2.6 ‰ and 0.38 ‰ for δ^{2} H and δ^{18} O, respectively. 56

57 Condensation within the sample system can lead to unreliable data. This can be either prevented by

Thus, under conditions where the ambient temperature is significant warmer then the soil temperature 1 2 3 a simple valve controlled membrane inlet will be sufficient for an indirect determination of isotopes in unsaturated zone or saturated zone water. During day time this is the case at the presented study site, 4 but changes drastically overnight as described. Dilution of the vapor concentration can be done by 5 providing dry gas at the other end of the available probes. In the case of pure diffusion sampling the 6 maximum dilution rate depends upon the absolute amount of water molecules in the vapor and is 7 controlled by the length of the probe, their diffusion properties, the flow velocity and the temperature at 8 depth. The flow velocity can be different depending on the laser spectrometer that is used. Adding a 9 mixing chamber at the head of the probe has the distinct advantage of additional mixing directly before 10 the vapor enters the sample line (Volkman and Weiler, 2014). This leads to independence on flow 11 velocity, probe length and membrane diffusion properties in terms of water content. However, under 12 very dry conditions it might be useful to increase probe length for an increase of resolution, since the 13 soil volume around the probe affected by the measurement will be reduced.

14 Another critical point is the long term application of membrane based methods. The pore space of the 15 probes can be altered over time which might increase the memory effect of the system. Further, the 16 calibration of the in-situ methods of Volkmann and Weiler (2014) and this study used prior oven dried 17 substrate for the calibration. This procedure assumes that all water is evaporated during oven drying 18 and only the added standard water will be measured afterwards. The same assumption is made using 19 the equilibration bag method if the standards are treated in the same way as described. However, 20 Interlayer water or adsorbed water of clay minerals is commonly removed under vacuum heating the 21 sample to 200 to 300 °C for several hours (VanDeVelde and Bowen, 2013). These adsorbed and 22 interlayer water is bound on the mineral surface and exchanges with atmospheric water vapor within 23 hours (Savinand and Epstein, 1970). Hence, for soils containing clay minerals a calibration procedure 24 using previosly oven dried soil materials might mislead. A direct comparison of the cryogenic vacuum 25 extraction with a membrane based in-situ measurement showed that this calibration procedure is 26 applicable for fine sand. However, it will probably lead to insufficient data applying this calibration 27 procedure to soil samples with finer texture, especially if clay and/or salt contents are high (Oerter et 28 al., 2014). " 29

Reviewer 1:

In general, the revised manuscript still comes along with a lot of typos and mistakes (e.g. Volkmann and Weiler 2014 instead of 2013; Table instead of table and Figure instead of figure etc.) and some sections would need additional references and editing (e.g p. 9, 20, 21).

35 Answer:36 We revise

We revised the typos and hope that all mistakes could be removed.

37 38

30 31

39 Reviewer 240

This is the second time that I am reviewing Gaj et al. manuscript on "In-situ unsaturated zone stable water isotope (2H and 18O) measurements in semi-arid environments using tunable off-axis integrated cavity output spectroscopy".

The authors have added new sections written as it seems in quite a hurry (please find below a sample of the typos / missing words that I could notice). The level of English is at some places surprisingly poor, e.g., the authors should avoid use of colloquial formulations, e.g., "basically", "besides", and seem to get "thus" and "though" mixed up. The uploaded version also does not contain all the modifications (i.e., parts that were removed) brought to the manuscript. But more importantly, the authors have only answered the first part of my specific comments (answers to pages C2689-C2693 are lacking).

Nevertheless I salute the effort to provide some quantitative numbers (mass balance section), even though – again – sloppily written.

Answer:

It is true that the review was done in quite a hurry. Therefore we excuse that many sentences were sloppily written. Further that the last part of the recommendations were not considered without any

recognition that it was missing. We highly appreciate the recommendations of both reviewers, it improved the manuscript substantially. We hope that, after this second review the manuscript will meet the requirements to be published in HESS. Please find the complete revision and answers to your comments in the following.

