

Article

Groundwater Recharge and Circulation in Dolomitic Aquifer Located in Semi-Arid Region: Evidence from the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ Record, South Africa

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Abstract: Dolomitic aquifers are regarded as important groundwater storage sites in South Africa. Since these aquifers occur in a semi-arid climatic setting with low rainfall, often characterized by a torrential downpour and high potential evapotranspiration, the occurrence of active recharge is very limited (<5% of mean annual rainfall) as compared with the rainfall amount. The Malmani dolomites that have undergone greenschist metamorphism contain widespread caves and open karst structures at shallow levels, which facilitate groundwater recharge, circulation, storage and spring occurrence. However, the open karst structures receive recharge that passes through fractures in the vadose zone, which regulates the recharge through retardation and mixing processes. The integrated approach involving major ions and stable isotopes of water was applied to understand the recharge mechanism. The cave drip water samples were represented by the $\delta^{18}\text{O}$ values of -3.95‰ to 3.32‰ and the $\delta^2\text{H}$ values ranging from -11.0‰ to 27.7‰ . On the other hand, the rainfall isotope results for $\delta^{18}\text{O}$ fall between -16.11‰ and 5.38‰ , while the $\delta^2\text{H}$ values fall between -105.7‰ and 35.6‰ . The most depleted Malapa springs contain $\delta^{18}\text{O}$ of -5.64‰ and $\delta^2\text{H}$ of -32.4‰ . Based on the results, the mixing of water in the vadose zone could be considered as an indicator of the dominance of a slow-diffusive flow process in the aquifer as a result of poor fracture permeability. However, regional groundwater circulation through faults and dykes besides interconnected karst structures helps in generating highly productive karst springs in the region characterized by low rainfall.

Keywords: dolomitic aquifers; diffusive flow; cave drip water; microstructures; Johannesburg



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1. Introduction

In the Republic of South Africa, groundwater is an important resource that has rescued the country during several drought years in the 1980s and recently in 2015 and 2016 (due to El Niño), as well as its dominance in the agricultural sector with over 80% of irrigation water contribution [1]. Whenever there is a shortage of municipal water supply, groundwater is the prominent and reliable source both in urban and rural areas. It is obvious that in order to utilize groundwater, aquifers have to be sustained with active recharge owing to the presence of favorable media for recharged water to circulate with ease. The Johannesburg region receives an average rainfall of about 710 mm/year, which falls sporadically between October and March [2], and the region has high potential evapotranspiration of 1600 mm/year [3] which does not guarantee substantial recharge to the crystalline aquifers [4].

One of the environmental factors with an immediate impact on humans is climatic variability that affects the water supply sector. Slight changes in rainfall and temperature can be felt by humans and the economic sector; hence, competition for the available water resources could be intensified. This is where groundwater from dolomitic aquifers plays a significant role in supplementing the current water supply. There were various efforts by the Department of Water and Sanitation to systematically document and manage aquifers across the country, which recognized the dolomitic aquifers as one of the national

groundwater reservoirs [5,6]. As a result of an increase in water demand due to rapid population growth, the expansion of the industrial, agricultural and mining sectors and high levels of water pollution, South Africa has difficulty in attaining water security for its population and economic sector, which is aggravated due to its location in the arid and semi-arid climatic setting that provides low groundwater recharge. Recently, the impact of untreated municipal wastewater disposal in the water supply dam resulted in the cholera outbreak that claimed over 47 lives in the Hammaskraal and Parys towns, South Africa [7], which was attributed to poorly treated water at the water supply treatment plant.

Groundwater recharge from rainfall and surface water sources could take place either directly or indirectly, which is an important process for the renewability of scarce water resources. This can be conducted through a comparison of stable isotope records with global and local meteoric water lines [8,9]. For rainfall to reach the zone of saturation, it must be facilitated by the hydraulic parameters including porosity, hydraulic conductivity and transmissivity that regulate the recharging water and mixing process. The variability in the hydraulic characteristics could affect the effective rainfall to pass through the vadose zone and reach the aquifer, hencecausing the mixing of stable isotopes during the circulation process [2].

The spatial and temporal isotope variability in rainfall is influenced by the stable isotope effects, which are a function of the climate (temperature, humidity and amount of rainfall) and physical characteristics (elevation, distance from ocean, rainfall moisture sources and temperature) [8]. This affects the stable isotope composition of rainfall that eventually recharges the aquifers.

In line with this challenge, the main objective of the current work was to investigate the role of the vadose zone and understand if rainfall is transferred directly to the water table or delayed based on the fracture network. Often, the groundwater flow in a karst structure is complex that varies from advective flow in an open structure to diffusive flow in microstructures. Since dolomites are declared as strategic aquifers in the country, it is important to look at the renewability of the system because water users are taping historic storage, which will help to guide the groundwater management system. If karst systems are directly open to the atmosphere and receive recharge from rainfall, advective flow is expected to take place. However, it is essential to know how permeable the system is for groundwater to appear as a big spring. With a major focus on the West Rand region, which is situated west of Johannesburg, the current work tries to understand the groundwater recharge characteristics based on an integrated approach that involves physicochemical parameters, major ions and stable isotopes of water (^{18}O and ^2H).

2. Geological Setting

The current monitoring work was conducted in the dolomitic region which is situated along the western margin of the Johannesburg Dome; a near-circular, antiformal structure covered by Mesoarchaeon (>3.1 Ga) basement gneiss surrounded by outward dipping volcano-sedimentary cover rocks of Neoarchaeon to Paleoproterozoic age (3.0–2.1 Ga) [10,11]. The cover sequence is represented by the Transvaal Supergroup, which includes stromatolite-rich dolomite with abundant chert of the Late Archaeon (2.64–2.50 Ga) Malmani Subgroup dolomites [12] (Figure 1), which is composed of five Formations (from base to top: the Oaktree, Monte Christo, Lyttelton, Eccles and Frisco Formations) based on variations in stromatolite morphology, chert content and the presence of shale and chert-breccia horizons [13]. The dolomite units had experienced greenschist facies metamorphism and bedding-parallel shear along mylonite zones in dolomite and interbedded shale units [14]. The dolomites were intruded by diorite sills and dykes that were later subjected to low-grade metamorphism.

