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Hydrogeochemical and isotope study of perched aquifers in the Cuvelai-Etosha Basin, Namibia

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\textbf{ABSTRACT}

A hydrogeochemical and stable isotope study (\textsuperscript{2}H and \textsuperscript{18}O) was carried out in the Cuvelai-Etosha Basin in order to characterize available groundwater and to identify possible recharge mechanisms for the perched aquifers. Data were collected during seven field campaigns between 2013 and 2015 from a total of 24 shallow and deep groundwater hand-dug wells. In the investigated groundwaters, hydrogen carbonate is the dominating anion in both well types, whereas cations vary between calcium and magnesium in deep wells, and sodium and potassium in shallow wells. Groundwater chemistry is controlled by dissolution of carbonate minerals, silicate weathering and ion exchange. Stable isotopic composition suggests that deep groundwater is recharged by high-intensity/large rainfall events, whereas the shallow wells can even be recharged by less-intense/small rainfall events. Water in deep wells reflect a mixture of water influenced by evaporation during or before infiltration and water that infiltrated through fast preferential pathways, whereas shallow wells are strongly influenced by evaporation. The findings of this research contribute to improve the understanding of hydrogeochemistry, recharge paths and temporal variations of perched aquifers.

\textbf{1. Introduction}

Groundwater is the main water source for most communities in semi-arid regions \cite{1,2}. For effective planning, management and utilization of the groundwater resources addressing water supply sustainability and water quality, a comprehensive understanding of the groundwater system through integrated hydrogeological investigations is obligatory \cite{3}. The Cuvelai-Etosha Basin (CEB) located in northern central Namibia (Figure 1) is home to approximately 40\% of the Namibian population; more than 80\% of this population live in rural areas where they depend on groundwater for drinking water and livestock watering \cite{4}. Groundwater in this region occurs in both deep and perched aquifers. Freeze and Cherry \cite{5} and Fetter \cite{6} defined perched aquifers as bodies of groundwater (a saturated zone) that is unconfined and open to the overlying unsaturated zone but is

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separated from an underlying main body of groundwater by an unsaturated zone. In other words, perched aquifers occur as discontinuous small water bodies trapped by impermeable layers within the unsaturated zone. In the CEB, these perched aquifers are tapped by traditional hand-dug wells, which are owned and managed by individual families, and thus, each village might have more than 10 wells in one well-field. Normally these hand-dug wells are unprotected and not covered, and therefore, contaminants including animal faeces are washed from the surface and migrate to the wells, making the wells highly vulnerable to pollution [7]. Consequently, having several open wells not only promotes over-exploitation of groundwater resources on a local scale, but also increases the risk of groundwater contamination. High population density, rapidly growing population and lack of infrastructure in rural areas add further pressure on the limited groundwater resources. In recent years, the German Federal Institute for Geosciences and Natural Resources (BGR) has carried out extensive research on groundwater in the study area; however, their focus concentrates on the exploration and utilization of deep aquifers [8]. For the perched aquifers it was found that the water quality in these wells is inappropriate for human consumption due to high amounts of fluoride, nitrate, sulphate and total dissolved solids (TDS) [9,10]. Additionally, perched aquifers are susceptible to contamination not only because of their shallow water level, but also because of improper well designs [7]. Recharge rates estimated in the study area are higher than 100 mm/a in some areas [11], which was described as exceptional for specific sites and hence cannot be up scaled to the CEB [10]. Beyer et al. [12,13] estimated recharge rates of 0 and 29 mm/a using a peak displacement technique for two subsequent years. Gaj et al. [14]
calculated a soil water balance using unsaturated zone water stable isotopes and estimated recharge rates between 4 and 5 mm/a. It was further shown that transpiration is responsible for most of the depletion in soil water storage [14]. However, hydrochemical processes and recharge mechanisms of perched aquifers are not yet understood and to the authors’ knowledge have not been investigated thoroughly. Consequently, little is known about the perched aquifer in the CEB, though its temporal and spatial evolution can be related to direct infiltration of rainfall [8].