GENERAL COMMENT

Answer:

If the precision is abnormal high depends upon what is taken for comparison. For an improved discussion we added the following paragraph to the discussion section:

"Results show that the precision of the in-situ approach is better than 0.8 ‰ and 2.5 ‰ for δ^{18} O and δ^{2} H, respectively. This is a feasible precision if it is compared to the precision for isotope values derived with the cryogenic vacuum extraction method with 0.8 ‰ and 3.5 ‰ for δ^{18} O and δ^{2} H, respectively. It is still much worse compared to the precision that can be reached measuring stable isotopes directly from water samples (0.2 ‰ and 0.8 ‰ for δ^{18} O and δ^{2} H). However, it needs to be considered that such laser spectrometers are in general mounted in a temperature controlled laboratory. In this study, accuracy and precision of 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 with a similar or even better precision compared to destructive sampling and a subsequent soil water extraction in the laboratory."

SPECIFIC COMMENTS TITLE Reviewer 2

"water stable isotopes" and not "stable water isotopes"!

Answer: We changed to: "In-situ unsaturated zone water stable isotope (²H and ¹⁸O) measurements in semi-arid environments using tunable off-axis integrated cavity output spectroscopy."

ABSTRACT

Reviewer 2 P2L2. Precise to what "directly" refers to here.

Answer:

"Directly" referred to the measurement of stable isotopes in the field. We removed the word and rewrote the sentence as follows:

"Stable isotopes (deuterium, ²H, and oxygen-18, ¹⁸O) of soil pore water were measured in the field using liquid water isotope analyser (tunable off-axis integrated cavity output spectroscopy, OA-ICOS, LGR) and commercially available soil gas probes (BGL-30, UMS, Munich) in a semi-arid region of the Cuvelai-Etosha-Basin (CEB), Namibia."

INTRODUCTION

Reviewer 2

In general, this should be substantially shortened. It reads like a mini-review while should go straight to the point after a short introductory §. Your study is a technical one. This is not reflected by the Introduction until P4L21. The "hypotheses" P6L4-8 should be stated as clear "objectives". The bullet point list should incorporate the "mass balance" objective.

Answer: We substantially shortened the introduction section:

"Stable isotopes of water have been successfully used for decades as powerful proxies for the description of water fluxes such as infiltration in humid (Saxena, 1987) or semi arid regions (Dincer et al., 1974; Allison and Hughes, 1983), evapotranspiration (Barnes and Allison, 1988, Skrzypek et al., 2015), plant root water uptake (Dawson and Ehleringer, 1991; Ehleringer and Dawson, 1992; Dawson, 1996; Yang et al., 2010), hydraulic redistribution (Dawson, 1993; Caldwell et al., 1998), and in

catchment hydrology (e.g., Sklash and Farvolden, 1979; Richard and Shoemaker, 1986; Tetzlaff et al., 2007; Kendall and McDonnell, 2012). Water stable isotopes provide information on flow paths way and mixing within the unsaturated zone (Gazis and Feng, 2004; Stumpp and Maloszewski, 2010; Garvelmann et al., 2012; Mueller et al., 2014). Soil 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 stable isotopes for quantitative recharge estimations which are actively discussed in early and recent reviews (e.g., Allison et al., 1994; Scanlon et al., 2002). But the usefulness of evaporation profiles to determine recharge remains debatable (Herczeg et al, 2011).

In all unsaturated zone studies manual removal of soil samples and a subsequent extraction of soil water in the laboratory was necessary using either vacuum extraction (e.g., West et al., 2006; Koeniger et al., 2011; Orlowski et al., 2013), equilibration (e.g., Wassenaar et al., 2008), mechanical sqeezing, azeotropic distillation or centrifugation methods (e.g., Walker et al., 1994; Kelln et al., 2001). These methods cause both disturbance to the integrity of the natural soil system and possible evaporation during the sampling procedure. The latter is 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 state variables such as soil moisture or matrix potential. Indeed, there are suction cup installations which allow a removal of soil water non-destructively but they are not applicable in arid environments. This is especially true during the dry season where vapor transport (i.e. evaporation) is the dominant driver for water fluxes in the unsaturated zone. In this context, the determination of stable isotope from sampling the vapor of the pore space appears useful.

