

Abstract

Stable isotopes (deuterium, ^2H , and oxygen-18, ^{18}O) 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-Etосha-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 $\delta^2\text{H}$ and ^{18}O , respectively. Mean Accuracy using quality check standards was 5 and 0.3‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, 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, ^{18}O) compared to other tracers is the areal input through precipitation which shows a linear relationship between ^2H and ^{18}O on a global scale known as the global meteoric water line (GMWL) (Craig, 1961). Meteoric water tends to be more depleted in ^2H and ^{18}O 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 fractionation is given if water remains in a closed system without any removal of vapor.

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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 landscape 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).

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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.

2 Study site and methods

The study area is located in the north of Namibia and is part of the Cuvelai-Etoshabasin (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 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 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 aquifer (Lindenmaier and Christelis, 2012; Lindenmaier et al., 2014). Groundwater recharge mechanisms concerning both, the shallow and the deep aquifer are not yet fully understood. The shallow aquifer

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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 a < 63 μm sieve. The sand fraction (63–2000 μm) was dried again and the amount of material < 63 μm was calculated by difference between initial and recovered sample mass. The grain size analysis of the dried sand was performed using an optically based instrument (Camsizer, Retsch). The instrument employs two digital cameras (CCD) to record falling particles (dynamic image analysis) in the grain size of 0.03–30.0 mm. 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 cryogenically using a slightly modified method of the cryogenic-vacuum extraction described by Koeniger et al. (2011). Instead of a water bath heated by a hot plate an isolated aluminium block tempered 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. δ¹⁸O and δ²H) and are normalized to the international scale using Eq. (1):

$$\delta = \left[\left(\frac{R_{\text{sample}}}{R_{\text{reference}}} \right) - 1 \right] \cdot 1000\text{‰} \quad (1)$$

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

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5 dard Mean Ocean Water (VSMOW) and Standard light Antarctic Precipitation (SLAP) scale by assigning values of 0 and -55.5% ($\delta^{18}\text{O}$) and 0 and -428% ($\delta^2\text{H}$) to VSMOW and SLAP, respectively. Further two laboratory standards that were calibrated directly against VSMOW and SLAP were measured in each run. All values were corrected 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 $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. Subscripts are used to distinguish between either the in-situ (I) and the cryogenically (C) derived isotope values in the remaining text.

10 For the determination of $\delta^2\text{H}_I$ and $\delta^{18}\text{O}_I$, 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). A simplified wiring diagram is illustrated in 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 positioned above the loading area of the pick-up truck where the analyser is mounted. Power supply was maintained using a common 230 V generator.

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

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3.3 Campaign 2

During the second campaign these variations were much smaller (daytime $\sim 35^{\circ}\text{C}_{\text{max}}$ and $30\%_{\text{min}}$; night $\sim 20^{\circ}\text{C}_{\text{min}}$ and $\sim 90\%_{\text{max}}$). Two rainfall events were recorded (12 November 2014: 12 mm morning, 13 November 2014: 30 mm morning) at the climate 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 $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. Another event (4 mm) was sampled at the 19 November 2014 with isotope values of 3.6 and 28.8% for $\delta^{18}\text{O}$ and $\delta^2\text{H}$.

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 un-vegetated plot of the second campaign (E2.7, see Fig. 4 right hand side and Table 2) is used to compare the in-situ and the laboratory results as an example with higher water contents. The water contents range between 4.4 and 6.8% with maximum values between 12.5 and 25 cm (Fig. 4, right). Strongest enrichment of $\delta^{18}\text{O}$ is in the top layer declining exponentially with depth for both methods. There is good agreement between $\delta^{18}\text{O}_I$ and $\delta^{18}\text{O}_C$ except for the depth at 30 and 50 cm. In contrast, there are substantial differences between $\delta^2\text{H}_I$ and $\delta^2\text{H}_C$. Above 25 cm values of $\delta^2\text{H}_C$ are more enriched (-15.5 to -22.6%) than for $\delta^2\text{H}_I$ (-25.0 to -29.2%), and vice versa depleted below 25 cm with -23.4 to -15.2% for $\delta^2\text{H}_C$ and -11.6 to -5.1% for $\delta^2\text{H}_I$, respectively.

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

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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.

4 Discussion

The data presented here shows advantages, limitations and improvements that are valuable for further in-situ applications investigating unsaturated zone processes. At 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. 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.

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).

