Article

Determining Water Isotope Compositions for the IAEA WICO and North West Villages, South Africa

Joseph Mathuthu ^{1,*} , Naomi Dikeledi Mokhine ¹ , Namhla Mkiva ², Samuel Che Nde ^{1,2} , Ingrid Dennis ³, Johan Hendriks ³, Lobina Palamuleni ² , Tebogo Gilbert Kupi ¹ and Manny Mathuthu ¹

- ¹ Centre for Applied Radiation Science and Technology, Mafikeng Campus, North West University, Mahikeng 2790, South Africa; dikeledi.mokhine@gmail.com (N.D.M.); Samuel.Nde@nwu.ac.za (S.C.N.); Tebogo.Kupi@nwu.ac.za (T.G.K.); Manny.Mathuthu@nwu.ac.za (M.M.)
- ² Department of Geography and Environmental Sciences, Mafikeng Campus, School of Geo and Spatial Sciences, North West University, Mahikeng 2790, South Africa; namhla.mkiva@nwu.ac.za (N.M.); lobina.palamuleni@nwu.ac.za (L.P.)
- ³ Centre for Water Sciences and Management, Potchefstroom Campus, North-West University, Potchefstroom 2520, South Africa; Ingrid.Dennis@nwu.ac.za (I.D.); Johan.Hendriks@nwu.ac.za (J.H.)
- * Correspondence: mp18797@gmail.com

Abstract: Deuterium (^2H) and oxygen 18 (^{18}O) stable isotopes in water are the key indicators of hydrological and ecological patterns and processes. The water isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ have been employed widely as tracers in hydrological and ecological research, as they are integrated into geological and biological systems in a predictable manner. The aim of this study was to determine the water isotope composition of the International Atomic Energy Agency's (IAEA) Water Isotope Inter-laboratory Comparison (WICO) samples and to determine the Local Meteoric Water Line for North West Province (NWP) villages in South Africa. The IAEA WICO 2020 samples were obtained from the IAEA, Vienna, and borehole water samples from selected villages in the North West province of South Africa were randomly collected to investigate the relationship between the stable isotopes (^{18}O and ^2H) and the climate in underground water aquifers. A cavity ring-down spectroscopy analyzer with laser-current-tuned cavity resonance, Picarro L2140-i, was used to measure triple water–isotope ratios with high precision. The IAEA WICO results obtained for the d-excess were in a satisfactory range and the margins of error were close to those required by the IAEA. The $\delta^2\text{H}$ values ranged between -33.00‰ and -8.00‰ , while the $\delta^{18}\text{O}$ values ranged between -5.50‰ and -2.00‰ . The results of this work have shown that our water science and management lab is capable of undertaking inter-laboratory comparisons for the IAEA.

Keywords: water isotope compositions; deuterium-excess; Local Meteorological Water Line

Citation: Mathuthu, J.; Mokhine, N.D.; Mkiva, N.; Nde, S.C.; Dennis, I.; Hendriks, J.; Palamuleni, L.; Kupi, T.G.; Mathuthu, M. Determining Water Isotope Compositions for the IAEA WICO and North West Villages, South Africa. *Water* **2021**, *13*, 2801. <https://doi.org/10.3390/w13202801>

Academic Editor: David Widory

Received: 3 September 2021

Accepted: 5 October 2021

Published: 9 October 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Groundwater is a critical resource for both humanity and biota. Its usage has increased in recent decades, principally due to unpredictable climate changes and increased population growth. Due to the imbalance in water availability and supply, groundwater is over-utilized. Special attention should be paid to the reduction and deterioration of water resources, particularly in areas where human activity has increased [1]. The physico-chemical constituents of groundwater play a major role in the water's quality. Researchers are paying more attention to stable isotopes in these circumstances, since they can be utilized to analyze the hydrological processes in various watersheds [2]. The stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are “fingerprints” of water flow, such as rainfall, infiltration, subsurface movement, and stream discharge. These isotopes can help researchers better understand the water cycle, runoff mechanisms, flow patterns, water–rock interactions, and residence time [3,4]. Hence, water stable isotopes (SIs), $\delta^2\text{H}$ and $\delta^{18}\text{O}$, have been widely used to study a variety of meteorological and catchment-scale processes. Identifying diverse moisture

sources, quantifying recycled moisture fractions, predicting groundwater recharge sources, studying groundwater flow patterns, and understanding surface water and groundwater interaction are all part of this process [4]. The SIs of water have also been used to assess hydrological processes under extreme circumstances, such as drought and flooding [4,5].