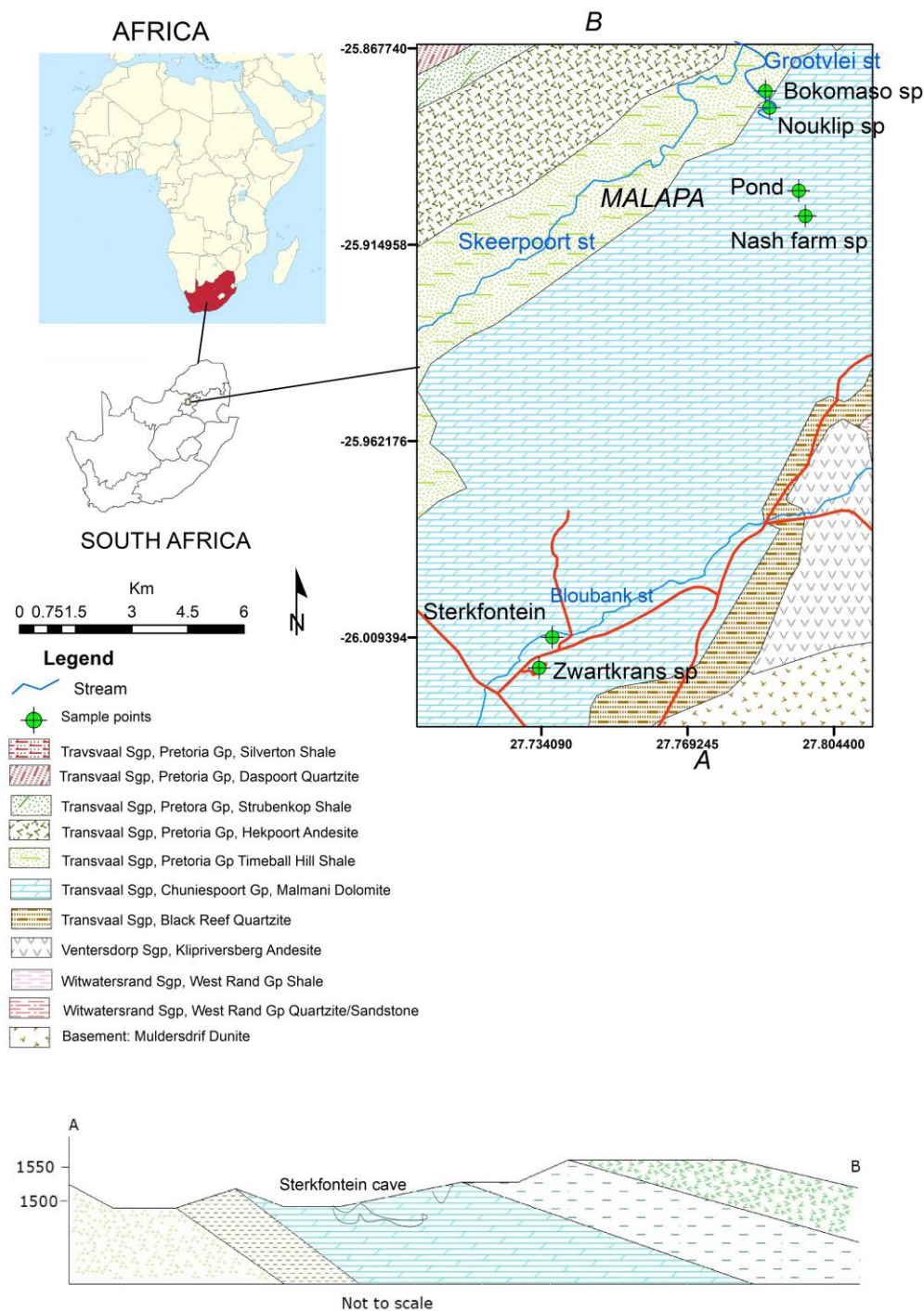


Figure 1. Simplified geological, sample location map and schematic geological cross-section (A-B) (sp stands for spring, st stands for a stream, the vertical scale is in m).

3. Karst Structures and Groundwater Occurrence

The widespread occurrence of geological structures such as joints, faults, dykes and dissolution cavities provide suitable media for groundwater circulation in dolomites. Dolomitic aquifers have high importance for water supply in the country [15], where the regional assessment of the dolomitic aquifers has been conducted through different projects [3,5,6,16]. These studies revealed that the dolomites of the Malmani Subgroup act as the main aquifer in the north-central and western parts of the country and are characterized by an extreme spatial heterogeneity that strongly influences the hydraulic behavior of the aquifer [17].

The West Rand region has a very attractive landscape with rolling hills and stream channels that are characterized by the occurrence of caves and springs. The dolomitic aquifers are typically known for the high-discharging springs that often emerge along structural boundaries and in places where the contact between the chert layer and dolomites is prominent. In the dolomitic areas, cave formation was influenced by lithological variation and cross-cutting fracture systems [18,19]. Caves are more evident in dolomites that are relatively chert poor, which could be attributed to the fact that chert layers restrict the circulation of groundwater and hence less possibility for the progression of dissolution.

Hydrogeological domains that are often identified as compartments in the dolomites were bounded by crosscutting dykes and faults often forming structurally controlled groundwater reservoirs. Since geological structures are regionally extensive, the dolomitic compartments are interconnected that allow regional groundwater circulation through different aquifer layers and drive the mixing of recharging water.

Dolomitic compartments are hydrogeologically distinct units with similar characteristics isolated from each other by steeply dipping to vertical dolerite and syenite dykes, silicified faults and layer-parallel shear zones and shale horizons [6,20,21]. Transmissivity values between and within compartments range from 1 to 25,000 m²/day [21] reflecting the heterogeneous nature of the dolomitic aquifers and variation in the open karst structures with high water storage capacity. The limited local recharge, which is mostly <5% of the mean annual rainfall (<35.5 mm/year of recharge from 710 mm/yr of rainfall), complicates the renewability of the dolomitic aquifer at a local scale unless the hydrogeological system is regionally open and extensive so that a chance for recharging water could increase.

Since geological structures such as dykes and faults are regionally extensive, they play a significant role in regulating regional groundwater circulation. Often, the cross-cutting structures form compartments and facilitate regional groundwater circulation, hence generating springs with a discharge of more than 100 L/s that may not be possible with limited local recharge.

The main focus areas in the dolomitic region include the Zwartkrans compartment, which is represented by the Zwartkrans spring located ~1.4 km north-east (downstream) of Sterkfontein Cave and the Tweefontein compartment that includes high-yielding springs such as the Nash farm and Nouklip springs, as well as several small springs in the area.

The importance of a karst aquifer depends on the interaction between recharging water and circulation that regulate the storage, owing to the presence of fractures and the exchange of water between different layers and compartments.

