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

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Abstract

Stable isotopes (deuterium, ²H, and oxygen-18, ¹⁸O) of soil pore water were measured directly in the field using tunable off-axis integrated cavity output spectroscopy (OA-ICOS) and commercially available soil gas probes in a semi-arid region of the Cuvelai-Etosha-Basin, Namibia. High spatial and temporal resolution was achieved in the study area with reasonable accuracy and measurements were in agreement with laboratory-based cryogenic vacuum extraction and subsequent cavity ring down laser

- spectroscopic isotope analysis (CRDS). After drift correction of the isotope data, mean precision for over 140 measurements of two consecutive field campaigns in June and November 2014 were 1.8 and 0.46% for δ^2 H and ¹⁸O, respectively. Mean Accuracy using quality check standards was 5 and 0.3% for δ^2 H and δ^{18} O, respectively. Results support the applicability of an in-situ measurement system for the determination of stable isotopes in soil pore water. Spatio-temporal variability could be deduced with the observed data in an extremely dry evaporation dominated environment which was sporadically affected by intermittent rainfall.
 - 1 Introduction

The advantage of stable water isotopes (e.g. deuterium, ²H and oxygen-18, ¹⁸O) compared to other tracers is the areal input through precipitation which shows a linear relationship between ²H and ¹⁸O on a global scale known as the global meteoric water line (GMWL) (Craig, 1961). Meteoric water tends to be more depleted in ²H and ¹⁸O in higher latitudes. This can also be observed when they are moving further inwards a continent (Dansgaard, 1964). For this reason, local meteoric water plots on a line that has a slightly different slope known as the local meteoric water line (LMWL). This is due to equilibrium and kinetic fractionation effects. The condition of equilibrium frac-



In contrast, kinetic fractionation occurs due to the removal of water from a reservoir, consequently the reservoir will be enriched in heavy isotopes.

General isotopic composition of precipitation in any region is, driven primarily by local altitude and seasonal climatic patterns, while single event variation is caused by the

- type of event. For example, short and heavy rainfall events (e.g., convective) tend to be more enriched than those with longer duration. This is known as the amount effect and leads to distinguishable isotopic composition of single events (Clark and Fritz, 1997). Hence, the stable isotope composition of precipitation reveals information of single and local events as well as of seasonal and continental circulation patterns. However this
- input signal is altered during infiltration through evaporation, dispersion and mixing of water with different isotopic composition. Evaporation leads to enrichment in the remaining reservoir and changes in deuterium excess values. Heterogeneous flow paths and variable storage capacities in different subsurface reservoirs contain old water with potentially different isotopic composition as the new input. Soil types, and different land-
- scape positions characterize evaporation patterns and therewith enrichment of water on its way through and into the unsaturated zone.

Further, stable isotopes 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), plant root water uptake (Dawson and Ehleringer, 1991; Ehleringer and Dawson, 1992, 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). Stable water 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).



Isotope profiles in the unsaturated zone of arid and semi-arid regions are dominated by evaporation effects overprinting the input signal of precipitation. Evaporation can be determined within these profiles by applying analytical solutions developed by Barnes and Allison (1983). Evaporation from water stored in the unsaturated zone initially plot-

ted on the LMWL tends to fall on a specific evaporation line with a slope dependent on atmospheric temperature and relative humidity as well as the substrate (Allison et al., 1983; Barnes and Allison, 1988). The intersection of that evaporation line with the LMWL is known to be the mean isotopic composition of the originating water.

Intensive work has been done to use stable isotopes for quantitative recharge estimations and is intensively discussed in early and recent reviews (e.g., Allison et al., 1994; Scanlon et al., 2002; Koeniger et al., 2015).

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.,

- ¹⁵ 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 intense and expensive which is limiting the use
- of stable isotopes compared to the other state variables such as soil moisture or suction tension. Suction cup installations allow a removal of soil water non-destructively but are not applicable in arid environments.

However, recent developments in laser spectroscopy allow the measurement of stable isotopes with much higher throughput and even continuously (Berman et al., 2009;

Herbstritt et al., 2012). Such measurements are desirable while facing questions concerning eco-hydrological interactions within the soil plant atmosphere which are not yet fully understood (McDonnell, 2014). In atmospheric studies their sensitivity to vapor concentrations as well as their long-term behavior was already addressed (Wang et al., 2009; Sturm and Knohl, 2010; Rambo et al., 2011; Aemisegger et al., 2012).