Principles to sample soil air for the determination of stable isotopes were already indicated by 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-100) is presented in a recent review by Soderberg et al., (2012). The first study monitoring 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 a cavity-ring-down spectrometer (CRDS) (L1102-I, Picarro, CA, USA) calibrated with liquid water injections using a vaporizer unit. Volkmann and Weiler, (2014) developed custom built poly-ethylene (PE) probes with an equilibration chamber allowing additional mixing of the vapor to prevent condensation in the sample line. They further proposed a sophisticated system with a CRDS device (Picarro L2120-i, CA, USA) calibrated with standards prepared on previously oven dried local substrate.

In the present study in-situ usability of commercially available PP-membranes (BGL-30, 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 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 presents I.) an improved automatization with minimal technical modification of commercially available parts. II.) We demonstrate that in-situ measurements are comparable to data derived from cryogenic vacuum extractions. But also, differences exist at the transition to the atmosphere and will be discussed. Such a comparison seems to be useful since a cryogenic extraction is a direct determination of the soil water isotopic composition. III.) Finally, derived isotope data is used quantitatively to determine a soil water balance of a thick sandy unsaturated zone and to separate soil evaporation from transpiration."

STUDY

AND

METHODS

Reviewer 2

P8L2-7. This can be detailed and moved to some appendix but in the text a reference is enough (e.g., Altuhafi et al. 2013).

SITE

Answer: We changed as follows: "In the laboratory grain size analyses was conducted on 10 g material from the extracted samples with a method of Altuhafi et al. (2013)."

Reviewer 2

P9L18. "rate" is missing after "flow". Also throughout the text "velocity" should be replaced with "rate". **Answer:**

We changed as recommended: "volumetric flow" to "volumetric flow rate" and also "velocity" by "rate" if appropriate.

Reviewer 2 P9L31. "®" and not "©". Answer: We changed as recommended.

Reviewer 2

Soil water balance (should have its own section) **Answer:** Soil water balance has its own subsection. **Reviewer 2** P10L11. Provide unit for "Recharge rate". **Answer:** *"Recharge rates were determined in mm/y using a simple empirical relationship […]"* To Equations 2 and 3:

Reviewer 2

1/ how were they empirically found? At a first glance, "22" and "3" do not look like empirical factors to me. Provide peer-review reference(s) associated with these equations;

Answer:

We added as follows:

"The relationship is proposed by Allison et al., 1984 and for $\delta^2 H$ given here as in Clark and Fritz, 1997:"

Reviewer 2

2/ Provide clear definition of δshift.

Answer:

"Recharge rates were determined in mm/y using a simple empirical relationship applied to the data of the deep isotope depth profiles. Therefore the difference between the deuterium excess of the LMWL and the intercept of the linear regression to isotope data of deep soil water is defined as $\delta^2 H_{shift}$ (Figure 4)."

Reviewer 2

To Equations 4 and 5: 1/ P10L20. You certainly mean "Thus" and not "Though"; 2/ they require steady state conditions. This hypothesis must be mentioned; 3/ Provide definitions and unit for all terms, 4/ justify value for tortuosity factor; 5/ which value do you take for δEF?

Answer:

To 1:

Yes this was confused. Thus, we changed if appropriate.

To 2:

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

To 3 and 4:

"Thus, evaporation can be determined providing the relative humidity h_a [-], the saturated water vapor pressure N_{sat} [hPa], the tortuosity with τ =0.67 [-], the diffusitivity of water vapor in air $D^v = 24 * 10^{-6}$ [m^2/s], the density of water ρ [kg/m^3], the porosity p and the soil water content θ_v [m^3/m^3]." These parameters are calibrated to fit the isotope depth profile.