The isotope effects that precede each step of the water cycle cause stable isotopic compositions to change during precipitation. Environmental temperature is considered the most important factor; however, other factors such as changes in the origins of air masses or rain generation mechanisms also have effects [5]. In most hydrological systems, precipitation is the primary source of groundwater. The choice of oxygen and hydrogen isotope tracers as fingerprints depends upon the isotopic composition of precipitation before and after the water recharge is known. In water, the compositions of ^{18}O and ^2H occur with mass abundances of 0.204% for all oxygen atoms and 0.015% for all hydrogen atoms, respectively [4].

Stable isotopes have been used in recent studies to highlight the changes in river water cycles caused by the impoundment of water in reservoirs. Craig [6] proposed a linear relationship for global precipitation between the stable isotope ratios of ^2H and ^{18}O , given by $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$, known as the Global Meteoric Water Line (GMWL) [6]. IAEA gives the definition of d-excess = $\delta^2\text{H} - 8 \times \delta^{18}\text{O}$ [7]. However, understanding changes in local precipitation requires the use of a Local Meteoric Water Line (LMWL).

The d-excess is an indication of local environmental conditions, such as the temperature of condensation, the amount of sub-cloud evaporation occurring during rainout, and the degree of local moisture recycling [8]. The deuterium excess reflects the slower diffusion of the ^2H and ^{18}O molecules, resulting in a relative enrichment of the water molecules in the less firmly bonded phase—for example, in the gas phase during the evaporation of water [9]. This slower movement can only result in detectable differences if the two phases do not have enough time to attain isotopic equilibrium. Isotopic values fluctuate seasonally due to sub-cloud evaporation and isotopic fractionation; thus, higher isotopic values are observed in summer and the most depleted values are observed in winter [10]. In addition, physical conditions such as humidity, air temperature, and sea surface temperature also directly affect the deuterium excess value. Bershaw [10] suggested that d-excess precipitation increases at relatively low temperatures of condensation at high elevations [10]. Rao and Kulkarni [11] stated that an identifiable isotopic characteristic is provided by the kinetic fractionation of ^2H and ^{18}O , occurring during condensation rather than evaporation [11].

The north west province of South Africa is a semi-arid region, and studies have revealed that the province is plagued by both surface and groundwater quality shortages. Suburbs such as Mafikeng, Setlagole, Lichtenburg, and Klerksdorp are engaged in different land-use practices that mostly rely on groundwater supply. What is most crucial is that no studies have investigated the compositions of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the area, influencing the level of instability of the consumed groundwater. West et al. [12] recommended the increased spatial sampling of precipitation—especially for high-elevation regions—and the temporal sampling of ground and tap water to considerably aid isotopic studies in this region [12].

As the first step in developing successful methods of maintaining long-term water supply and safeguarding water quality, determining the source of water is essential.

Since the 1990s, every four years the International Atomic Energy Agency (IAEA) has offered isotopic water analysis skill assessments to laboratories throughout the world. Water Isotope Inter-laboratory Comparison (WICO) test helps scientists to establish the stable isotope-measuring capabilities of their laboratories (precision, accuracy); the age of water; and to guess the origin of inter-comparison samples [13]. A comparison of the analytical performance of 25 laboratories was carried out by the IAEA in 2018, utilizing isotope ratio mass spectrometry and laser absorption spectrum analysis. Their results were observed in the ranges of -115‰ to 0‰ in $\delta^2\text{H}$ and -16‰ to 0‰ in $\delta^{18}\text{O}$ [14].

The main objectives of this study were to: (1) determine the groundwater isotope composition and construct the LMWL for the North West province's villages, and (2) determine the precision of the North West University's water isotope analyzer, the Picarro, by analyzing IAEA water samples. From these results, factors affecting the water cycle can be better understood through other comparable systems in this province.