Since new laser spectrometers are available, continuous measurements of the isotopic composition from transpired water is possible (Wang et al., 2012) and when combined with isotope depth profiles also a separation of evapotranspiration can be obtained (Dubbert, 2013). By now, using hydrophobic gas permeable membranes enables the measurement of stable isotopes in liquid water with a temporal resolution of less than a minute (Herbstritt et al., 2012).

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 water vapor 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. (ellymann and Weiler (2012) developed custom built poly athylang (PE) probability.
- ¹⁵ unit. Volkmann and Weiler (2013) 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 prior oven dried local substrate.

In the present study in-situ usability of commercially available PP-membranes (BGL-30), Umweltmesssysteme, Munich (UMS) using a water vapor analyzer (Los Gatos Research, DLT-100) for a determination of stable isotopes in soil pore water is demonstrated. In comparison to earlier in-situ studies this study presents an improved application with an OA-ICOS with minimal technical effort. The in-situ measurements are

²⁵ compared to data derived through cryogenic vacuum extraction in the laboratory and an active communication with the analyzer is developed. Besides, the proposed system is for the first time applied under semi-arid field conditions on dry sandy soils with moisture contents ranging from 0.3 to 6%. Infiltration and evaporation patterns as well as effects under high evaporative fluxes are shown. Hence, the present study shows



for the first time an application of in-situ measurements of stable water isotopes in the unsaturated zone under field conditions:

- in a semi-arid environment for water contents lower than 5 %
- in comparison to values from a cryogenic-vacuum extraction
- using commercially available PP-membrane probes.

Further unique is the type of automatization which allows a laboratory like operation. The potential and the limitations of such a system under dry conditions with high temperature and low humidity are discussed.

Study site and methods 2

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- The study area is located in the north of Namibia and is part of the Cuvelai-Etosha-10 Basin (CEB). The whole surface water catchment has an extent of about 173 000 km² where the northern part (approx. 52000 km²) belongs to Angola and the southern part to Namibia. This sedimentary basin is divided into four major sub-basins called lishana, 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 Fig. 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 in the CEB is a multilayer aquifer system in the Andoni formation with

a thickness of 6 to 80 m. The main groundwater flow is towards the Etosha pan with 20 an average gradient of 0.2% (Christelis and Struckmeier, 2001). Beside the shallow aquifer, recent studies identified an area of 500 km² potentially containing fresh groundwater at a depth of 200 m namely the Ohangwena II aguifer (Lindenmaier and Christelis, 2012; Lindenmaier et al., 2014). Groundwater recharge mechanisms concerning





system consists partly of freshwater lenses on brackish to saline groundwater mostly in the lishana region. Perched discontinuous aquifers are found in the eastern part of the basin and can develop on clay lenses in the subsurface 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 3000 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 the rainfall in the western part is less predictable.

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 m and has high saturated hydraulic conductivity (2304–2409 cm day⁻¹), high

- ¹⁵ porosity (0.4) and low field capacity (~ 3.5 %). Sampling and measurements were conducted during two field campaigns. The first field campaign was conducted between the 9 and 15 June 2014 and the second between 15 and 22 November 2014. To determine heterogeneity of infiltration and evaporation processes and to evaluate an in-situ approach determining stable isotopes in soil water nine plots within an area of 9000 m²
- ²⁰ were investigated. During the first campaign soil gas probes were installed at depths of 2, 5, 10, 15, 20, 25, 30, 40 and 50 cm. Two plots were established with different vegetation characteristics such that one was vegetated with shrubs and the other was exposed without any vegetation. During the second field campaign probes were installed horizontally 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 resolution especially for the top layer. In addition to the in-situ measurements samples were collected in head space glass vials for laboratory extraction and crimp sealed to avoid evaporation. 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. Samples were



transported via aircraft to the laboratory of the Federal Institute of Geosciences and Natural Resources (BGR) in Hannover, Germany and subsequently extracted.

In the laboratory grain size analyses was conducted on 10 g material from the extracted samples < 2000 μm was washed and particles < 63 μm were allowed to pass

- ¹⁰ The instrument images a falling curtain of sediment and determines the grain size of each particle in the image using two different cameras. Typically images of a few million grains were processed for each sample (Altuhafi et al., 2013).