Reviewer 2

To Equations 6 (and not 5):

1/ Is zEF determined with Equation 6 or 5? The problem with Equation 5 is that in order to get zEF, you need δEF ;

2/ give values for r1 and r2.

Answer:

to 1: we changed the formulation for clarification from:

"The isotope ratio δ at depth z_{ef} is then calculated from the isotope value of the reservoir δ_{res} and the isotope ratio at the evaporating front δ_{ef} ."

to

"The data of the isotope depth profile δ is calculated from the fitted parameters z_{ef} , the isotope value of the reservoir δ_{res} and the isotope ratio at the evaporating front δ_{ef} ."

to 2: "Values of z_{ef} are between 110 and 290 mm/y 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 texture, we derive a depth of the evaporation front of 210 and 118 mm for $r^1 = 63 - 112 \mu m$ and $r^2 = 630 - 1120 \mu m$, respectively."

Reviewer 2

P11L7: "with the surface tension of water (α) calculated at 24°C". **Answer:**

We changed : "with the surface tension of water α calculated at 24°C," to "with the surface tension of water α calculated at 24°C,"

RESULTS

Reviewer 2 Keep with paste tense!

Reviewer 2

Figure 5 is described before Figure 4. In this context I do not understand what informative value contains the deuterium excess that does not contain each isotope composition individually... From the text it is also not clear.

Answer:

We changed the order of the Figure 5 and Figure 4 and wrote:

"The shape of the isotope depth profiles is different for δ^{18} O and δ^2 H within the upper 5 to 10 cm. For instance, the maximum isotope values of δ^2 H_c and δ^{18} Oc are at 15 cm. In contrast, the maximum isotope values of δ^2 H_i and δ^{18} O_i are at 10 cm." And

"In comparison to the isotope depth profiles the deuterium excess depth profiles have its minima at 10 cm for both methods excluding profile E2.7."

This cannot be observed by the $\delta^{18}O$ and δ^2H plot only.

Reviewer 2

P12L24. δ values cannot be "enriched/depleted" but are "higher/lower than"

Answer:

We changed:

"Above 25 cm values of $\delta^2 H_c$ are more enriched (-15.5 to -22.6 ‰) than for $\delta^2 H_l$ (-25.0 to -29.2 ‰), and vice versa depleted below 25 cm with -23.4 to -15.2 ‰ for $\delta^2 H_c$ and -11.6 to -5.1 ‰ for $\delta^2 H_l$, respectively."

То

"Above 25 cm values of $\delta^2 H_C$ are higher (-15.5 to -22.6 ‰) than for $\delta^2 H_I$ (-25.0 to -29.2 ‰), and vice versa lower below 25 cm with -23.4 to -15.2 ‰ for $\delta^2 H_C$ and -11.6 to -5.1 ‰ for $\delta^2 H_I$, respectively."

Reviewer 2

P13L7. Where can the reader find the mentioned values in Table 3? **Answer:** It can be found in Table 2: *"A compilation of the quality check standards for* $\delta^2 H_{qc}$ *and* $\delta^{18}O_{qc}$ *of the two campaigns is shown in Table 2."*

Soil water balance

Reviewer 2

Please use abbreviations to match with the Equations and help the reader (e.g., R, zEF). How where T and ET determined?? This comes as a surprise at this point of the manuscript... **Answer:** We added the abbreviation in the text and clarified as follows:

"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 between R = 4 - 5 mm derived from $\delta^2 H_{shift}$ and $\delta^{18} O_{shift}$, respectively. The soil water storage (S) is derived from the soil moisture depth profile and the evaporation front is 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_{ef} using the isotope depth profiles. The mean of all results from E1.1 and E1.2 is 120 ±50 mm/y. Then, Recharge (R), soil water storage (S) and soil evaporation (E) are subtracted from precipitation (P). The remainder is potentially available for transpiration (T) with 510 ±50 mm/y. Runoff can be neglected because it was not observed at the experimental site. Hence, there is a contribution of transpiration to evapotranspiration (E/T_{pot}) of 77 ±7 %. The potential contribution of transpiration (E/T_{pot}) or root water uptake at the inter-canopy plot is between 76 and 92 %. At the site underneath the canopy and vegetated with shrubs E/T_{pot} is between 72 and 92 %. "

Reviewer 2 P15L1. "mm" instead of "mm/y".