In several dolomitic terrains across the world, groundwater occurs in complex geological and hydrogeological settings. For example, the groundwater flow in the Precambrian dolomite of Kabwe (Zambia) which is located in a semi-arid climate zone, is controlled by fissures which decline rapidly below 80 m depth. Transmissivity is generally over 1000 m²/day and locally up to 3500 m²/day, which is associated with fracture development [22]. The occurrence of more than 50 springs in the karstic aquifer in Iran was attributed to water that seeps from the Seymareh Dam, where average groundwater velocity ranges from 0.2 to more than 14 m/h [23]. This indicates that the karst structures act as an open system. Similarly, water from the Niagara River above Niagara Falls, USA was found to be infiltrating into a fractured dolomite aquifer, where a large portion of the water flows into a tunnel excavated in dolomites, which suggests an open fracture system [24]. Another study from the São Miguel karst-dominated watershed in Brazil [25] reported strong influences of regional geological structures in the karst water flow directions, high concentrations of major ions, karstification processes and aquifer recharge that are more active during the rainy season, while in the dry season, the watershed is fed by groundwater. The hydrogeology of dolomites in the Pale di San Martino Mountains (Northern Italy) was found to be represented by two flow systems due to variations in the fracture and karst-related permeability. The upper flow occurs in a karstic zone with a fast flow and is active during periods of high recharge; while the lower flow is slower and passes through the diffused fracture system [26].

Both local and international studies underline the fact that groundwater circulation in dolomites is not always facilitated by fractures and karst structures that vary with depth and geological setting. Often, due to the prevalence of karst structures, groundwater recharge is considered as a straightforward process in carbonate rocks. However, this work tries to demonstrate that the presence of limited recharge in dolomitic aquifers is due to the localization of fractures.

4. Study Area

The study area is part of the West Rand region situated west of the city of Johannesburg. Particular focus was given to the areas dominated by dolomitic caves in order to conduct water sampling. For stable isotopes of water (^{18}O and ^2H) analysis, drip samples were collected inside the caves at about 15 m below the surface in the Sterkfontein area (Figure 2) in addition to major springs in the Malapa area (see Figure 1).



Figure 2. Inside the dolomite cave, about 15 m below the surface where drip samples were collected.

The Sterkfontein area is drained by the Bloubank stream and the Malapa area is drained by the Skeerpoort stream (with Grootvlei stream as its tributary) which feed into the Crocodile River, an important tributary of the Limpopo River. The Nash farm spring, Nouklip spring and Bokomaso spring feed the Grootvlei stream. Springs are common in dolomitic areas owing to the fact that the rocks are fractured and weathered with abundant vegetation cover along the valleys that allow the retention of runoff by favoring delayed recharge. Even though the area is characterized by low rainfall occurrence, the perennial discharge of springs, flow of acid mine drainage and disposal of municipal wastewater sustained stream flow throughout the year, which often complicates the hydrological system and water quality in the area.

Springs with various yields (from less than 1 L/s to >100 L/s) are a characteristic feature of the West Rand region. Small springs are more frequent than big springs. They manifest in the form of patches of wet areas throughout the region. A notable pattern for the occurrence of big springs is characterized by a relatively constant high yield and they occur along structural lines. The most prominent dolomitic outcrop in the West Rand area contains deformed chert layers (Figure 3a). Some big springs such as the Nash farm spring discharge about 30 L/s [27]. Water from this spring is captured in the old farm dam located 200 m downstream from the spring site, and the overflow disappears into an open fracture system at about 500 m below the dam. Then, water appears as a Nouklip spring

with a discharge of over 150 L/s. The Grootvlei stream starts its journey from this spring (Figure 3b). A small Bokomaso spring, with a discharge of about 4.5 L/s, also joins the Grootvlei stream at about 150 m downstream of the Nouklip spring. Along the Grootvlei stream, travertine is actively deposited in the stream channel forming a damming effect resulting in small rapids (Figure 3d). The schematic cross-section (Figure 4) is helpful in depicting the field occurrence of the Malapa springs and Grootvlei stream.

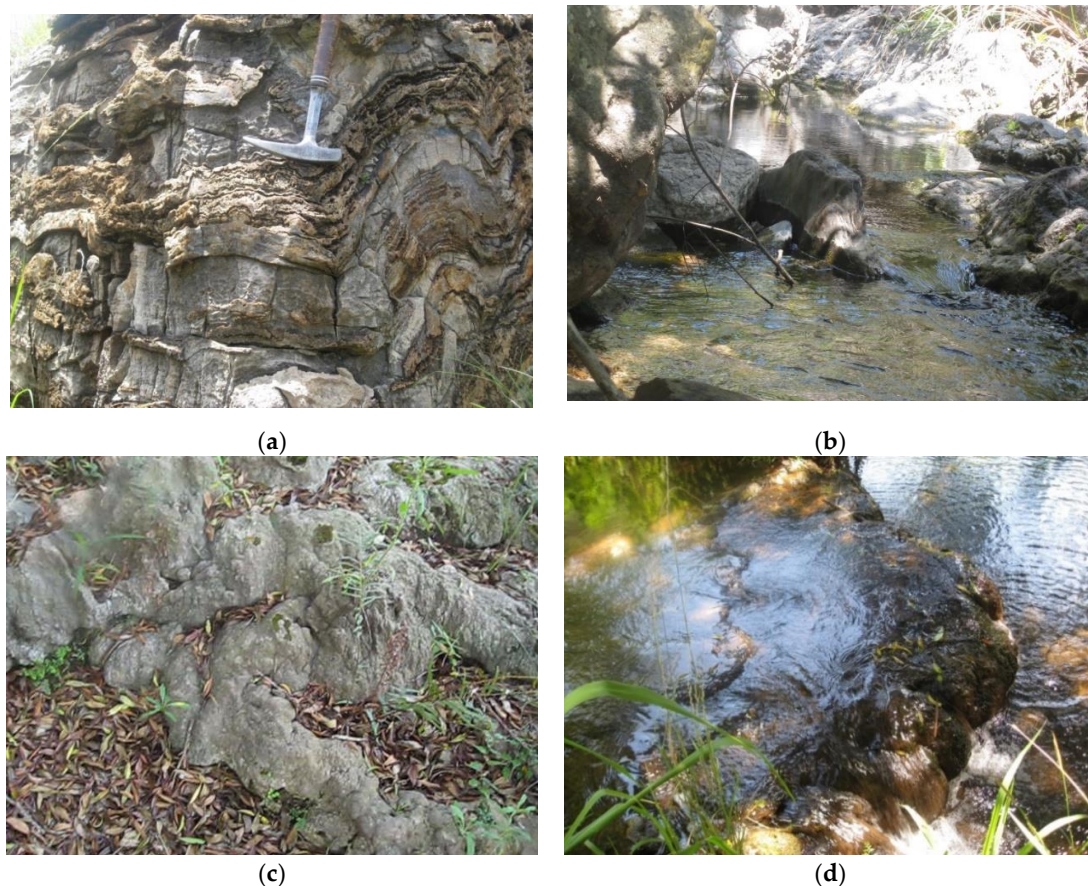


Figure 3. (a) Deformed chert layers within the dolomite outcrop, (b) Nouklip spring discharge point, (c) Travertine deposit and (d) Small rapid formed due to the damming effect of the travertine along the Grootvlei stream channel.