Tracer methods and isotope tracers in particular have been extensively used in hydrogeology. For determining groundwater age often radioactive isotopes are applied (e.g. tritium or carbon-14), whereas stable isotopes (e.g. carbon-13, nitrogen-15) are powerful parameters to decipher biogeochemical processes or problems concerning pollution of groundwater. Methods based on stable isotopes and hydrochemical techniques have been used in hydrogeological studies around the globe to provide substantial information about groundwater origin [15,16], recharge mechanisms [17,18], biogeochemical processes in groundwater [19], water flow directions [20,21], residence time distributions of groundwater [22], salinization of aquifers [23,24], intermixing of aquifers [25], the nature of the aquifer through which the water has circulated [26,27], as well as anthropogenic influences affecting the groundwater system [28]. Generally, the understanding of geochemical processes and recharge mechanisms often leads to an understanding of groundwater quality and quantity and can potentially initiate valuable predictions such as presented in [29]. This study is focusing on the perched aquifers in the CEB, which are of crucial importance for local communities but hydrogeology and hydrology are poorly understood. The aim of this study is to characterize the groundwater chemistry and isotopic composition of oxygen ($\delta^{18}$O) and hydrogen ($\delta^{2}$H) to understand mechanisms of groundwater dynamics and quality of groundwater. A particular focus is given on origin of groundwater in perched aquifers and a potential evaluation of recharge processes.

2. Study site

The CEB is the Namibian part of the Cuvelai catchment (Figure 1), which is a vast sedimentary basin extending from the southern Angola highlands into northern central Namibia covering 165,000 km$^2$ [4,30]. Perennial tributaries within the Cuvelai catchment are limited to the Angolan part, whereas tributaries (locally known as lishana) in Namibia are generally ephemeral [31]. The topographic gradient is extremely low, with elevation ranging between 1092 and 1110 metres above sea level (m a.s.l.) [31]. All drainage is directed towards the saline Etosha pan, which is the lowest point in the basin. The majority of the population in the basin lives in rural areas and uses groundwater wells that tap both shallow and deep aquifers. The CEB climate is characterized as semi-arid with low annual rainfall ranging from 250 mm in the west and up to 550 mm in the east [4]. Mean annual temperatures range from 17 °C in June and July to 25 °C from October to December [4]. The mean potential evaporation rate can be as high as 3000 mm/a, which is five times higher than the precipitation [31]. The rainy season lasts from November to April; however, the amount and distribution of rain are quite variable [32]. The CEB is divided into four major sub-basins called lishana, Niipele, Olushandja and Tsumeb. In this study, core sites were chosen in the Niipele sub-basin, in the proximity of Okongo town (Figure 1).
The hydrogeological system in the study area is called Ohangwena multi-layered aquifer system. This system is made up of three major hydrogeological units that are contained within the unconsolidated to semi-consolidated sediments of the Andoni and Olu-konda Formations [14,33]:

(i) The upper aquifer is the discontinuous shallow perched aquifer (KOH-0) characterized by well-sorted, fine- to medium-grained sands with minor silt. It occurs within the unsaturated zone as small water body trapped by an impermeable base above the regional water table. The thickness of the aquifer ranges between 1 and 40 m.

(ii) The subsequent aquifer is the regional Ohangwena I aquifer (KOH-I). It is characterized by fine-grained sands with varying silt and clay contents. The aquifer lies between 60 and 160 m b.g.l.

(iii) The deep-seated aquifer is the recently discovered Ohangwena II aquifer (KOH-II), occurring at the depth of 250–350 m b.g.l and is made up of well-sorted, fine-grained sands, mixed with calcrites, silicretes and dolocretes.

This study pays particular attention to the perched aquifers. In the CEB, the perched aquifers are widely present underneath pans and depressions. Pans are geomorphological features that appear as shallow sub-circular to sub-elliptical isolated depressions; they are predominantly associated with crescent dunes which can rise to a height of 30–40 m above the pan floor [34]. Depressions have physical properties similar to those of pans, but lack crescent dunes in their proximity. Burrough et al. [35] and Nash and McLaren [36] argued that even though pans have a similar morphology as some landforms that occur in temperate regions, for example, karst depressions or permanent lake systems, they are characteristic for dry land because of the set of processes that are involved in their formation. Bowler [37] suggested that pans can serve as either discharge or recharge point, depending on the present hydrologic dynamics and their soil hydraulic properties. Moreover, their ground surface may be covered or partly covered by grass, bare clay and/ or calcrite with few shrubs mainly from the acacia species, while the dunes are covered by thick forest.