Answer:

we changed "Values of z_{ef} are between 110 and 290 mm/y" to "Values of z_{ef} are between 110 and 290 mm".

Reviewer 2

P15L5. Did you mean "67 - 79 mm/y and 161- 201 mm/y."?

Answer:

Indeed: "Calculated soil evaporation rates for profiles from June 2014 are between 67 - 79 mm/y and 161 - 201 mm/y. "

Reviewer 2

P16L6. Remove "be" from the sentence.

Answer: We rewrote that section.

Reviewer 2

P16L8-9. This is not comprehensible...

Answer:

We agree and therefore we rewrote that section.

Comparison with destructive sampling

Reviewer 2

P18L22-23. Water can move from high to low water potential. Since soil water potential is negative, the sentence becomes: "In this case water from deeper soil layers with higher water potential can move through the root system to soil layers with lower water potential (Dawson et al., 1993)". **Answer:** Thus we changed:

"In this case water from deeper soil layers with lower water potential can move through the root system to soil layers with high water potential (Dawson et al., 1993)."

То

"In this case water from deeper soil layers with higher water potential can move through the root system to soil layers with lower water potential (Dawson et al., 1993)".

Reviewer 2

P18L31. "Those" should refer to more than one study (i.e., Sutanto et al. 2014). **Answer:** Therefore we changed as follows:

"Those suggest a contribution of transpiration of more than 70 % to the total evapotranspiration flux (Sutanto et al., 2014)."

То

"Those suggest a contribution of transpiration of more than 70 % to the total evapotranspiration flux as Sutanto et al. (2014) discussed in a recent review."

Reviewer 2

P20L16-21. This is not comprehensible...

Answer:

We could not properly address isotopic differences between methods with the following: "However, it appears that it behaves different to δ 180 and soil moisture as well as δ 180 values show a different pattern as soil moisture. This might be reasonable considering the difference in physical properties of the two isotopologues (Merlivat, 1978). However, the intention to show isotope depth profiles for each transect with their standard deviation for isotopes and soil moisture was to show the difference between the two. The variability within the isotope depth profiles shows a much more heterogeneous pattern than that of the soil moisture data."

Therefore we rewrote as follows:

"However, it appears that it behaves different for $\delta^2 H$ and $\delta^{18} O$ values compared to soil moisture. The differences might be related to vapor diffusion processes or to biological processes. For instance, Dawson et al. (2002) discussed the isotopic composition of different carbon and water pools. Soil respired (CO₂) will equilibrate with the abundant soil water and might cause additional changes of the isotopic composition of the soil pore water."

Reviewer 2

P20L23. "Soil respired CO2...". **Answer:** We changed : "Since soil respiration (CO_2)" to "Soil respired (CO_2)"

Potential, limitations and future research

Reviewer 2

P20L27-28. Can be removed.

Answer: We removed as recommended and renamed "Potential, limitations and future research" to "Potential Limitations"

restructured the section as follows:

"Water vapor mixing ratio dependencies (Sturm and Knohl, 2010; Aemisegger et al., 2012) are of minor importance in this study, because the water content was maintained within the density of approximately 2- 4*10¹⁶ molecules cm³ as recommended by Los Gatos Research. However, it is assumed that small variations will be reflected in the standard deviation of the measurements. Additionally, inference through organic 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 due to high salt concentrations or chemical reactions as observed by Oerter et al. (2014) are negligible, because the cation exchange capacity of the sand was 0.5 meq/100g and total organic carbon (TOC) 0.22 %.