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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 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, 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-

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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 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 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 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 $\delta^2\text{H}_I$ below 30 cm are more enriched compared to $\delta^2\text{H}_C$. Therefore, observed differences between $\delta^2\text{H}_I$ and $\delta^2\text{H}_C$ 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

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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 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 $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ 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 spatio-temporal variability was investigated. Comparing the quality check standards of the two campaigns the precision within one series (σ_{rep}) of $\delta^2\text{H}$ is one-third better than the long term accuracy. However, the accuracy of $\delta^{18}\text{O}$ 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 diffusivity to gas (Merlivat et al., 1979). 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) present values of 2.6 and 0.38‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, 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).

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

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

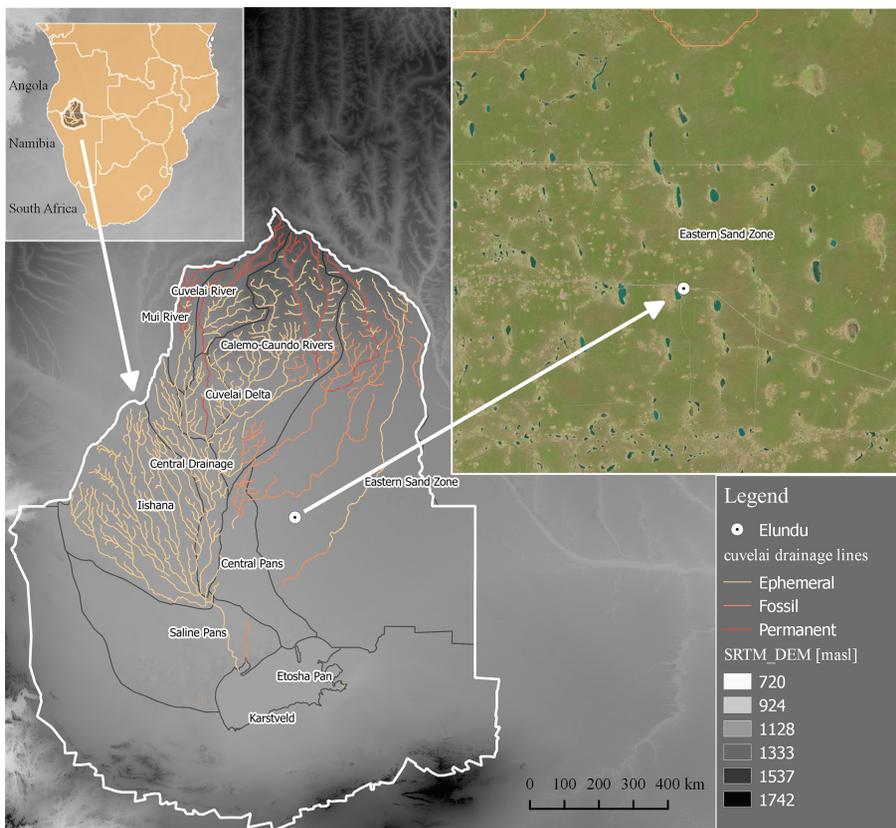


Figure 1. The study area is located in the northern part of the Cuvelai-Etосha-Basin (CEB), which is subdivided by the political border between Angola and Namibia (left). Sampling was conducted in Elundu located in the center of the CEB (center, right).

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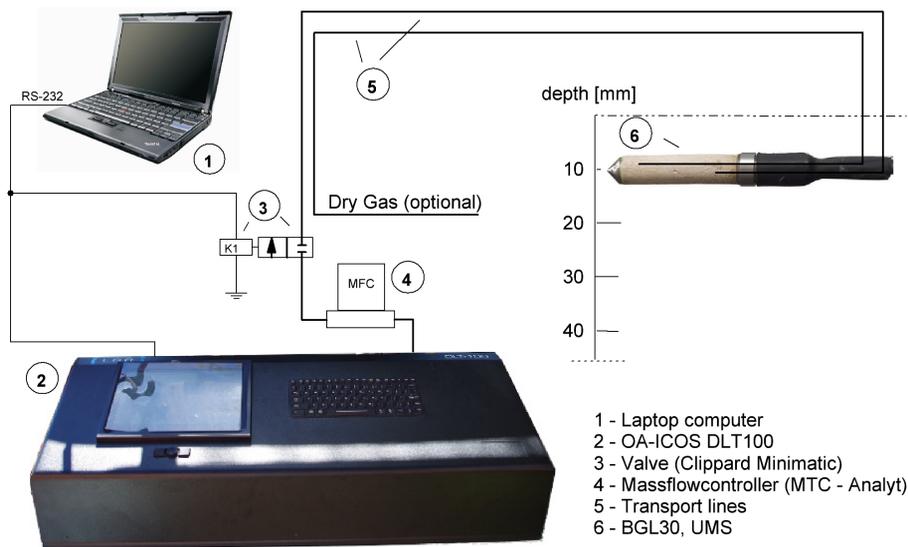