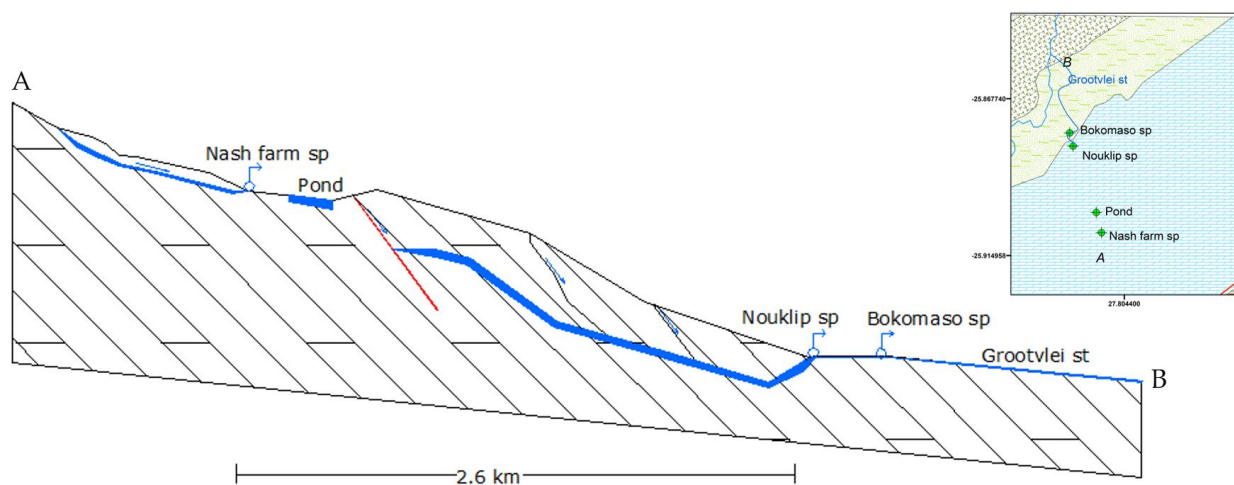


Figure 4. Schematic cross-section along A-B that portrays the occurrence of springs in the Malapa area (for the lithology of the inset map, refer to Figure 1).

In the Sterkfontein area, the discharge of the Zwarkrans spring is in the order of 100 L/s [27] that feeds the Bloubank stream, which flows into the Crocodile River (see Figure 1).

The chemical and isotopic study helps to explain if indeed the open karst structures are responsible for high spring discharge or groundwater that circulates predominantly within the microfractures and weathered zones recharge the regional dolomitic aquifer. It is also essential to understand if the groundwater flow in the dolomitic aquifer is taking place either through advective (fast flow) or diffusive (slow flow) processes in the vadose zone based on the nature of fracturing and weathering.

5. Methods

A relevant sampling strategy was designed to collect representative water samples for major ions and environmental isotope analyses. One dolomite cave was selected based on access and safety requirements. Cave drip samples were collected at least twice a month (for one year) in the Sterkfontein area for stable isotope analysis. This was conducted by placing a pre-rinsed 500 mL flask to capture the water that drips from the roof of the cave. This was intended to obtain mixed water that was collected over 12 h, in order to coincide with the rainfall event at the time of sampling. There were several points where water was dripping in the cave, so a random approach was followed based on the accessibility of the sampling point. On the other hand, samples from the Malapa area were used to analyze the major ions and stable isotopes of water.

Four prominent springs in the area were considered in this study (Figure 1). Samples for the stable isotopes of ^{18}O and ^2H analysis were pipetted into a 1.5 mL vial for analysis on the Liquid Water Isotope Analyzer-model 45-EP, Laser machine at the University of the Witwatersrand, South Africa. The machine is known for providing acceptable results with a precision of approximately 1‰ for $\delta^2\text{H}$ and 0.2‰ for $\delta^{18}\text{O}$ in liquid water samples of up to at least 1000 mg/L dissolved salt concentration.

The physicochemical parameters were measured in the field with a pre-calibrated Orion Star A214 pH/ISE multi-parameter probe. During fieldwork, the appropriate quality control (QC) procedure was followed by regularly calibrating the instrument as the ambient temperature varies and conducting a test with a predefined buffer solution (pH 4.0 and 7.0) to verify if the multimeter is in good order.

6. Results and Discussion

The physicochemical and chemical data from the Malapa area indicate the presence of less mineralized springs that circulate in the dolomite. The water temperature of the Nash farm and Nouklip springs (SP1 and SP2) was 22.1 °C and 21.6 °C, with an electrical conductivity (EC) of 360 $\mu\text{S}/\text{cm}$ and 420 $\mu\text{S}/\text{cm}$, respectively. Even though the ambient temperature at the time of measurement in August was below 10 °C, the temperature of the water was high, which shows the aquifer temperature has not been impacted by the local weather condition implying the possibility of deep circulation. The influence of equilibria between the solute and gaseous phases of CO_2 on carbonate dissolution and precipitation processes greatly depends on the pH and water temperature. Once deep circulating water appears as a spring, atmospheric conditions influence the CO_2 liberation and, hence, the pH changes (increases), which influences the precipitation of travertine from the spring. As the Nouklip spring flows downstream, EC shows a decreasing trend (Table 1) due to calcite precipitation in the form of travertine and possible mixing with shallow springs that joins the stream, from ST1 to ST5 (Figure 5). In some places, the travertine deposit has a thickness of up to 15 m with a lateral extent of up to 200 m. The spring samples maintain high EC values with a near-neutral pH. High EC values were recorded for springs at a discharging (emergence) point (cluster A) and low values for the stream samples after travertine deposition (cluster B) due to the precipitation of calcite along the flow path.

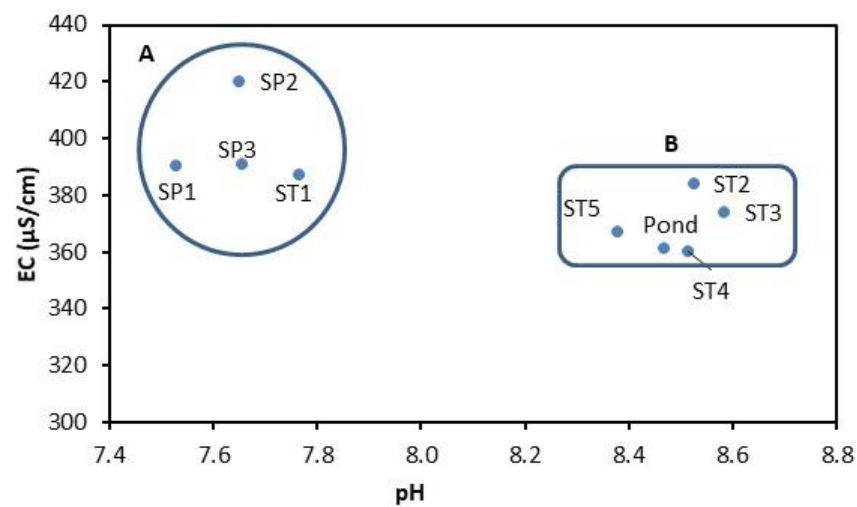


Figure 5. The EC and pH variation in the water samples grouped as cluster A and cluster B.