2. Methodology

2.1. Study Area

The research was conducted using samples from four selected villages in North West Province, South Africa (Figure 1). Generally, the geology of the area comprises nine lithological stratigraphic classes—namely, Swazian, Kalahari, Dwyka, Malmari, Allanridge, Kraaipan, Kameeldooms, Blackreef, and Klipriviersberg. The Swazian category, which consists of granite and gneiss, is the dominant geological structure in the study area. These are very important, increasing the occurrence of groundwater due to the fractures present. The Malmari is made up of limestone, subordinate chert, minor carbonaceous shale, quartzite, and dolomite. The chert-rich formations are significant in the formation of groundwater's main aquifers. In the Blackreef, some fractures experience low permeability [15]. The Kalahari is the most dominant geological landscape, with superficial deposits consisting of gravels, clays, sandstone, silcrete, calcrete, and aeolian sand. Groundwater occurs mostly in crystalline rocks that are weathered near the surface and are later siphoned to fractured zones in deeper portions [16]. In the study area, groundwater recharge occurs as a diffused process which is viewed as the direct movement of water from the land surface as a result of precipitation infiltrating and percolating through the unsaturated zones. The quality of the groundwater is influenced by the nature of the geological formations [17]. Similar to other environments, the mineral weathering of these geological rocks releases trace elements and mobile elements (e.g., alkali) into the water [18].

Figure 1. A map of the study area in the four selected villages of the North West province. (A) is a map of South Africa showing the North West province highlighted in red, (B) is a map showing the municipality districts in the province, and (C) shows the four studied villages in their districts.

The climate of the study area is influenced by two ecological regions—namely, the Highveld and the Southern Kalahari. The Highveld can be described as sub-humid, with low to moderate relief from the western side towards the eastern landscapes [14,19]. The study area is semi-arid and records a mean annual rainfall of 400 mm. The area experiences mean summer temperatures, with the maximum in January, at approximately 35 °C. Winters can be cool, with mean night temperatures in June of sometimes below 0 °C. The rate of evaporation exceeds that of precipitation. The relative humidity is between 64% and 66% in February and about 28–32% in July. Having a flat topography, the study area is underlain by a low to medium drainage density. Surface water is limited, and groundwater has become the only reliable water supply.

2.2. IAEA WICO Samples

Six water samples (OH-25–OH-30) were received by the North West University (NWU) Centre for Applied Radiation Science and Technology (CARST) from the Radio-analytical Laboratory of IAEA (WICO project Ref# 20318A) to perform water isotope inter-laboratory comparison tests.

2.3. Sampling Technique and Analysis

Forty (40) borehole water samples—SM1-10; SL1, SL3, SL4, SL5, SL7, SL9, SL10, SL11, SL12, SL13; SK1, SK5, SK6, SK11, SK12, SK13, SK14, SK15, SK16, SK18, SK19, SK20; and C, D, E, S2K, S3K, S7K, S10K, S17K, respectively—were collected from Mafikeng, Lichtenburg, Klerksdorp, and Setlagole villages in North West province, South Africa, in the months of March to April 2021. These samples were collected in summer during the rainy season. A handheld GPS (Garmin etrex 30, by Garmin Southern Africa (PTY) Ltd., Johannesburg, South Africa) was used to record the coordinates for each of the sampling points. The pump was operated for at least 5 min to allow the water to flush the fittings and pipes. Then, each sample of water was collected by allowing the water from the pump to flow directly into the sample bottle. The bottle cap and cover were carefully replaced. All the water samples were collected in 500 mL polyethylene bottles and carried to our Centre for Water Sciences and Management laboratory. Two of the boreholes in Mafikeng, sample SM7 and SM9, were 40 m deep, and the borehole SM10 was 30 m deep. The samples were not acidified, as this would have affected the isotopic composition of the water.