These perched aquifers are tapped mainly by two types of hand-dug wells; the shallow wells, locally known as ‘Omifima’ (funnel-shaped hand-dug wells) and the deep wells known as ‘Eendungu’ (cylindrical-shaped hand-dug wells). The shallow hand-dug wells have a water table ranging from the topographic surface to a depth of maximum 5 m b.g.l. In contrast, the deep hand-dug wells have depths of water levels ranging between 5 and 30 m b.g.l. The deep wells are equipped with rope and bucket, which are used to abstract water from the aquifer. Whereas the deep wells are mainly found in areas where a distinct impermeable caliche layer close to the soil surface is present, the shallow wells are mainly concentrated in areas with deep sheet sands. The terms ‘shallow wells’ and ‘deep wells’ will be used in the subsequent sections for differentiating the type of wells in this paper.

3. Sampling and methods

Water samples were collected from 24 hand-dug wells, of which 10 are shallow and 14 are deep wells. Seven sampling campaigns were carried out with the first in November
2013, followed by campaigns in March, June and September in 2014 and in March, June and August in 2015. Some wells were not sampled at all times because they were not in use and dry during the particular field campaign; thus sampling would have been unrepresentative. The rainy season data were collected during March; June campaigns denote after rainy season data. In addition, samples collected in August/September represent the dry season. Samples from November comprise dry/beginning of rainy season data. In the field, the physical parameters pH, electrical conductivity (EC), redox potential (Redox), oxygen content ($O_2$) and temperature ($T$) were measured with Hach field portable instruments (HQ 11d pH meter, HQ 14d conductivity meter, HQ 40d multimeter). The water level was measured with an electrical contact gauge. Three samples were taken at each well: a 100 ml polypropylene bottle for cations, a 500 ml polypropylene bottle for anions and a 50 ml glass bottle for stable isotopes. The glass bottle for stable isotopes was carefully sealed to prevent evaporation during transport. The cation samples were filtered through 0.45-µm filters and subsequently preserved with nitric acid, whereas anion samples were kept cool using a cooler box and refrigerator until analysed in the laboratory. Rain samples were collected as monthly cumulative rain samples at collectors in Okongo and Eenhana. Occasionally, event samples were collected for isotope analysis.

Chemical analyses were performed at the Analytical Laboratory Services in Windhoek, Namibia, and at the hydrochemistry laboratory of BGR in Hanover, Germany. The methods used at each laboratory are summarized in Table 1. The reliability of the analyses was checked by an ion charge balance error on all 98 samples. A total of 51 samples were within 5 % error while the rest were above; however, it was observed that mainly samples from the shallow wells were having high errors as a result of high total organic compounds (TOC) in samples. TOC was measured for numerous samples and explains the relative high ion charge balance error. TOC reflect anion behaviour but is not considered as anion during measurements, which results in lower anion concentrations in comparison to cation concentrations. Therefore, all samples were used to characterize water types despite some having a charge balance error above 5 %.

Stable isotopes were measured at the University of Namibia (UNAM) and BGR laboratories using an off-axis integrated cavity output spectrooscope (OA-ICOS, Los Gatos DLT-100) and a cavity ring down spectrometer (CRDS, model L2120-i, Picarro Inc.), respectively. All values are given as δ-values in per mil (‰) against the international standard Vienna

<table>
<thead>
<tr>
<th>Table 1. Analytical methods used for analyses of major ions.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group</strong></td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>Anions</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Cations</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Standard Mean Ocean Water (V-SMOW, normalized to V-SMOW/SLAP scale) as defined by Equation (1):

\[
\delta = \left[ \frac{R_{\text{SA}}}{R_{\text{ST}}} - 1 \right] \times 1000, \tag{1}
\]

where \(R_{\text{SA}}\) denotes the isotope ratio of \(^2\text{H}/\text{H}\) or \(^{18}\text{O}/^{16}\text{O}\) of the sample and \(R_{\text{ST}}\) of the standard, respectively. Analytical errors of a quality check sample measured within each run are better than 0.20 \(\%\) for \(\delta^{18}\text{O}\) and 0.8 \(\%\) for \(\delta^{2}\text{H}\) measurements.