Table 1. Physicochemical, major ion and isotopic results for spring samples (SP: spring, ST: stream).

		SP1	Pond	SP2	SP3	ST1	ST2	ST3	ST4	ST5
Parameter	Unit	Nash Farm		Nouklip Spring	Bokomaso Spring	50 m below SP2	150 m below SP2	300 m below SP2	Tributary 1	Tributary 2
Elevation	m. a.s.l	1450	1440	1323	1319	1320	1300	1290	1290	1290
pH		7.50	8.11	7.65	7.66	7.77	8.53	8.59	8.52	8.38
T	°C	22.10	21.30	21.60	21.30	21.50	21.50	20.80	21.10	19.20
EC	μS/cm	390.0	361.0	420.0	391.0	387	384.0	374.0	360	367
TDS	mg/L	293.0	271.0	315.0	294.0	290	278.0	280.0	270	275
ORP	mV	−15.7	−64.5	−22.2	−31.0	−29.5	−73.2	−75.2	−76.5	−63.1
Ca	mg/L	38.0	32.0	41.0	38.0		34.0	31.0		
Mg	mg/L	23.0	24.0	26.0	24.0		24.0	20.0		
Na	mg/L	1.6	1.5	1.5	1.5		1.3	1.8		
K	mg/L	0.5	0.2	0.4	0.3		0.3	0.4		
HCO ₃	mg/L	224.0	207.0	243.0	226.0		221.0	219.0		
CO ₃	mg/L	0.0	1.0	0.0	2.0		4.0	5.0		
Cl	mg/L	2.4	2.4	1.4	1.0		1.4	2.0		
SO ₄	mg/L	2.9	2.4	2.1	0.6		1.9	1.0		
δ ² H	‰	−29.0	−27.3	−31.0	−32.4	−31.2	−30.4	−30.1	−29.6	−29.2
δ ¹⁸ O	‰	−5.17	−4.75	−5.42	−5.64	−5.40	−5.39	−5.23	−5.11	−5.17

The pH records show a relatively increasing trend from pH 7.6 to pH 8.5 along the stream flow path. The increase in pH downstream is a typical characteristic of the degassing of deep circulating springs [28,29] when water is exposed to an oxic condition ($\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2^-$). The low pH values (cluster A, Figure 5) represent springs at the emergence point while higher values (alkaline pH) represent the travertine deposition down the valley. This process facilitates the removal of CO_2 from the spring water and favors the precipitation of travertine.

The variation in the EC values could be linked to the maturity of the Nouklip spring through deep circulation and prolonged water–rock interaction process as compared to the upstream Nash farm spring. The hydrochemical analysis of the springs also revealed high Mg and Ca content for SP1, SP2 and SP3 that range between 23 mg/L and 26 mg/L and 38 mg/L to 41 mg/L, respectively. The Nouklip spring has distinctly high Mg and Ca content, which confirms the dolomites as a host. The spring water has relatively low Na, K, SO_4 and Cl concentrations in the range of 0.5 mg/L to 3.3 mg/L. All springs have a relatively constant Na concentration with an average of 1.5 mg/L, suggesting the absence of sodium-bearing minerals in the aquifer system.

The Zwartkrans spring (Table 2) has a high EC value (840 μS/cm) as compared with other springs in the area. Owing to its host, dolomite, it has a high bicarbonate content (195 mg/L). However, the high sulphate concentration of 154 mg/L, could be attributed to

the impact of acid mine drainage that flows through the Bloubank stream and seeps into the dolomitic aquifer. The annual seepage from the Bloubank stream was estimated at 30 million m³ [30] into the dolomitic aquifer upstream of the Zwartkrans spring that affected the spring water chemistry with a high sulphate content.

Table 2. Chemical and isotope data for the Zwartkrans spring in 2010 [27].

Parameter	Zwartkrans Spring
pH	7.5
EC (µS/cm)	840
Ca (mg/L)	66
Mg (mg/L)	37
Na (mg/L)	36
K (mg/L)	1.5
Cl (mg/L)	57
SO ₄ (mg/L)	154
HCO ₃ (mg/L)	195
δ ² H (‰)	−16.8
δ ¹⁸ O (‰)	−3.17

The water type of samples in Table 1 falls under Ca–Mg–HCO₃ type water (dark circle), while the Zwartkrans spring (Table 2) is identified as Ca–Mg–SO₄ (dark square) (Figure 6).

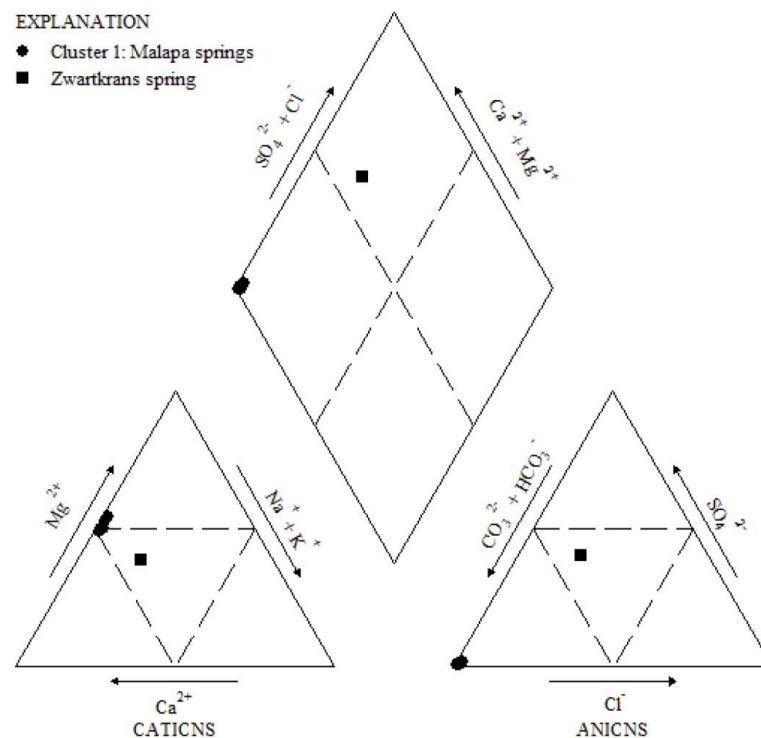


Figure 6. Two distinct facies in the Piper plot are based on the water quality data in Tables 1 and 2.