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 precision within one series (orep) of δ 2H is one-third better than the long term accuracy. However, the accuracy of δ 18O is three times greater than the mean precision (Table 2). This can likely be improved by utilizing a more sophisticated technical setup e.g. temperature controlled conditions, standard preparation and frequent cleaning of the probes. Another reason could be the difference in the physical properties of the probe pores such as the diffusitivity of gas (Merlivat et al., 1979). Though there is no chemical data available it is unlikely that chemical properties are responsible, since the sandy soil has a very low CEC. Mote likely are biological processes that are introduced due to the sudden availability of water. Nevertheless, there is no data (i.e CO2 measurements) available to support this assumption. 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) with values of 2.6 ‰ and 0.38 ‰ for δ ²H and δ 18O, respectively.

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 dilution of the sample. Thus, under conditions where the ambient temperature is significant warmer then the soil temperature a simple valve controlled membrane inlet will be sufficient for an indirect determination of isotopes in unsaturated zone or saturated zone water. During day time this is the case at the presented study site, but changes drastically overnight as described. Dilution of the vapor concentration can be done by providing dry gas at the other end of the available probes. In the case of pure diffusion sampling the maximum dilution rate depends upon the absolute amount of water molecules in the vapor and is controlled by the length of the probe, their diffusion properties, the flow velocity and the temperature at depth. 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 directly before

the vapor enters the sample line (Volkman and Weiler, 2014). This leads to independence on flow velocity, probe length and membrane diffusion properties in terms of water content. However, under very dry conditions it might be useful to increase probe length for an increase of resolution, since the soil volume around the probe affected by the measurement will be reduced.

A critical point is the long term application of membrane based methods. The pore space of the probes can be altered over time which might increase the memory effect of the system. Further, the calibration of the in-situ methods of Volkmann and Weiler (2014) and Gaj et al. (this study) used prior oven dried substrate for the calibration. This procedure assumes that all water is evaporated during oven drying and only the added standard water will be measured 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 minerals is commonly removed under vacuum heating the sample to 200 to 300 °C for several hours (VanDeVelde and Bowen, 2013). These adsorbed and interlayer water is bound on the mineral surface and exchanges with atmospheric water vapor within hours (Savinand and Epstein, 1970). Hence, for soils containing clay minerals a calibration procedure using 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)."

Reviewer 2

P21L5. "Thus, .." instead of "Hence, ...". Answer: We changed: "Thus,..." instead of "Hence, ...".

Reviewer 2

P21L7. "isotope compositions of unsaturated and saturated zone waters". **Answer:** We rewrote: "... indirect determination of isotopes in unsaturated zone or saturated zone water."

To "... indirect determination of isotope compositions of unsaturated zone or saturated zone water."

Reviewer 2

P21L8. Do you mean "site"? **Answer: Indeed. Thanks.**

Reviewer 2

P21L8. "overnight". Answer: changed "over night" to "overnight"

Reviewer 2

P21L12. What is meant here by "absolute humidity"? **Answer:** The absolute amount of water molecules in the vapor phase. Thus we changed: "In the case of pure diffusion sampling the maximum dilution rate under absolute humidity..." to "In the case of pure diffusion sampling the maximum dilution rate depends upon the absolute amount

"In the case of pure diffusion sampling the maximum dilution rate depends upon the absolute amount of water molecules in the vapor..."

Reviewer 2

P21L23. You certainly mean "Thus" and not "Though". **Answer: Indeed. Thanks.**

CONCLUSION

Reviewer 2

P22L2. Avoid use of "summing up".

Answer: We rewrote to avoid summing up:

"The present study demonstrates that high resolution in-situ sampling of stable isotopes in the unsaturated zone is feasible."

Reviewer 2

P23L1. I don't understand the mention of isotopic fractionation factors all of sudden... These should not be measured with such a setup (!)

Answer:

We agree and removed that sentence.

Reviewer 2

P23L6. "Additionally, the direct determination of soil water isotope compositions" **Answer:** We changed as recommended: "Additionally, the direct determination of soil water..." to "Additionally, the direct determination of soil water isotopic composition..."

TABLES AND FIGURES

Reviewer 2

In general, all information presented should be carefully defined in the captions. **Answer:** We rewrote the captions for clarification.

- 2
- 3
- 4