For stable isotope analysis of soil water triplicate soil samples were prepared and scaled before and after the water extraction procedure. Soil water was extracted cryo-

¹⁵ genically using a slightly modified method of the cryogenic-vacuum extraction decribed by Koeniger et al. (2011). Instead of a water bath heated by a hot plate an isolated aluminium block temperated to 105 °C was used. Each sample was evacuated at –3 mbar vacuum and extracted for 15 min. After extraction soil samples were oven dried at 105 °C for 24 h and weighted again. Results before and after oven drying are compared as a measure of extraction success.

The water samples were subsequently measured with a cavity ring-down spectrometer (CRDS, model L2120-i, manufactured by Picarro Inc.). Isotope values are expressed as parts per thousand in δ -notation (e.g. δ^{18} O and δ^{2} H) and are normalized to the international scale using Eq. (1):

$$\mathcal{E}_{25} \quad \delta = \left[\left(\frac{R_{\text{sample}}}{R_{\text{reference}}} \right) - 1 \right] \cdot 1000\% \tag{1}$$

where R_{sample} (-) denotes the isotope ratio of ${}^{18}\text{O}/{}^{16}\text{O}$ or ${}^{2}\text{H/H}$ of a sample and R_{Standard} (-) those of the standard. The data sets were normalized to the Vienna Stan-



dard Mean Ocean Water (VSMOW) and Standard light Antarctic Precipitation (SLAP) scale by assigning values of 0 and -55.5% (δ^{18} O) and 0 and -428% (δ^{2} H) to VS-MOW and SLAP, respectively. Further two laboratory standards that were calibrated directly against VSMOW and SLAP were measured in each run. All values where corrected for drift and mean and scale protocol and scale protocol.

⁵ rected for drift and memory applying a method proposed by.van Geldern 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 soil extractions has to be taken into account which is better than 0.8 and 4‰ for δ^{18} O and δ^{2} H, respectively. Subscripts are used to distinguish between either the in-situ (I) and the cryogenically (C) derived isotope values in the remaining text.

For the determination of $\delta^2 H_1$ and $\delta^{18}O_1$, 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). A simplified wiring diagram is illustrated in

- ¹⁵ Fig. 2. Each probe is separated from the main transport line with a valve (Clippard Minimatic, USA) which in turn is controlled by a laptop. In addition, the laptop is communicating with the OA-ICOS through an RS-232 connection. The laptop mimics the behavior of a laboratory auto sampler via an interface programmed in python. To avoid over heating of the analyser during day time by direct sun radiation a gazebo was po-
- ²⁰ sitioned above the loading area of the pick-up truck where the analyser is mounted. Power supply was maintained using a common 230 V generator.

Four repetitive measurements at each depth were performed during the first campaign. During the second campaign six consecutive measurements were performed at each depth. A measurement cycle consists of three steps: (i) a flushing phase were the cavity is evacuated, (ii) the sample intake opening a particular valve and (iii) the measurement of the sample. Flushing introduces a vacuum of 0.1 torr or less. The

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sample intake is controlled by valves which are opened for 10 s for each measurement allowing a volumetric flow between 95 and 110 mLmin⁻¹. The transported gas volume is measured with a flow control device (Analyt-MTC 0–200 mLmin⁻¹). The Probe and



transport lines to the analyser have a volume of approximately 40 mL. The lines are made of steel and are connected with Swagelok[®] connectors. After six consecutive measurements at one depth, the sampled soil volume is approximately 120 mL. Assuming that the soil volume around the 300 mm long probe is sampled equally over the

- ⁵ hole length, a diameter of 1 cm around the probe will be directly affected by the measurement. Hence the top layer is measured with reasonable accuracy for this particular setup. The measurement of a 1 m deep profile considering 16 different depths with 6 repetitions and a resolution down to 2.5 cm for the top 20 cm takes about 4.5 h. The OA-ICOS device needs an additional warm up of about two hours.
- Standard preparation of 200 g prior oven dried sandy substrate was used. It has been transported in aluminium bags (WEBA bags ©) and was spiked with 5 mL of standard before the experiment at the day of measurement. Normalization to the international scale is done using one low standard (HGLA) and one high standard (HMER). In addition one standard for drift correction (HDES) and a quality check standard (HLAU)
- ¹⁵ were used. All standards were measured at the beginning of each experimental sequence; additionally HDES and HLAU were measured at the end of each sequence. Isotope values of the used standards are illustrated in Table 1. The standards were used only for two consecutive measurement series and then new standards were prepared to avoid potentially enrichment through evaporation. Calibration standards were light in flacks with a diameter of 0 am and a leagth of 50 am. Calibration standards were
- kept in flasks with a diameter of 2 cm and a length of 50 cm. Soil gas probes were subsequently entered and the flasks sealed to avoid evaporation.