Based on the stable isotope results (Table 3), it was clear that the cave drip samples fall within the range of rainfall records. The stable isotopes of ¹⁸O and ²H have been plotted along with the Johannesburg Local Meteoric Water Line (JLMWL) which was defined by $\delta^2\text{H} = 6.7\delta^{18}\text{O} + 10\text{‰}$ [31] and the Global Meteoric Water Line ($\delta^2\text{H} = 7.9\delta^{18}\text{O} + 8.72\text{‰}$, [32]) (Figure 7). In this plot, the cave drip water samples are represented by the $\delta^{18}\text{O}$ values of

−3.95‰ to 3.32‰ (ave. −1.90‰) while the $\delta^2\text{H}$ values range from −11.0‰ to 27.7‰ (ave. 0.4‰). On the other hand, the rainfall isotope results for $\delta^{18}\text{O}$ fall between −16.11‰ and 5.38‰ (ave. −4.63‰), while the $\delta^2\text{H}$ values fall between −105.7‰ and 35.6‰ (ave. −19.2‰).

Table 3. Stable isotope data for cave drip samples at Sterkfontein and rainfall at Johannesburg.

Code	$\delta^{18}\text{O}$ (‰)	$\pm$ (‰)	$\delta^2\text{H}$ (‰)	$\pm$ (‰)	Code and Date	$\delta^{18}\text{O}$ (‰)	$\pm$ (‰)	$\delta^2\text{H}$ (‰)	$\pm$ (‰)
CAVE 05 01 2021	−3.10	0.1	−7.1	0.6	RF 06 01 2021	−10.80	0.3	−71.9	1.1
CAVE 20 01 2021	−2.76	0.1	−5.6	0.3					
CAVE 05 02 2021	2.01	0.1	10.9	0.9	RF 02 02 2021	−16.11	0.2	−105.7	1.2
CAVE 20 02 2021	−0.24	0.1	10.3	0.5					
CAVE 05 03 2021	−1.68	0.1	2.3	0.3	RF 04 03 2021	−2.14	0.1	−1.3	1.2
CAVE 20 03 2021	−2.17	0.1	1.3	0.3					
CAVE 05 04 2021	−3.23	0.1	−4.4	0.3					
CAVE 20 04 2021	−3.90	0.1	−8.9	0.3	RF 06 04 2021	−5.88	0.25	−16.1	1.3
CAVE 05 05 2021	−1.81	0.1	−2.6	0.3					
CAVE 20 05 2021	−3.72	0.1	−9.6	0.3					
CAVE 05 07 2021	−2.20	0.1	−8.7	0.7					
CAVE 20 07 2021	−1.15	0.1	17.9	1.0					
CAVE 05 09 2021	3.32	0.1	27.7	0.5	RF 30 09 2021	5.38	0.3	35.6	1.5
CAVE 20 09 2021	−3.95	0.0	−11.0	0.4					
CAVE 05 10 2021	−1.31	0.1	−0.4	0.3	RF 02 10 2021	−0.94	0.0	6.5	0.3
CAVE 20 10 2021	−0.98	0.1	10.9	0.3					
CAVE 05 11 2021	−3.03	0.1	−3.9	0.3	RF 07 11 2021	−2.60	0.1	6.8	1.1
CAVE 20 11 2021	−3.71	0.2	−7.7	0.3					
CAVE 05 12 2021	−3.07	0.0	−6.6	0.3	RF 02 12 2021	−3.95	0.0	−7.6	0.3
CAVE 20 12 2021	−1.32	0.1	3.9	0.3					
Average	−1.90		0.4			−4.63		−19.2	

According to the plot in Figure 7, the “cave drip water” reflects a similar isotopic composition as rainfall, where some rainfall samples contain highly depleted $\delta^{18}\text{O}$ value of −16.11‰ and $\delta^2\text{H}$ value of −105.7‰ that depict high latitude moisture sources such as from Antarctica, and highly enriched $\delta^{18}\text{O}$ value of 5.38‰ and $\delta^2\text{H}$ value of 35.6‰ that reveal the presence of localized moisture source for rainfall sourced from the southern Indian and tropical Ocean regions. This suggests that the Johannesburg area is receiving moisture from different sources dictated by moisture trajectory due to seasonal changes. The average values for the cave drip samples show more enrichment than the rain samples due to mixing and recharge that took place after evaporation. The cave drip samples do not reflect the extreme values measured in the rainfall samples, which could signify that they might have been recharged by different rainfall in previous years with a delayed circulation in the vadose zone which might have undergone a mixing process. The drips in the cave take place irrespective of the seasons throughout the year. This could suggest the possibility of retention or delay in the circulation of the recharged rainfall in the vadose zone. This could be attributed to a retarded flow as a result of microfractures in the dolomites.

The Malapa spring samples contain depleted $\delta^2\text{H}$ values that range between −32.4‰ and −29.6‰ (excluding −27.3‰ for the pond sample due to evaporation) and $\delta^{18}\text{O}$ values that range between −5.64‰ and −5.11‰ (excluding −4.75‰ for the pond sample due to evaporation).

The position of the Zwartkrans spring in Figure 7 with relatively enriched ^{18}O and ^2H values as compared with the Nash farm and Nouklip springs suggests the recharge from the evaporated seepage water from the Bloubank stream in the dolomitic aquifer owing to the presence of highly permeable structures. The springs that have not been affected or mixed with recent water were plotted in the depleted isotopic region (see the position of the Nash farm and Nouklip springs that include the Pond, Bokomaso springs and streams). The similarity in the stable isotope composition could confirm the similarity in the hydrogeological basin and recharge history. A past study [33] reported that the mean residence time of groundwater that emerges through springs in the Malapa area ranges from 1650 ± 50 to 1850 ± 50 years, where about 200 years was the time needed for

groundwater circulation between the two springs. Consequently, the springs' discharge always remains high throughout the year irrespective of the season as a result of regionally dominated groundwater circulation through geological structures.