4. Results and discussion

4.1. Physico-chemical parameters

The physical and chemical parameters of 98 groundwater samples measured in the field are summarized in Table 2. The temperature of the collected groundwater samples ranges between 15 and 36 °C with lowest temperatures recorded during mornings in winter while summer afternoons displayed the highest temperatures. The average temperature is 25 °C, which is close to the mean annual air temperature of the study area. Low temperatures during mornings in winter and high temperatures during summer afternoons reflect a direct relationship between groundwater and air temperature. The EC values indicate that the deep wells are highly mineralized in comparison to shallow wells with EC values ranging from 489 to 1199 µS/cm and 52 to 296 µS/cm respectively (Table 2). The TDS were calculated from EC; thus they show the same trend as EC, higher in deep wells than in shallow wells. No temporal variation could be established; each well has similar values in all the campaigns. The mean pH is 7.1 for shallow wells and 7.6 for deep wells; however, they both range from slightly acidic to slightly basic. Values for both TDS and pH are within drinking water threshold of the world health organization (WHO) guideline [38]. The shallow wells are highly turbid with values ranging from 27 to 255 Nephelometric Turbidity Units (NTU) indicating the presence of many undissolved particles in the water. Deep wells have a lower turbidity ranging between 1 and 20 NTU (Table 2). According to the Namibian water cooperation guidelines (NAMWATER) [39], turbidity should not be higher than 10 NTU in drinking water and all the shallow wells have turbidity values above 10 NTU and thus classifying them as not suitable for human consumption.

Table 2. Minimum, mean and maximum values for the physio-chemical parameters at all the sampling sites.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Shallow wells ((n = 43))</th>
<th>Deep wells ((n = 55))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
</tr>
<tr>
<td>Water level (m)</td>
<td>0.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>15.0</td>
<td>36.0</td>
</tr>
<tr>
<td>(\text{O}_2) (mg/l)</td>
<td>4.2</td>
<td>20.0</td>
</tr>
<tr>
<td>Redox potential (mV)</td>
<td>29.0</td>
<td>177.0</td>
</tr>
<tr>
<td>pH</td>
<td>4.8</td>
<td>10.0</td>
</tr>
<tr>
<td>EC (µS/cm)</td>
<td>52</td>
<td>296</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>27</td>
<td>255</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>35</td>
<td>198</td>
</tr>
</tbody>
</table>
4.2. Major ion geochemistry

4.2.1. Deep wells
Ca\(^{2+}\) is the dominant cation in deep wells, with 64.3\% of the samples being Ca\(^{2+}\)-rich water while the remaining 35.7\% either have no dominant cation or are Na\(^{+}\)-dominated. The concentration of the alkaline earth Ca\(^{2+}\) and Mg\(^{2+}\) ions range from 6.2 to 117.7 mg/l and 9.5 to 41.0 mg/l with a mean of 68.6 and 24.8 mg/l, respectively (Figure 2). Concentration of the alkali ions (Na\(^{+}\) and K\(^{+}\)) ranges from 0.7 to 75.0 mg/l and 2.7 to 114.0 mg/l with a mean value of 29.7 and 25.9 mg/l, respectively. The dominant anion in all deep wells is HCO\(_3\)^\(-\), which has concentrations ranging from 223 to 783 mg/l with a mean of 326.7 mg/l. Concentrations of the anions Cl\(^-\), F\(^-\), SO\(_4\)^{2-} and NO\(_3\)^- range from 0.7 to 25.1 mg/l, 0.3 to 4.5 mg/l, 1.0 to 6.7 mg/l and 0.1 to 296 mg/l, respectively, with mean values of 7.4, 1.9, 3.4 and 64.7 mg/l, respectively. Therefore the abundance of major ions in deep wells can be grouped in the order Ca\(^{2+}\) > Mg\(^{2+}\) > Na\(^{+}\) > K\(^{+}\) for cations and HCO\(_3\)^\(-\) > NO\(_3\)^- > Cl\(^-\) > SO\(_4\)^{2-} > F\(^-\) for anions. Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\), Cl\(^-\), SO\(_4\)^{2-} concentrations fall within the WHO limits of 200, 100, 100, 1000 and 400 mg/l, respectively; however, a number of samples for K\(^{+}\), NO\(_3\)^- and F\(^-\) show concentrations above permissible limits of 10, 50 and 1.5 mg/l, respectively, as recommended by WHO [38] (Figure 2).