Figure 2. Simplified diagram of the technical setup. The laptop (1) mimics the behavior of a laboratory autosampler communicating with the analyser (2). The transport line (5) is interrupted by a valve (3) which is controlled by the laptop computer. Soil pore water is transported through the transport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

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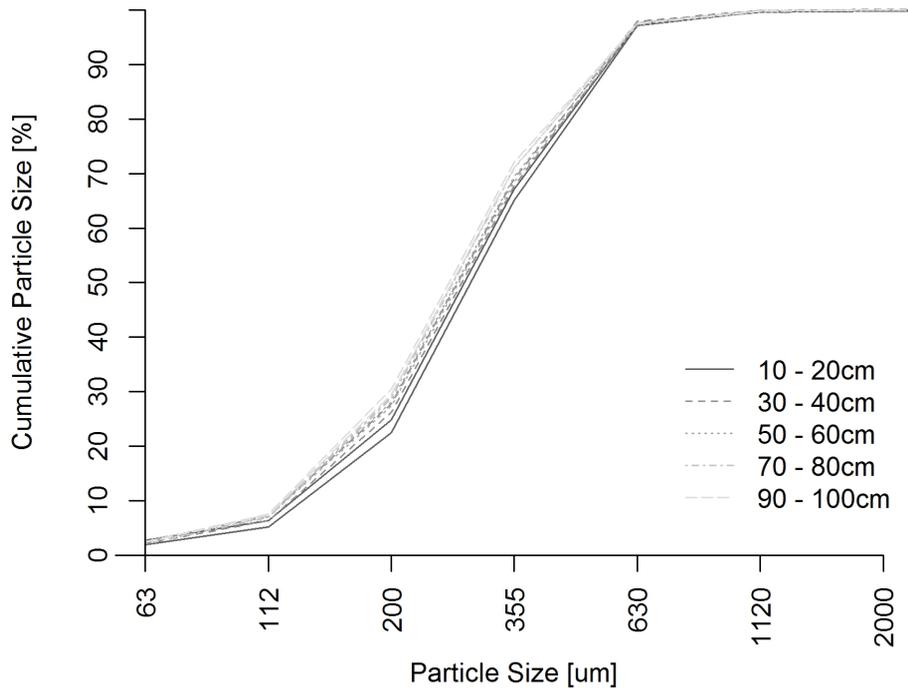


Figure 3. Grain size distribution of a 1 m deep profile at Elundu, Cuvelai-Etосha-Basin (CEB), Namibia.

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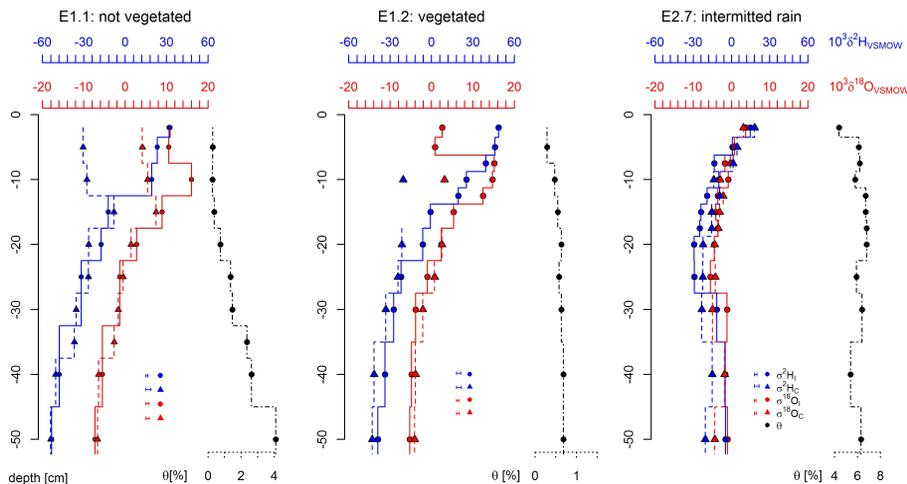


Figure 4. Depths profiles of the field campaign in June 2014 (E1.1, E1.2) and the field campaign in November 2014 (E2.7) are shown. Compared are isotope depth profiles extracted with the cryogenic vacuum extraction (dashed, triangles) and measured in-situ (straight, dots). $\delta^2\text{H}$ is given in blue and $\delta^{18}\text{O}$ 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.