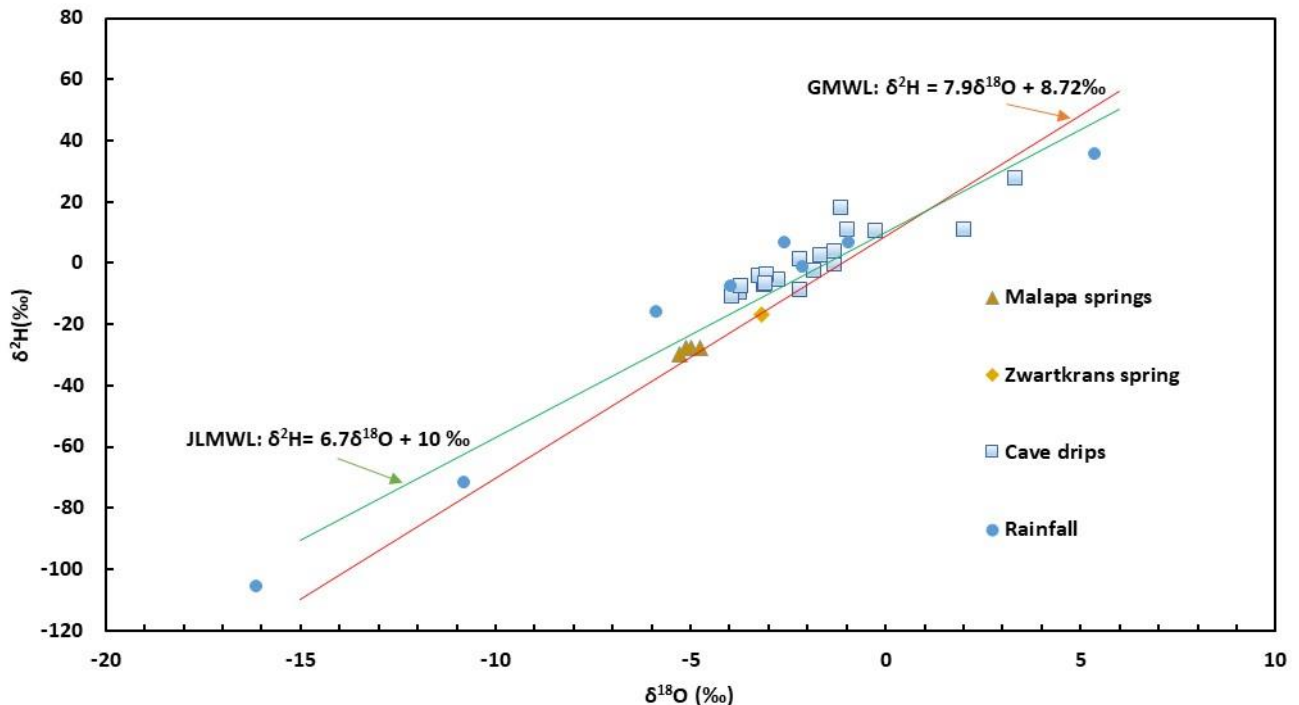


Figure 7. Stable isotope plot with respect to the Johannesburg Local Meteoric Water line ($\delta^2\text{H} = 6.78\delta^{18}\text{O} + 10\text{‰}$, [31]) and the Global Meteoric Water Line ($\delta^2\text{H} = 7.96\delta^{18}\text{O} + 8.72\text{‰}$, [32]).

7. Conclusions

The circulation of recharged rainfall through dolomitic microfractures in the vadose zone reflects its important role in delaying the flow that appears in the caves. Even though the stable isotope plot for the cave drip samples shows a similar signature to rainfall, it does not reflect the presence of extreme isotopic values that were recorded in rainfall, suggesting the possibility of a delay in circulation that could result in the mixing of recharged water in the vadose zone. Considering the spatial separation of 2.6 km between SP1 (Nash farm spring) and SP2 (Nouklip spring) and the residence time difference of about 200 years [33], this confirms the retardation process in the dolomites and poorly developed groundwater circulation media and the heterogeneous nature of the dolomite. This also helps the storage of groundwater to take place from one compartment to the other along the boundaries of the compartment. Even though the area is characterized by low rainfall and high evapotranspiration, there are high-yielding springs as much as 150 L/s in the area, which indicate the role of regional structures that connect different compartments and allow regional groundwater circulation rather than local recharge which is insignificant.

The deposition of travertine is a very good indicator of carbonate saturation and change in the alkalinity of water in the springs as a result of prolonged water–rock interaction in the dolomite. Weathering zones and fractures are the primary media for recharge to take place that facilitate the widespread occurrence of small springs. However, faults and dissolution cavities (karst structures) are most widely associated with large springs. In general, the findings of the current work help to contribute to the understanding of the delayed recharge in dolomites besides the need to be cautious in using the millennia-old groundwater for various economic uses since the aquifers are not readily recharged with recent rainfall.