2.4. Quality Control and Quality Assurance

The water samples were taken for analysis to the Center for Water Sciences and Management at NWU Potchefstroom Campus, South Africa. For the assessment of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, all the water samples were evaluated using a cavity ring-down spectrometer with laser-current-tuned cavity resonance (Picarro L2130-*i* Isotope H_2O , Picarro Inc., Santa Clara, CA, USA) [12]. To calibrate and monitor the equipment, three internal laboratory standards (Picarro Inc., Santa Clara, CA, USA), developed at Picarro's stable isotope laboratory—Picarro Zero ($\delta^{18}\text{O} = 0.3\text{‰}$, $\sigma \pm 0.2\text{‰}$; $\delta^2\text{H} = 1.8\text{‰}$, $\sigma \pm 0.9\text{‰}$), Picarro Mid ($\delta^{18}\text{O} = -20.6\text{‰}$, $\sigma \pm 0.2\text{‰}$; $\delta^2\text{H} = -159.0\text{‰}$, $\sigma \pm 1.3\text{‰}$), and Picarro Depl ($\delta^{18}\text{O} = -29.6\text{‰}$, $\sigma \pm 0.2\text{‰}$; $\delta^2\text{H} = -235.0\text{‰}$, $\sigma \pm 1.8\text{‰}$)—were evaluated after every 20 water samples. The Picarro standards were calibrated against the Vienna Standard Mean Ocean Water (VSMOW) standard. Nine injections per sample vial were analyzed using an SGE 10 μL syringe (Picarro Inc., Santa Clara, CA, USA), and the average of the last 4 replicates was recorded by the Isotopic Water Analyzer Software (Picarro Inc., Santa Clara, CA, USA).

3. Results and Discussion

3.1. Results for IAEA WICO Samples

The plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ for the WICO water samples is shown in Figure 2. These results, obtained from the Picarro L2130-*i*, were sent to Vienna for verification against the IAEA reference standard. As seen from Table 1, the results obtained for the d-excess were

in a satisfactory range and the margins of error were close to those required by the IAEA. From the isotope composition values, we can conclude that the water samples OH-26, OH-28, and OH-30 may have been collected from vapor, while the water samples OH-25 and OH-27 may have been collected from rain and OH-29 may have been collected from the ocean [20]. The precision of our $\delta^2\text{H}$ measurement is satisfactory and comparable to the IAEA reference values, as shown in Table 1.

Figure 2. Plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ for the IAEA WICO 2020 samples.

Table 1. Evaluation of the d-excess for the IAEA WICO samples compared to the IAEA reference standard.

Sample	Reference Value			Submitted Result		Evaluation			Comment
	$\delta^2\text{H}$	Unc.	σp	$\delta^2\text{H}$	Unc.	D	z-test	ζ -test	
OH25	6.4	0.2	1.1	6.0	0.3	−0.4	−0.34	−1.14	-
OH26	11.6	0.2	1.1	11.4	0.2	−0.2	−0.14	−0.57	-
OH27	8.3	0.3	1.1	7.4	0.4	−0.9	−0.80	−1.92	-
OH28	14.6	0.4	1.1	14.1	0.6	−0.5	−0.49	−0.75	-
OH29	10.2	0.2	1.1	10.6	0.3	0.3	0.30	0.92	-
OH30	11.8	0.3	1.1	11.9	0.3	0.1	0.08	0.20	-

Colour Codes			Overall performance		
	Satisfactory		Avg $ z $ $\delta^2\text{H}$	0.36	-
	Questionable		Avg $ \zeta $ $\delta^2\text{H}$	0.92	-
	Unsatisfactory		SD of D $\delta^2\text{H}$	0.45	-

From the supplementary file (Tables S1–S5, Figures S1–S4), our results for $\delta^{18}\text{O}$ show a good accuracy but poor precision ($|z| < 2$ and $|\zeta| \geq 3$). However, the overall performance is satisfactory, although we may have underestimated or overlooked some relevant sources of uncertainty. $|\zeta| \geq 3$ shows that the precision was overestimated for one or more of the samples analyzed.

The s-plots for the $\delta^{18}\text{O}$ results in Figure 3 show that the difference between the measured and the “true” values, expressed in terms of the z-scores, lies between 2 and −2 and that the results are in the satisfactory (green) range. Thus, the $\delta^{18}\text{O}$ results obtained with the Picarro were consistent with the six WICO 2020 inter-comparison samples [21].

Figure 3. The s-plots vs the mean $|z|$ score for the $\delta^{18}\text{O}$ of the IAEA WICO samples OH-28–OH-30. Mean $|z|$ scores below the green line show overall Satisfactory performance (i.e., mean $|z| < 2$ for either $\delta^{18}\text{O}$ and $\delta^2\text{H}$). A result falling above the orange line is considered to be Unsatisfactory overall performance (i.e., mean $|z| \geq 3$ for either $\delta^{18}\text{O}$ and $\delta^2\text{H}$).