3 Results

3.1 Campaign 1

The first field campaign was conducted short after the rainy season. No rain occurred during that campaign. The texture (medium sand) was uniform throughout the depth profile (Fig. 3). No changes in Texture were observed for the other investigated plots.



Temperature and humidity variability within the sampling period between daytime (~ $30\degree C_{max}$ and $15\%_{min}$) and night (~ $9\degree C_{min}$ and ~ $90\%_{max}$) was high during the first campaign.

3.2 Isotope depth profiles

- ⁵ During the first campaign (15 June 2014) measurements were taken at two plots (E1.1, E1.2) at a distance of 25 m on the same day. The measurement at E1.1 started at 09:30 UTC+1 and later at 16:00 UTC+1 at plot E1.2. Plot E1.1 is not vegetated and has a thin soil crust in the top first centimeter. Volumetric water content increases from 0.3% at the top to 4.1% at 50 cm depth (Fig. 4, left). Plot E1.2 is vegetated, a dense
 ¹⁰ root mat is visible in the upper 10 cm. In contrast to E1.1 water contents are much lower increasing from 0.3% at the surface to 0.7% at 50 cm depth (Fig. 4, center). The isotope depth profiles are of similar shape and magnitude for both profiles with a maximum at 10 cm and an exponential decline down to the maximum depth. Due to low water contents in the upper 15 cm of the vegetated plot, not enough water could
 ¹⁵ be extracted with the cryogenic extraction method. However, at 10 cm depth the same pattern as for profile E1.1 can be absorved. The absorved the profiles are of profiles.
- pattern as for profile E1.1 can be observed. The shape of the isotope depth profiles is different for δ^{18} O and δ^{2} H within the upper 5 to 10 cm. As depicted in Fig. 6, the deuterium excess for both profiles shows a maximum at 10 cm depth and are exponentially decline down to 50 cm. At the vegetated plot deuterium excess values are positive
- ²⁰ within the top 7.5 cm. Comparing deuterium excess values of the cryogenic extraction with those from the in-situ measurements it can be found that they agree well for the bare soil plot, but not at 10 and 15 cm depth. In contrast, all values measured in the field below 10 cm of the vegetated plot, which has very low water contents (< 1 %), are shifted towards more positive values.



3.3 Campaign 2

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During the second campaign these variations were much smaller (daytime $\sim 35 \degree C_{max}$ and $30\%_{min}$; night ~ $20^{\circ}C_{min}$ and ~ $90\%_{max}$). Two rainfall events were recorded (12 November 2014: 12 mm morning, 13 November 2014: 30 mm morning) at the cli-⁵ mate station in Eenhana which is approximately 15 km west of the experimental site. However, no isotope data is available for these events. Later during the campaign small rain events (16 mm) could be sampled for isotopes on the 17 November 2014 at 8 a.m. with -0.6 and 3.0% were measured for δ^{18} O and δ^{2} H, respectively. Another event (4 mm) was sampled at the 19 November 2014 with isotope values of 3.6 and 28.8% for δ^{18} O and δ^{2} H.

3.4 Isotope depth profiles

In contrast to the plots measured during the first campaign, the plots in November (rainy season) show higher water contents and variable vegetation patterns. One unvegetated plot of the second campaign (E2.7, see Fig. 4 right hand side and Table 2) is used to compare the in-situ and the laboratory results as an example with higher 15 water contents. The water contents range between 4.4 and 6.8% with maximum values between 12.5 and 25 cm (Fig. 4, right). Strongest enrichment of δ^{18} O is in the top layer declining exponentially with depth for both methods. There is good agreement between $\delta^{18}O_1$ and $\delta^{18}O_2$ except for the depth at 30 and 50 cm. In contrast, there are substantial differences between $\delta^2 H_1$ and $\delta^2 H_c$. Above 25 cm values of $\delta^2 H_c$ are 20 more enriched (-15.5 to -22.6 ‰) than for $\delta^2 H_1$ (-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 $\delta^2 H_i$, respectively.