4.2.2. Shallow wells
Shallow wells are dominated by the alkali ions Na\(^{+}\) and K\(^{+}\) with concentrations ranging from 0.8 to 39 mg/l and 2 to 30 mg/l with mean values of 14 and 11.3 mg/l, respectively (Figure 2). The alkaline earth Ca\(^{2+}\) and Mg\(^{2+}\) have concentrations between 0.9 and

[Figure 2. Boxplot showing maximum, minimum and median values of cation and anion of deep wells (in open colour) and shallow wells (in grey colour). The box outlines the interval between the 25th and 75th percentiles. Circles indicate outliers. The black diamond symbol indicates the WHO guideline values.]
16.8 mg/l and 0.5 and 4.6 mg/l with mean values of 7.7 and 2.5 mg/l, respectively. HCO$_3^-$ is the dominant anion in 65% of the samples while the remainder percentage is water dominated by Cl$^-$ and SO$_4^{2-}$. Concentrations of all anions range from 1.8 to 90.3 mg/l for HCO$_3^-$, 0.8 to 28.0 mg/l for Cl$^-$, 0.01 to 0.6 mg/l for F$^-$, 0 to 50 mg/l for SO$_4^{2-}$ and 0.5 to 46.3 mg/l for NO$_3^-$ with mean values of 35.8, 8.3, 0.2, 12.4 and 8.7 mg/l, respectively. The abundance of major ions in shallow wells is in the order of Na$^+$ > Ca$^{2+}$ > K$^+$ > Mg$^{2+}$ for cations and HCO$_3^-$ > NO$_3^-$ > SO$_4^{2-}$ > Cl$^-$ > F$^-$ for anions. All cations and anions concentrations are within permissible WHO limits, with an exception of K$^+$, which is above the limit in 50% of the samples (Figure 2).

4.2.3. Geochemical processes in groundwater

In Figures 3 and 4, a Piper diagram [40] and a Gibbs plot [41] are illustrated. Subsequently, the ionic relationships of major ions are discussed in regard to hydrochemical evolution and grouping. Piper diagrams are widely used in order to interpret the chemistry of water samples and to identify different water types [40]. Gibbs plots enable an assessment of precipitation, rock weathering and evaporation effects on the geochemical evolution of groundwater in semi-arid and arid areas [41]. Since the wells were sampled multiple times and no strong temporal difference was found (indicated by TDS values; Figure 5), average values for each well were used. The Piper diagram (Figure 3) suggests two water types in the deep wells; Ca$^{2+}$-Mg$^{2+}$-HCO$_3^-$ and Na$^+$-K$^+$-HCO$_3^-$, with Ca$^{2+}$-Mg$^{2+}$-HCO$_3^-$ being the dominant type. Shallow wells are characterized by three water types; the mixed water type with neither a dominant cation nor anion, Na$^+$-K$^+$-HCO$_3^-$ and Ca$^{2+}$-Mg$^{2+}$-HCO$_3^-$ water types. Ca$^{2+}$-Mg$^{2+}$-HCO$_3^-$ water type indicates that groundwater is formed in carbonate-rich rocks or derived from an active recharge zone with short residence times [42]. Therefore it can be argued that the Ca$^{2+}$-Mg$^{2+}$-HCO$_3^-$ water type in deep wells is a