3.2. Results for North West Villages Samples

The results in Figure 4 show the plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ for the North West villages Mafikeng, Lichtenburg, Klerksdorp, and Setlagole. The $\delta^2\text{H}$ values of the groundwater varied from -32.03‰ to -9.41‰ , and the $\delta^{18}\text{O}$ values ranged from -5.34‰ to -2.04‰ . Groundwater samples from this research location, which is located in a hot, semi-arid part of the country, are predicted to have high isotope levels of ^2H and ^{18}O . Most samples show d-excess values below 10‰ , perhaps suggesting groundwater replenished by rainfall whose moisture underwent long-term circulation in North West's warm atmosphere. Samples with a significant d-excess above 10‰ might be a sign of groundwater recharge, by way of rainfall precipitation episodes that underwent long-term circulation in colder atmospheres [22].

Figure 4 shows the isotopic composition of the groundwater. The slope, m , of the LMWL of Mafikeng (Figure 4) is similar to that of the GMWL [6] due to the closeness of the gradient (7.53 versus 8.00), while the slopes of Lichtenburg, Klerksdorp, and Setlagole are significantly lower than that of the GMWL (5.47 versus 7.06 versus 6.41 versus 8.00, respectively), reflecting the influence of evaporation under relatively semi-arid conditions. The GMWL and LMWLs are widely used as references for interpreting the isotopic composition of surface water and groundwater, respectively [23].

Figure 4. Plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ for Setlagole, Mafikeng, Lichtenburg, and Klerksdorp villages.

The groundwater samples were used to determine the LMWL (Figure 4) for the North West villages. This LMWL is used as a reference to better understand the isotopic composition that leads to the creation of water resources in this location. The average d-excess value in Figure 4 is +4.40‰, and it is within the range (−10.30‰ to +16.90‰) found by other researchers for the southern hemisphere [9,12]. This might be due to partial evaporation, occurring during storage or as the precipitation falls from the clouds. The low d-excess values are a result of higher temperatures in the area. This is in agreement with the findings of [12]. The low d-excess values could also be a result of the evaporation of surface water. The North West province of South Africa is one of the driest and hottest regions in Southern Africa. Hence, our values are in good agreement with the climatic conditions in this province.

The slope of the Local Meteoric Water Line (LMWL) of the NW villages (Figure 4) is lower than that of the Global Meteoric Water Line (GMWL), at 6.8 ± 0.03 versus 8.00. This is a result of the greater isotopic fractionation of ^{18}O than ^2H with evaporation during rainfall, possibly caused by higher temperatures during the rainy season. The samples reflected that they were of meteoric origin, and the LMWL is not very far from the Global Meteoric Water Line ($\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$) [12]. The results from all four villages show that the water samples were depleted of heavy isotopes, as shown by the low values in the equations of the LMWLs. This might be due to the fact that they were collected during a warmer season, resulting in less evaporation and precipitation. Due to evaporation and differences in the humidity of the vapor source, d-excess values can vary.

4. Conclusions and Recommendations

In this study, the water composition of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and the water isotope inter-laboratory comparison (IAEA WICO 2020) were studied. The IAEA WICO results have shown that our laboratory at the Center for Water Science and Management is capable of undertaking inter-laboratory comparisons for the IAEA. The slope of the LMWL of Mafikeng (Figure 4) is similar to that of the GMWL (7.53 versus 8), while the slopes of Lichtenburg, Klerksdorp, and Setlagole are significantly lower than that of the GMWL (5.47 versus 7.06 versus 6.41 versus 8, respectively). The slope of the Local Meteoric Water Line (LMWL) of the NW villages is lower than that of the Global Meteoric Water Line (GMWL) at 6.84 ± 0.03 versus 8.00. Thus, it might be concluded that this was caused by hot climatic conditions in the province where the samples were collected, resulting in more evaporation

and precipitation taking place. From Figure 4, the $\delta^2\text{H}$ values ranged between -33‰ and -8‰ , while the $\delta^{18}\text{O}$ values ranged between -2‰ and $+5.5\text{‰}$, and both ranges are within those found by [12], whose $\delta^2\text{H}_{\text{ground}}$ range was from -57‰ to $+5.6\text{‰}$. For $\delta^{18}\text{O}_{\text{ground}}$, the range was from -6.8‰ to $+1.1\text{‰}$. The groundwater deuterium excess (calculated as $d_{\text{ground}} = \delta^2\text{H}_{\text{ground}} - 8 \times \delta^{18}\text{O}_{\text{ground}}$) ranged between -10.3‰ and $+16.9\text{‰}$.