Both isotope depth profiles of the first campaign show good agreement between 15 and 50 cm (δ^{18} O RMSE = 3.9; δ^{2} H RMSE = 9.2) but diverge at shallower depth 25 with more enriched values for the in-situ measurements (δ^{18} O RMSE = 7.0; δ^{2} H RMSE = 43.4). In general, better agreement can be observed for δ^{18} O compared to



 δ^2 H values. Both isotope 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 this maximum at 10 cm, but only for $\delta^{18}O_1$. The profile of the second campaign does show good agreement within the top 25 cm ⁵ for $\delta^{18}O_1$ but for δ^2H only within the upper 10 cm. In terms of accuracy for the set of these three profiles we obtain 6.86 and 1.87% for $\delta^2 H_1$ and $\delta^{18} O_1$ respectively.

A compilation of the quality check standards of the presented campaigns is shown in Table 2. The standard deviation of the repetitive measurements for each depth is a measure of measurement precision. After drift correction and normalisation of the isotope depth profile E1.1 the precision (σ_{qc}) of the quality check standard (HLAU) was 5.2 ‰ δ^2 H and 0.66 ‰ δ^{18} O. The mean precision of the repetitive measurements (σ_{rep}) is two times better for $\delta^2 H_1$ than for the precision of the repetitive measurements (σ_{crv}) for values derived with the cryogenic vacuum extraction $\delta^2 H_c$. Values of δ^{18} O show more similarity (refer to Table 2). The measurement of the second profile E1.2 is less precise for $\delta^2 H_1$ but in the same range as $\delta^2 H_c$. Similar precision as profile E1.1 is 15 found for the third profile E2.7 for both δ^2 H and δ^{18} O, respectively.

3.5 δ^{18} O vs. δ^{2} H

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In Fig. 5 the δ^{18} O to δ^{2} H relationship is shown. The LMWL consist of historical data collected in the CEB and has a slope of 7.3 ($R^2 = 0.96$). Additionally samples of local groundwater and deep soil water are represented as mean values. Soil water from the 20 first field campaign derived from the cryogenic vacuum extraction plots along an evaporation line with a slope of 2.4 ($R^2 = 0.79$) for the non-vegetated plot and 3.1 ($R^2 = 0.96$) for the vegetated plot. In-situ measurements of the non-vegetated plot have a slope of 3.9 ($R^2 = 0.84$). Excluding the first 10 cm of the unvegetated profile the slope is 2.9 $(R^2 = 0.73)$. Values of the vegetated site derived from the in-situ measurements have 25 a slope of 3 (R = 0.464) and are shifted towards more positive δ^2 H values. Excluding the top 15 cm of the in-situ measurement the slope remains the same but with $R^2 = 0.9$.



Values from the second campaign show a much higher slope with 5.29 ($R^2 = 0.75$) for the in-situ measurement and 5.1 ($R^2 = 0.96$) for the cryogenic vacuum extraction and are plotting close to the LMWL.

3.6 Spatio-temporal variability

⁵ Each profile of the second campaign is measured at 18 different depths and each depth with 6 repetitions. After drift correction of the isotope data, the mean precision considering the quality check measurements (σ_{qc}) for more than 140 measurement points is 2.15% for $\delta^2 H_1$ and 0.36% for $\delta^{18} O_1$ (Table 2). Mean standard deviation of the repetitive measurements (σ_{rep}) of each depth is 1.86% for $\delta^2 H_1$ and 0.46% for $\delta^{18} O_1$, respectively. As shown in Table 2, the mean standard deviation of the repetitive measurements are similar to those derived from the quality check standards. Differences are observed between σ_{qc} and σ_{rep} . However, the precision of $\delta^2 H$ is within the range of the mean accuracy of 5.1%. The mean accuracy of $\delta^{18} O$ is much higher with 0.3%. There are two outliers (E2.8, E2.9) which were not considered for the mean precision 15 or accuracy.