Figure 3. Piper plot showing hydrogeochemical facies in meq/l.
result of dissolution of calcrete, which is outcropping in some areas of the pans, as well as weathering of the silicate minerals. Most deep wells are located in depressions and pans characterized by layers of calcrete embedded into unconsolidated sands. Higher EC in deep wells can be interpreted as a result of longer residence times in deep groundwater than in the shallow groundwater. Obiefuna and Orazulike [43] state that evaporation increases the concentration of ions in the remaining water and leads to precipitation and deposition of evaporates. Therefore, the data tend to suggest that evaporation processes are responsible for the observed geochemical composition in the CEB especially in the shallow wells. Furthermore, a widely accepted view is that in semi-arid regions, low rainfall and high evaporation rate cause evaporates to be leached into the saturated zone and this reduces dilution effects on groundwater. Conversely, Na\(^+\)–K\(^+\)–HCO\(_3\)\(^-\) demonstrates that groundwater formed in formations where alkali carbonates are present. The mixed water, where no particular water type could be identified, indicates cation exchange as the main process responsible for the groundwater chemistry.

The relationship of different ions was further used to distinguish between different geochemical processes that control groundwater chemistry. In carbonate rocks, dissolution is both the simplest and most common weathering reaction which is specified by a 1:2 ratio of Ca\(^{2+}\)/HCO\(_3\)\(^-\) [44]. The plots of Ca\(^{2+}\) vs. HCO\(_3\)\(^-\) (Figure 6(a) and (b)) point out that a majority of the shallow well samples plot near the 1:4 and 1:2 lines while samples from deep wells are scattered without a particular trend; however, all plot above the 1:2 regression. Plotting of Ca\(^{2+}\) + Mg\(^{2+}\) vs. HCO\(_3\)\(^-\) + SO\(_4\)\(^2-\) (Figure 6(c) and (d)) was used to indicate where these ions derived from. When data points plot along the 1:1 line, samples are influenced by
carbonate dissolution and weathering while data points shifting away from this line indicate either one of these process as dominant. Excess $\text{HCO}_3^- + \text{SO}_4^{2-}$ over $\text{Ca}^{2+} + \text{Mg}^{2+}$ in the groundwater suggests weathering of Ca–Mg-bearing minerals such as calcite and plagioclase feldspars, while excess $\text{Ca}^{2+} + \text{Mg}^{2+}$ indicates reverse ion exchange process [45,46].

The ionic exchange between $\text{Ca}^{2+}$ and $\text{Na}^+$ is explained by the following adsorption equation [44]:

$$[0.5\text{Ca}^{2+} - \text{Adsorber}_2] + \text{Na}^+ \leftrightarrow 0.5\text{Ca}^{2+} + [\text{Na} - \text{Adsorber}].$$

During ion exchange, there is excess $\text{HCO}_3^- + \text{SO}_4^{2-}$; therefore $\text{Ca}^{2+}$ is desorbed from the absorber and released into solution whilst $\text{Na}^+$ is adsorbed. During carbonate dissolution, there is an excess of $\text{Ca}^{2+} + \text{Mg}^{2+}$; therefore $\text{Ca}^{2+}$ is adsorbed while $\text{Na}^+$ is released into solution. In this study, shallow wells are clustered around the 1:2 line, while deep wells are