In the groundwater from the study area of the North West province, isotope signatures indicated that the dominant sources had undergone an evaporation process. The results revealed the percolation of surface water to the lower aquifer as the recharge mechanism for the groundwater. This baseline information could contribute to the good planning and sustainable development of water systems in the North West province.

It is recommended that this study be extended to all the provinces of South Africa. Such information is crucial to the IAEA and its member states in terms of the management of global underground water resources.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w13202801/s1>: Table S1: Results $\delta^{18}\text{O}$, Figure S1: The s-plots vs the mean $|z|$ score for the $\delta^{18}\text{O}$ of the IAEA WICO samples OH-28–OH-30, Table S2: Results $\delta^2\text{H}$, Figure S2: The s-plots vs the mean $|z|$ score for the $\delta^2\text{H}$ of the IAEA WICO samples OH-28–OH-30, Table S3: Results d-excess, Table S4: Reference Values vs. Bias, Figure S3: A plot of $\delta^{18}\text{O}$ Bias vs. reference value, Table S5: Internal Reproducibility OH-26 vs. OH-30, Figure S4: Plot of ^2H [‰] vs $\delta^{18}\text{O}$ [‰].

Author Contributions: Conceptualization, J.M., N.D.M., M.M. and S.C.N.; methodology, J.M., N.D.M., N.M., J.H. and S.C.N.; validation, I.D. and L.P.; formal analysis, J.M.; investigation, M.M.; resources, I.D.; writing—original draft preparation, J.M.; writing—review and editing, N.D.M. and S.C.N.; supervision, N.D.M. and S.C.N.; project administration, M.M. and L.P.; lab quality assurance manager, T.G.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in the supplementary materials file.

Acknowledgments: The authors would like to acknowledge the IAEA Isotope Hydrology Laboratory for allowing them to participate in the water isotope inter-laboratory comparison (IAEA WICO 2020) and also allowing them to publish these results.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Cozma, A.I.; Baci, C.; Moldovan, M.; Pop, I.-C. Using Natural Tracers to Track the Groundwater Flow in a Mining Area. *Procedia Environ. Sci.* **2016**, *32*, 211–220. [\[CrossRef\]](#)
- Kumar, A.; Sanyal, P.; Agrawal, S. Spatial distribution of $\delta^{18}\text{O}$ values of water in the Ganga river basin: Insight into the hydrological processes. *J. Hydrol.* **2019**, *571*, 225–234. [\[CrossRef\]](#)
- Kendall, C.; McDonnell, J.J. Preface. In *Isotope Tracers in Catchment Hydrology*; Kendall, C., McDonnell, J.J., Eds.; Elsevier: Amsterdam, The Netherlands, 1998; pp. vii–ix.
- McGuire, K.; McDonnell, J. Stable Isotope Tracers in Watershed Hydrology. In *Stable Isotopes in Ecology and Environmental Science*; Wiley-Blackwell: Johannesburg, South Africa, 2007; pp. 334–374.
- Chiogna, G.; Skrobaneck, P.; Narany, T.S.; Ludwig, R.; Stumpp, C. Effects of the 2017 drought on isotopic and geochemical gradients in the Adige catchment, Italy. *Sci. Total Environ.* **2018**, *645*, 924–936. [\[CrossRef\]](#) [\[PubMed\]](#)
- Craig, H. Isotopic Variations in Meteoric Waters. *Science* **1961**, *133*, 1702–1703. [\[CrossRef\]](#) [\[PubMed\]](#)
- Froehlich, K.; Gibson, J.; Aggarwal, P. *Deuterium Excess in Precipitation and Its Climatological Significance*; International Atomic Energy Agency (IAEA): Vienna, Austria, 2002.
- Bershaw, J.; Hansen, D.D.; Schauer, A.J. Deuterium excess and ^{17}O -excess variability in meteoric water across the Pacific Northwest, USA. *Tellus B Chem. Phys. Meteorol.* **2020**, *72*, 1–17. [\[CrossRef\]](#)
- Pfahl, S.; Sodemann, H. What controls deuterium excess in global precipitation? *Clim. Past* **2014**, *10*, 771–781. [\[CrossRef\]](#)
- Bagheri, R.; Karami, G.; Jafari, H.; Eggenkamp, H.G.M.; Shamsi, A. Isotope hydrology and geothermometry of the thermal springs, Damavand volcanic region, Iran. *J. Volcanol. Geotherm. Res.* **2019**, *389*, 106745. [\[CrossRef\]](#)