Three rows are measured consisting of 3 plots. Each row is 150 m in distance from each other as well as each profile within one row. Each row is further named as one transect. Transects consist of bare plots as well as vegetated plots (Table 2). However, lateral roots could be found at each plot. Mean values of each transect are shown

- to illustrate an averaged temporal development with intermittent rainfall (Fig. 7) for this particular area. The first transect is affected only from the first set of rain events (E2.1 to E2.3) and was measured within two consecutive days. The next transect (E2.4 to E2.6) is affected by the 16 mm event (17 November 2014) where isotope data is available and were measured in a period of three days. Finally, the last three plots (E2.7 to E2.7) to E2.8 measured in a period of three days.
- E2.9) had the longest time to recover from the first rain events and experienced only additional precipitation on the 19 November 2014 with an amount of 4 mm. Maximum infiltration depth varied between 65 and 95 cm. Water content varied between 0.5 and



9.5%. Comparing the three transects it can be observed that variability of isotope depth profiles decreases from the first to the last transect and an evaporation profile developd.

Discussion 4

The data presented here shows advantages, limitations and improvements that are valuable for further in-situ applications investigating unsaturated zone processes. At 5 our location we found that especially the interaction between the top 20 cm of the soil profile and the atmosphere needs further investigation. Additionally, the transport of water vapor after rain events and its influence to isotope values of depth profiles is not yet fully understood. This is also valid to spatial variability which can be caused by heterogeneous rainfall even on a small scale, interception and preferential flow paths. 10 It could be shown that, spatial and temporal variability of isotope depth profiles and can be high compared to soil moisture profiles. Currently in-situ measurements are limited to measure one profile at a time. It would be necessary to setup more than one laser spectrometer or to find a way for higher measurement frequency to overcome this limitation.

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However some pitfalls outlined in other studies can be neglected for the present application. For instance, water vapor mixing ratio dependencies can be corrected for which is necessary if humidity is low (Sturm and Knohl, 2010; Aemisegger et al., 2012). This can be neglected in the present study because the water content was maintained within the density of approximately $2-4 \times 10^{16}$ molecules cm⁻³ 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).



4.1 Validation with destructive sampling

Results of the first field campaign demonstrates good agreement of the isotope depth profiles between different methods for lower parts but also a divergence in the top 15 cm. This could be caused by several reasons. An incomplete extraction of water will result in depleted isotope values of the extracted water. However, this is unlikely for fine sand with very low matrix potential and very low abundance of fine pores. While measuring with the soil gas probe in a very coarse material atmospheric vapor or even vapor from other parts of the soil can lead to a mixed sample. However, the extracted air volume is very low and a divergence of isotope values is only visible within the top 15 cm of the dry profiles (Fig. 4, left and center). Evaporation is reflected in the deuterium excess (d_{ex}) (Figs. 5 and 6) and could be enhanced by the uptake of air through the measurement. 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 would suggest to have enriched values

- ¹⁵ for deeper parts of the vegetated profile (Fig. 4, center). Therefore it might be rather attributed to kinetic processes because vapor transport (evaporation) will be higher at shallow depths (Braud et al., 2009). Beside this fact, it has to be noted, that destructive sampling was conducted one day after the in-situ measurements because it was assumed that the isotope profiles are in steady state after the dry season (Barnes and
- Allison, 1988). Therefore another explanation can be that high temperature and low humidity during the day causes a dry out of the top layer due to vapor transport into the atmosphere. During the night, temperatures decrease and humidity increases. Low soil water contents and a back diffusion of vapor into the upper part of the soil might cause condensation, which can significantly increase soil water content (Henschel and Seely,
- 25 2008) and 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 evaporation can be large depending on the energy budget at the surface but the influence on iso-



tope concentrations needs to be further investigated especially under field conditions (Braud et al., 2005).

Differences between the two sites of the first field campaign are small regarding the shape of the isotope depth profiles. Because of the shaded nature of plot E1.2 it

- ⁵ could be expected that less evaporation takes place and hence less enrichment and a lower deuterium excess would appear for the in-situ measurement (Fig. 6). 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). Interestingly, the water contents suggest root water uptake at sites with high shrub density even to values as
- 10 low as 0.5 % which can be of advantage for competition with other surrounding species. Depending on uptake rates this can affect infiltration amounts between wet spells, if a higher storage deficit in the soil has to be satisfied. Beside this, a dense root network in the upper 10 cm suggests that small rain events will be utilized by these plants. It is likely that even small amounts of water through dew deposition are accessible to plants

(Agam and Berliner, 2006).