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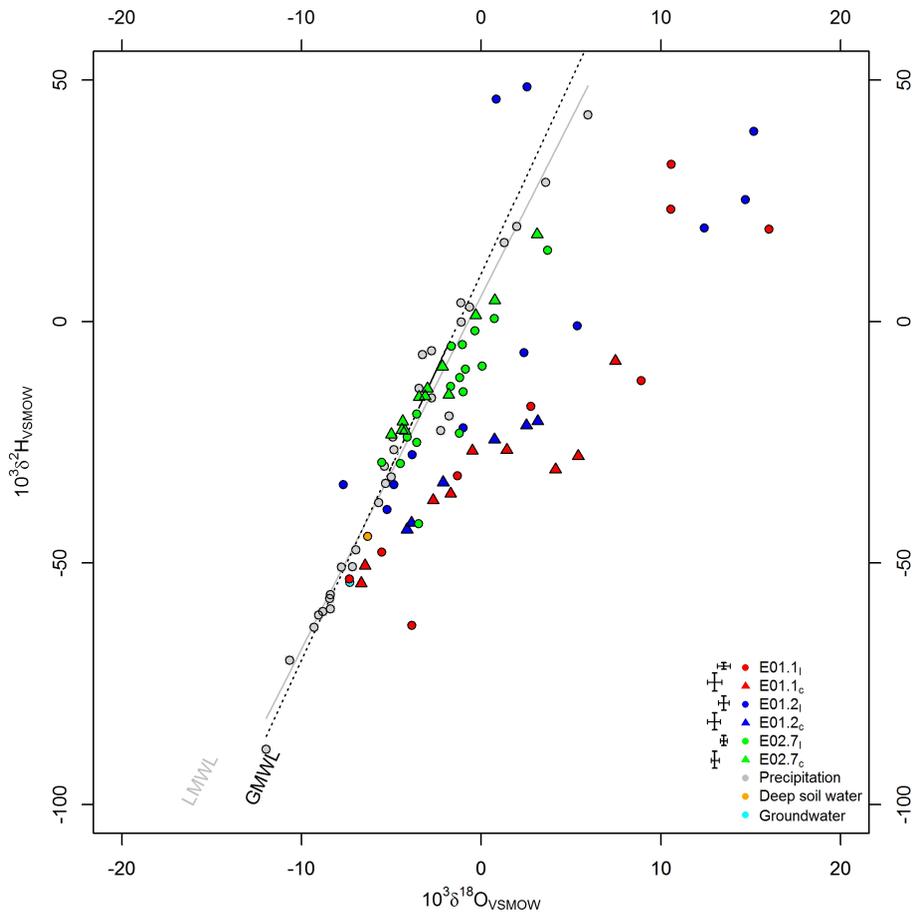


Figure 5. $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ plot of the profiles E01.1, E01.2, E02.7. Also shown is the LMWL for the northern part of Namibia as well as groundwater and soil water down to a depth of 4 m.

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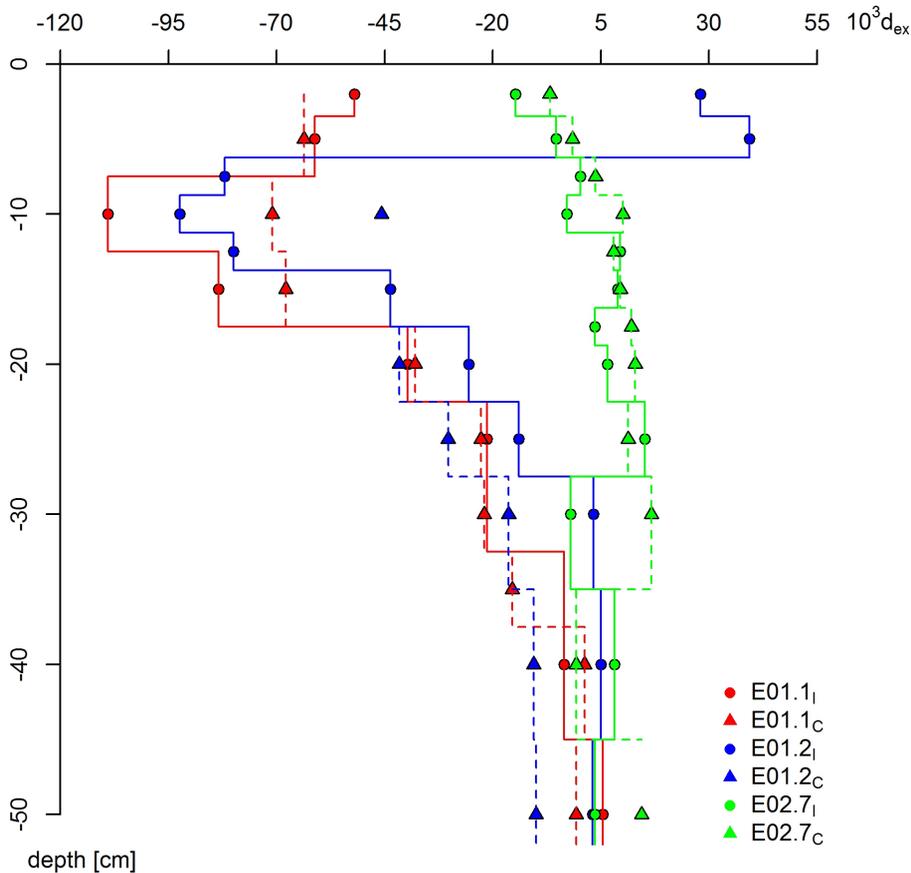