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**Figure 5.** Temporal variations of TDS in 10 of the sampled wells: (a) deep wells and (b) shallow wells.
Figure 6. Plots of ionic relationships to explain geochemical reactions. (a) and (b) Ca\(^{2+}\)/HCO\(_3^-\) plots, (c) and (d) Ca\(^{2+}\)+Mg\(^{2+}\)/HCO\(_3^-\)+SO\(_4^{2-}\) plots, and (e) and (f) Na\(^+\)+K\(^+\)–Cl\(^-\) vs. Ca\(^{2+}\)+Mg\(^{2+}\) and HCO\(_3^-\), respectively.
divided into two subgroups; one group plots along the 1:4 regression line while the other group plots around the 1:2 line. The two groups also correlate to differences in the depth to water table: all samples in the first group have a depth to water table of greater than 17 m b.g.l. and the second group reflects depths to water table shallower than 17 m b.g.l. Shallow wells are characterized by a high amount of Na\(^+\) (0.8–39 mg/l) and high amounts of HCO\(_3^-\) (1.8–90.3 mg/l). To determine whether this composition is a result of silicate weathering or cation ion exchange, Jahnke plots [47] were used. Jahnke [47] compared alkali excess over chloride (calculated as Na\(^+\) + K\(^+\) – Cl\(^-\)), to HCO\(_3^-\) and alkaline–earth metals (Ca\(^{2+}\) + Mg\(^{2+}\)). During cation exchange, Ca\(^{2+}\) + Mg\(^{2+}\) decreases at a 1:1 ratio while HCO\(_3^-\) remains uninfluenced compared to Na\(^+\) + K\(^+\) – Cl\(^-\). In contrast, Ca\(^{2+}\) + Mg\(^{2+}\) remains uninfluenced while HCO\(_3^-\) content increases at a 1:1 ratio compared to Na\(^+\) + K\(^+\) – Cl\(^-\) during silicate weathering. The Jahnke plots for the shallow wells have very low \(R^2\) (0.55 and 0.34), which shows that both processes are playing a major role in controlling the groundwater chemistry (Figure 6(e) and (f)). In a Gibbs plot (Figure 4), samples from shallow wells plot in the area of evaporation of rainfall, deep wells plot in two groups; one group with a low ratio of Na\(^+\) + K\(^+\) to Na\(^+\) + K\(^+\) + Ca\(^{2+}\) plots in the field of rock dominance, while the second group plots towards evaporation dominance.

### 4.3. Isotopic composition of oxygen (δ\(^{18}\)O) and hydrogen (δ\(^2\)H)

The isotopic composition of oxygen and hydrogen in shallow well water ranges from −6.95 to 0.86 ‰ and −49.1 to −7.6 ‰ for δ\(^{18}\)O and δ\(^2\)H, respectively. For deep wells, δ\(^{18}\)O values vary between −9.00 and −1.30 ‰ and for δ\(^2\)H between −61.5 and −22.1 ‰ (Table 3). Deuterium excess \(d\) varies between −16 and 11 ‰ for shallow wells and between 3 and 14 ‰ for deep wells. One deep well in Ongalangobe village was identified as an outlier and exhibits the lowest and highest \(d\)-excess values of −12 and 15 ‰, respectively. All groundwater samples are compiled in δ\(^2\)H vs. δ\(^{18}\)O space and plotted against the global meteoric water line (GMWL) as well as the local meteoric water line (LMWL) for the CEB (Figure 7). The CEB LMWL has a slope of 7.2 and an intercept of +4.4 (δ\(^2\)H = 7.2 δ\(^{18}\)O + 4.4; \(R^2 = 0.99\)) and was developed from rainfall data collected within SASSCAL between 2013 and 2015 and historic data compiled by Turewicz [48]. Most groundwater samples, particularly those from deep wells plot close to the LMWL (Figure 7), and this indicates that they originated from modern precipitation infiltration. The isotopic variations may be attributed to local climate factors [49,50].

All collected groundwater samples plot below both the LMWL and the GMWL; hence, they reflect a relative enrichment of heavier isotopes (Figure 7). The samples collected from shallow wells follow a regression line of \(\delta^2\)H = 4.66 δ\(^{18}\)O – 14.65; \(R^2 = 0.94\). Samples from deep wells plot on a regression line with an equation of \(\delta^2\)H = 6.01δ\(^{18}\)O + 7.88; \(R^2 = 0.93\). The intersection of the evaporation line with the GMWL or LMWL identifies the mean isotopic composition of the parent rainwater [51]. For the sampled locations, the two regression lines intersect with the LMWL at different points: (−7.48 ‰, −44.5 ‰) for shallow wells and (−10.31 ‰, −69.8 ‰) for deep wells. This shows that the parent water is different. The shallow aquifers are recharged by rainfall with lighter isotopic signature. This means even small/lighter rain events can replenish them. On the contrary, the regression line of deeper wells crosses the LMWL at a much lower point (−10.3 ‰, −69.8 ‰), indicating that only high amount of rain or intense
Table 3. Minimum, mean and maximum values for isotopes (in ‰ VSMOW) for all the sampling sites.