In contrast to the profiles of the first campaign the rain influenced profile E2.7 does not show such a divergence in the top layer. As shown in Fig. 6 the deuterium excess indicates that precipitation water is dominating. Good agreement is found in the top layer for both isotopes. Mixing with atmospheric vapor might be negligible considering

- ²⁰ the high soil water contents. Destructive sampling was done directly before the in-situ measurement started. It has to be noted that, in-situ measurements at 10 cm depth were done 90 min after the destructive sampling was conducted. In-situ measurements at 30 cm even after 120 min. Hence differences can be caused by the time lag between destructive sampling and in-situ measurement. Values of $\delta^2 H_1$ below 30 cm are more
- ²⁵ enriched compared to $\delta^2 H_c$. Therefore, observed differences between $\delta^2 H_l$ and $\delta^2 H_c$ for profile E2.7 (Fig. 4, right) might be attributed to the exchange between the evaporation depleted vapor that was transported from the deeper part (30 to 50 cm) to shallower depth (12.5 and 25 cm) due lower saturated water vapor pressure at shallower depth. The movement of water vapor is following temperature cycles if the vapour saturation



of soil air is similar over depth. If the soil air is not saturated there will be a transfer of vapour towards this dry zone which can be independent of temperature gradients as described in Abramova (1969).

Values for in-situ measurements and cryogenic extraction fall on evaporation lines ⁵ which are similar in slope, when the top part of the dry profiles is excluded. 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 discussed earlier, kinetic effects and diurnal variations in evaporation or condensation due to strong temperature changes are not yet fully understood. Hence the differences might be attributed to such effects which need further investigation in the future.

4.2 Spatio-temporal variability

During the second field campaign information on long term precision and spatiotemporal 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

- ¹⁵ the long term accuracy. However, the accuracy of δ^{18} O is three times greater than the mean precision (Table 2). This can likely be improved by utilizing a more sophisticate 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 to gas (Merlivat et al., 1979). ²⁰ However, the precision appears to be sufficient to monitor processes of a diurnal time scale which is comparable to other systems. e.g., Volkmann and Weiler et al. (2013)
- scale which is comparable to other systems, e.g., Volkmann and Weiler et al. (2013) present values of 2.6 and 0.38‰ for δ^{2} H and δ^{18} O, respectively.

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 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 the standard deviations within one transect (Fig. 7).



Other studies showed similar patterns in the context of a numerical experiment (Singleton et al., 2004). The first transect (Fig. 7, Transect 1) has variable isotope values throughout the whole depth. The isotope depth profile of transect one shows maxima and minima of isotope values which appears with a similar shape as a profile in a humid

- ⁵ climate. However, here it is 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 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 and 50 cm
- ¹⁰ (Fig. 7, 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.

Short time after rain the top part of the evaporation profile (Transect 1) was consider¹⁵ ably displaced as theoretically described by Allison et al. (1984). Variations of 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). 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-situ
²⁰ measurements have great potential to visualize theoretically discussed processes with

feasible accuracy under natural field conditions.

5 Conclusion

The present study demonstrates that a high resolution in-situ sampling of stable isotopes in the unsaturated zone is feasible. In-situ measurements can be applied with minimal technical effort for remote applications. They further show good agreement with values derived from cryogenic soil water extractions. Differences between the two methods are predominantly within the given accuracies of the methods. Divergence in



the upper soil layer between in-situ and destructive sampling suggest enhanced soilatmosphere interactions and kinetic processes due to high evaporation rates. However, evaporation induced by the measurement procedure needs further investigation for very low water contents to reduce limitations. Long term accuracy within the presented campaigns is about two times lower for $\delta^2 H$ and three times for $\delta^{18} O$ than for the short term precision of each profile.

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The presented in-situ measurements have great potential to investigate transient processes within the unsaturated zone of semi-arid environments which have not been able to study until now. The determination of stable water isotopes in the unsaturated zone directly in the field allows monitoring transient processes which would not be pos-

- ¹⁰ Zone directly in the field allows monitoring transient processes which would not be possible with destructive sampling strategies. This creates new possibilities to the design of tracer experiments with water of different isotopic composition as conservative tracer. However, this is limited to the measurement frequency of the provided system which is now at least feasible to capture diurnal processes with the presented vertical reso-
- ¹⁵ lution. In addition, a much higher spatial resolution can be achieved with much lower time consumption compared to conventional approaches. The proposed measurement offers the possibility to investigate unsolved questions regarding soil atmosphere interactions such as water vapor intrusion and transport plus effects of diurnal evaporation cycling on isotope depth profiles. Strategies of plant root water uptake in water scarce environments are not yet fully understood as well as the role of water vapor transport.