11. Rao, S.M.; Kulkarni, K.M. Isotope hydrology studies on water resources in western Rajasthan. *Curr. Sci. (Bangalore)* **1997**, *72*, 55–61.
12. West, A.G.; February, E.C.; Bowen, G.J. Spatial analysis of hydrogen and oxygen stable isotopes (“isoscapes”) in ground water and tap water across South Africa. *J. Geochem. Explor.* **2014**, *145*, 213–222. [[CrossRef](#)]
13. Ahmad, M.; Aggarwal, P.; Duren, M.v.; Poltenstein, L.; Araguas, L.; Kurttas, T.; Wassenaar, L.I. *Final Report on Fourth Interlaboratory Comparison Exercise for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ Analysis of Water Samples (WICO2011)*; IAEA: Vienna, Austria, 2012; p. 67.
14. Terzer-Wassmuth, S.; Ortega, L.; Araguás-Araguás, L.; Wassenaar, L.I. The first IAEA inter-laboratory comparison exercise in Latin America and the Caribbean for stable isotope analyses of water samples. *Isot. Environ. Health Stud.* **2020**, *56*, 391–401. [[CrossRef](#)] [[PubMed](#)]
15. Carney, J.N.; Aldiss, D.T.; Lock, N.P. *The Geology of Botswana*; Geological Survey Dept.: Lobatse, Botswana, 1994.
16. Duraisamy, S.; Govindhaswamy, V.; Duraisamy, K.; Krishinaraj, S.; Balasubramanian, A.; Thirumalaisamy, S. Hydrogeochemical characterization and evaluation of groundwater quality in Kangayam taluk, Tirupur district, Tamil Nadu, India, using GIS techniques. *Environ. Geochem. Health* **2019**, *41*, 851–873. [[CrossRef](#)] [[PubMed](#)]
17. Dedzo, M.G.; Tsozué, D.; Mimba, M.E.; Teddy, F.; Nembungwe, R.M.; Linida, S. Importance of Rocks and Their Weathering Products on Groundwater Quality in Central-East Cameroon. *Hydrology* **2017**, *4*, 23. [[CrossRef](#)]
18. Steinhilber, E.; Salbu, B. *Trace Elements in Natural Waters*; CRC Press: Boca Raton, FL, USA, 1995.
19. Dallas, H.; Fowler, J. *Delineation of River Types for Rivers of Mpumalanga, South Africa: The Establishment of a Spatial Framework for the Selection of Reference Sites*; Southern Waters Ecological Research and Consulting: Cape Town, South Africa, 2000.
20. Jung, H.; Koh, D.-C.; Kim, Y.S.; Jeon, S.-W.; Lee, J. Stable isotopes of water and nitrate for the identification of groundwater flowpaths: A review. *Water* **2020**, *12*, 138. [[CrossRef](#)]
21. IAEA. *WICO 2020 $\delta^{18}\text{O}/\delta^2\text{H}$ Intercomparison Test Laboratory Report*; IAEA: Vienna, Austria, 2020.
22. Leketa, K.; Abiye, T. Using Environmental Tracers to Characterize Groundwater Flow Mechanisms in the Fractured Crystalline and Karst Aquifers in Upper Crocodile River Basin, Johannesburg, South Africa. *Hydrology* **2021**, *8*, 50. [[CrossRef](#)]
23. Tessema, A.; Nzotta, U.; Chirenje, E. *Assessment of Groundwater Potential in Fractured Hard Rocks around Vryburg; North West Province, South Africa, WRC Project*; Water Research Commission: Pretoria, South Africa, 2014.