<table>
<thead>
<tr>
<th>Sample location</th>
<th>Well type</th>
<th>Minimum</th>
<th>Mean</th>
<th>Maximum</th>
<th>d-Excess</th>
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Notes: DW: deep well (14); SHW: shallow well (10).
rain events can recharge this aquifer. Samples from shallow wells plot further away from
parent water than those from deep wells. Moreover, shallow wells and rain events show
the same signature range of $\delta^{2}H$ and $\delta^{18}O$ which is highly enriched, and this is a sign
of water exchange and implies direct recharge for the shallow wells. However, highly
enriched isotope values might also indicate that shallow wells are influenced by evapor-
ation in comparison to deep wells. It should be noted, however, that the annual rainfall
is higher in the area with deep wells (500 mm) compared to the area with shallow wells
(450 mm). This might further influence the actual groundwater recharge rates, which
are also reflected by higher chloride concentrations (average 8.3 mg/l) in the area with
the shallow wells.

Under relative low humidity and semi-arid conditions, the slope of evaporation from an
open water body is characterized by 4.5–5 indicating evaporation as a major process.
Therefore, the observed slope of 4.6 in shallow wells indicates evaporation before or
during infiltration. The slope of 6.0 falls between a slope of evaporation of 4.6 and that
of the LMWL of 7.2. This indicates mixing of water influenced by evaporation and water
that infiltrates fast or along preferential paths through fractures and cracks in the calcrete
layers coinciding with observations during the field campaigns. Fractures and cracks cause
an increase of effective porosity and allow direct infiltration during high-intensity rainfall.
Large differences in $\delta^{18}O$ are observed in shallow wells rather than in deep wells (Figure 8).
However, there was no trend in the variation between the isotopic composition of

Figure 7. $\delta^{2}H$ vs. $\delta^{18}O$ plot including GMWL and LMWL and regression lines.
groundwater samples collected during the rainy and dry seasons. This point towards a lack of seasonal variation in isotopic composition of the parent water and also that processes after the rainy season are not influencing the isotopic composition of groundwater.

5. Conclusion

The study aimed to characterize the groundwater geochemistry and to understand recharge mechanisms of the perched aquifers using major ion chemistry and the stable water isotopes $\delta^{18}O$ and $^2H$. According to WHO recommendations, the water quality in most wells is (theoretically) not permissible for drinking and domestic purposes because of high turbidity, potassium, fluoride and nitrate values, which are above the accepted values for drinking water. This study shows that depth to water table plays a major role in groundwater chemistry and isotope hydrogeology of the perched aquifers as a clear
distinction can be made between the shallow and deep wells in the CEB. The deep wells are characterized by two water types – predominantly Ca\(^{2+}\)-Mg\(^{2+}\)-HCO\(_3^-\) and Na\(^+\)-K\(^+\)-HCO\(_3^-\), whereas shallow wells have three major groups; Na\(^+\)-K\(^+\)-HCO\(_3^-\), Ca\(^{2+}\)-Mg\(^{2+}\)-HCO\(_3^-\) and the mixed water type. Dissolution of carbonate minerals such as calcite and dolomite and silicate weathering and cation exchange are the dominant geochemical processes affecting the groundwater chemistry. The isotopic composition of the deep wells suggests distinguishing between two distinct recharge processes: (i) water that is affected by evaporation either before or after infiltration and (ii) water that infiltrates through fast preferential paths. The shallow well isotopic composition indicates evaporation. These isotopic compositions imply that groundwater is recharged under climatic conditions similar to the modern climate as they plot close to rainfall. It can also be concluded that deep groundwater must be recharged by high-intensity or large rainfall events while the shallow wells might also be recharged by lighter rainfall events. No temporal variation of the groundwater isotopic composition was identified. For a clear characterization of groundwater flow and recharge areas, it is necessary to further investigate spatial distribution and temporal variations of both groundwater chemistry and isotopic composition (both shallow and deep wells). Use of other tracers such as \(^3\)H and \(^14\)C would help us to determine ages of young and old groundwater but were not available for this work.

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