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Table 1. Standards used for normalization, drift correction, quality check and preparation of field standards.

Abbreviation	Description	$\delta^2 H$	σ	δ^{18} O	σ
HMER HDES HLAU	Hannover sea water Hannover distilled water Hannover lauretaner water	-3.1 -55.9 -64.6	±0.4 ±0.9 ±0.6	-0.4 -8.12 -9.73	±0.13 ±0.14 ±0.10
HGLA	Hannover glacier water	-152.1	±0.9	-20.27	±0.11

Table 2. Values for HLAU (qc) with the corresponding standard deviation of their repetitive mea-							
surements (σ_{ac}), the mean standard deviation of the repetitive measurements of each measure-							
ment point (σ_{rep}) and the corresponding values of the cryogenic vacuum extraction (σ_{crv}) from							
the campaigns June–November 2014. Bare plots (B) and vegetated plots (V) were measured.							

ID	Date	Init.Time		$10^3 \delta^2 H$		$\sigma_{ m qc}$	$\sigma_{\rm rep}$	$\sigma_{\rm cry}$	10 ³ δ ¹⁸ O		$\sigma_{ m qc}$	$\sigma_{\rm rep}$	$\sigma_{ m cry}$
E1.1	04.06.2014	09:30:00	В	-60.09	±	5.13	1.4	3.7	-10.04	±	0.66	0.7	0.8
E1.2	04.06.2014	15:30:00	V	-74.96	±	2.83	3	3.5	-13.16	±	0.01	0.6	0.6
					±	3.98	2.2	3.6		±	0.34	0.65	0.70
E2.1	15.11.2014	10:50:00	В	-73.25	±	0.87	1.17		-10.38	±	0.34	0.45	
E2.2	16.11.2014	08:00:00	В	-69.83	±	0.99	1.26		-8.05	±	0.48	0.35	
E2.3	16.11.2014	13:30:00	V	-71.11	±	0.49	2.21		-10.29	±	0.14	0.54	
E2.4	17.11.2014	11:00:00	V	-57.51	±	4.11	1.72		-8.45	±	0.14	0.28	
E2.5	18.11.2014	11:00:00	V	-64.82	±	1.86	1.52		-7.73	±	0.34	0.28	
E2.6	19.11.2014	07:30:00	В	-75.62	±	1.84	2.49		-6.81	±	0.81	0.5	
E2.7	19.11.2014	14:00:00	В	-79.35	±	1.27	1.93	3.5	-11.62	±	0.36	0.45	0.45
E2.8	20.11.2014	11:30:00	V	-25.24	±	2.53	1.45		-3.68	±	0.25	0.24	
E2.9	21.11.2014	11:30:00	V	-23.00	±	17.17	1.74		-15.59	±	4.17	0.37	
						2.15	1.86	3.57			0.36	0.46	0.62





Figure 1. The study area is located in the northern part of the Cuvelai-Etosha-Basin (CEB), which is subdivided by the political border between Angola and Namibia (left). Sampling was conducted in Elundu located in the center of the CEB (center, right).





Figure 2. Simplified diagram of the technical setup. The laptop (1) mimics the behavior of a laboratory autosampler communicating with the analyser (2). The transport line (5) is interrupted by a valve (3) which is controlled by the laptop computer. Soil pore water is transported through the transport lines (6) from soil gas probe to the ICOS device. The flow is measured with a massflowcontroller (4).





Figure 3. Grain size distribution of a 1 m deep profile at Elundu, Cuvelai-Etosha-Basin (CEB), Namibia.





Figure 4. 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. Standard deviation of each plot for each method are indicated by error bars in the legend of the plot.





Figure 5. δ^{18} O vs. δ^{2} H plot of the profiles E01.1, E01.2, E02.7. Also shown is the LMWL for the northern part of Namibia as well as groundwater and soil water down to a depth of 4 m.





Figure 6. Deuterium excess for the profiles E01.1, E01.2 sampled in June 2014 and E02.7 sampled in November 2014. Compared are values from the cryogenic vacuum extraction (triangles) and the in-situ measurements (circles).





Figure 7. 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.