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References

1. Abiye, T.A. Contribution of hydrogeology to solving community water supply problems in South Africa. *S. Afr. J. Sci.* **2023**, *119*, 14599. [CrossRef]
2. Abiye, T.A.; Demlie, M.B.; Mengistu, H. An overview of aquifer physiognomies and the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ distribution in the South African groundwaters. *Hydrology* **2021**, *8*, 68. [CrossRef]
3. Kafri, U.; Foster, M.B.J. Hydrology of the Malmani Dolomite in the Klip River and Natalspruit Basins, South Africa. *Environ. Geol. Water Sci.* **1989**, *13*, 153–166. [CrossRef]
4. Abiye, T.A. Synthesis on groundwater recharge in Southern Africa: A supporting tool for groundwater users. *Groundw. Sustain. Dev.* **2016**, *2*, 182–189. [CrossRef]
5. Department of Water Affairs and Forestry (DWAF). *A Guideline for the Assessment, Planning and Management of Groundwater Resources within Dolomitic Areas in South Africa*; Department of Water Affairs and Forestry (DWAF): Pretoria, South Africa, 2006; Volume 2, p. 187.
6. Meyer, R. *Hydrogeology of Groundwater Region 10: The Karst Belt*; WRC Report No. TT553/14; Water Research Commission: Pretoria, South Africa, 2014; p. 285.
7. Reliefweb, Cholera Death Toll in SA Rises to 47. Available online: <https://reliefweb.int/report/south-africa/cholera-death-toll-sa-rises-47-after-four-new-fatalities-recorded> (accessed on 21 June 2023).
8. Clark, I.D.; Fritz, P. *Environmental Isotopes in Hydrogeology*; Lewis Publishers: New York, NY, USA, 1997; 328p.
9. Harris, C.; Diamond, R. Oxygen and hydrogen isotopes record of cape town rainfall and its application to recharge studies of Table Mountain groundwater. In *The Use of Isotope Hydrology to Characterize and Assess Water Resources in South(ern) Africa*; Abiye, Ed.; WRC: Pretoria, South Africa, 2013; pp. 38–52. 210p.
10. Robb, L.; Meyer, F. The Witwatersrand Basin, South Africa: Geological Framework and Mineralization Processes. *Ore Geol. Rev.* **1995**, *10*, 67–94. [CrossRef]
11. Anhaeusser, C.R. Ultramafic and Mafic Intrusions of the Kaapvaal Craton. In *The Geology of South Africa*; Johnson, M.R., Anhaeusser, C.R., Tomas, R.J., Eds.; Council for Geosciences: Pretoria, South Africa, 2006; pp. 95–134.
12. Eriksson, P.G.; Altermann, W.; Hartzer, F.J. The Transvaal Supergroup and its precursors. In *The Geology of South Africa*; Johnson, M.R., Anhaeusser, C.R., Thomas, R.J., Eds.; Geological Society of South Africa and Council for Geoscience Publication: Pretoria, South Africa, 2006; pp. 237–260.
13. Eriksson, K.A.; Truswell, J.F. Stratotypes from the Malmani Subgroup North-West of Johannesburg, South Africa. *Trans. Geol. Soc. S. Afr.* **1974**, *77*, 311–323.
14. Alexandre, P.; Andreoli, M.A.G.; Jamison, A.; Gibson, R.L. $40\text{Ar}/^{39}\text{Ar}$ constraints on low-grade metamorphism and cleavage development in the Transvaal Supergroup (central Kaapvaal craton, South Africa): Implications for the tectonic setting of the Bushveld Complex. *S. Afr. J. Geol.* **2006**, *109*, 393–410. [CrossRef]
15. Winde, F. Challenges for sustainable water use in dolomitic mining regions of South Africa- a case study of Uranium pollution, Part 1: Sources and pathways. *Phys. Geogr.* **2006**, *27*, 333–347. [CrossRef]
16. Bredenkamp, D.B.; Vogel, J.C.; Wiegmanns, F.E.; Xu, Y.; van Reneburg, J. *Use of Natural Isotopes and Groundwater Quality for Improved Estimation of Recharge and Flow in Dolomitic Aquifers*; WRC Report; Water Research Commission: Pretoria, South Africa, 2007; p. 85.
17. Withüser, K.T.; Holland, M. Hydrogeology of the Cradle of Humankind World Heritage Site, South Africa. In Proceedings of the 12th International Conference of International Association for Computer Methods and Advances in Geomechanics (IACMAG), Goa, India, 1–6 October 2008.
18. Partridge, T.C. Geomorphological dating of cave opening at Makapansgat, Sterkfontein, Swartkrand and Taung. *Nature* **1973**, *246*, 75–79. [CrossRef]
19. Kavalieris, I.; Martini, J. Structural controls on some western Transvaal caves. *S. Afr. J. Sci.* **1976**, *72*, 308–309.
20. Bredenkamp, D.B.; Van der Westhuizen, C.; Wiegmanns, F.E.; Kuhn, C.M. *Groundwater Supply Potential of Dolomite Compartments West of Krugersdorp*; Technical Report Gh3440; DWAF: Pretoria, South Africa, 1986.
21. Holland, M.; Withüser, K.T.; Jamison, A.A. Hydrology of the Cradle of Humankind world heritage site: Geology, surface and groundwater. In *The Karst System of the Cradle of Humankind World Heritage Site*; WRC Report; The South African Karst Working Group, Water Research Commission: Pretoria, South Africa, 2010; pp. 125–140.
22. Houston, J.F.T. Rainfall and recharge to a dolomite aquifer in a semi-arid climate at Kabwe, Zambia. *J. Hydrol.* **1982**, *59*, 173–187. [CrossRef]

23. Peely, A.B.; Mohammadi, Z.; Raeisi, E.; Solgi, K.; Mosavi, M.J.; Kamali, M. Hydrogeological characterization of flow system in a karstic aquifer, Seymareh dam, Iran. *J. Afr. Earth Sci.* **2018**, *143*, 266–277. [[CrossRef](#)]
24. Yager, R.M.; Kappel, W.M. Infiltration and hydraulic connections from the Niagara River to a fractured-dolomite aquifer in Niagara Falls, New York. *J. Hydrol.* **1998**, *206*, 84–97. [[CrossRef](#)]
25. Lucon, T.N.; Costa, A.T.; Galvão, P.; Leite, M.G.P.; Madeira, T.; Nogueira, L.B. Recharge sources and hydraulic communication of karst aquifer, São Miguel watershed, MG, Brazil. *J. S. Am. Earth Sci.* **2020**, *100*, 102591. [[CrossRef](#)]
26. Lucianetti, G.; Mazza, R.; Mastroiello, L. Hydrogeology of a high Alpine carbonate aquifer (Pale di San Martino, Dolomites, Northern Italy). *J. Maps* **2019**, *15*, 448–459. [[CrossRef](#)]
27. Hobbs, P.J. (Ed.) *Situation Assessment of the Surface Water and Groundwater Resource Environments in the Cradle of Humankind World Heritage Site*; Report Prepared for the Management Authority; Department of Economic Development: Pretoria, South Africa, 2011; p. 424.
28. Liu, Z.; Zhang, M.; Li, Q.; You, S. Hydrochemical and isotope characteristics of spring water and travertine in the Baishuitai area (SW China) and their meaning for paleoenvironmental reconstruction. *Environ. Geol.* **2003**, *44*, 698–704. [[CrossRef](#)]
29. Deirmendjian, L.; Abril, G. Carbon dioxide degassing at the groundwater-stream-atmosphere interface: Isotopic equilibration and hydrological mass balance in a sandy watershed. *J. Hydrol.* **2018**, *558*, 129–143. [[CrossRef](#)]
30. Abiye, T.A.; Mengistu, H.; Masindi, K.; Demlie, M. Surface Water and Groundwater Interaction in the Upper Crocodile River Basin, Johannesburg, South Africa: Environmental Isotope Approach. *S. Afr. J. Geol.* **2015**, *118*, 109–118. [[CrossRef](#)]
31. Leketa, K.; Abiye, T.; Butler, M. Characterisation of groundwater recharge conditions and flow mechanisms in bedrock aquifers of the Johannesburg area, South Africa. *Environ. Earth Sci.* **2018**, *77*, 726–737. [[CrossRef](#)]
32. Terzer, S.; Wassenaar, L.I.; Araguás-Araguás, L.J.; Aggarwal, P.K. Global isoscapes for ^{18}O and ^2H in precipitation: Improved prediction using regionalized climatic regression models. *Hydrol. Earth Syst. Sci.* **2013**, *17*, 4713–4728. [[CrossRef](#)]
33. Abiye, T.A.; Leketa, K.C. The need for managing historic groundwater in the Limpopo River Basin, southern Africa: Based on the $\delta^{18}\text{O}$, $\delta^2\text{H}$ and ^{14}C data. *Groundw. Sustain. Dev.* **2021**, *14*, 100583. [[CrossRef](#)]

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