Figure 6. Deuterium excess for the profiles E01.1, E01.2 sampled in June 2014 and E02.7 sampled in November 2014. Compared are values from the cryogenic vacuum extraction (triangles) and the in-situ measurements (circles).

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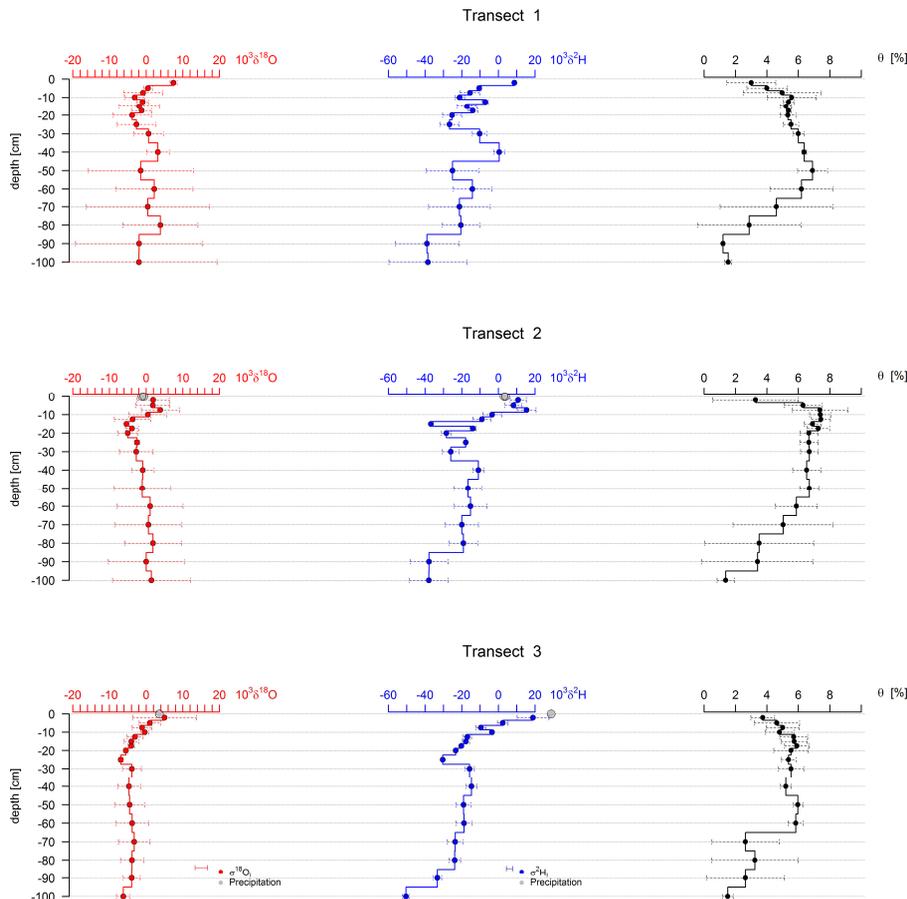


Figure 7. ^{18}O (red), ^2H (blue) and soil moisture (black) depth profiles. Shown are mean values for three transects consisting of three single profiles derived from in-situ measurements. Mean standard deviation σ of all quality check standards (qc) are shown in the legend. Rainfall isotope values are indicated on the x axes in grey.