

Article

Characterisation of Hydro-Geochemical Processes Influencing Groundwater Quality in Rural Areas: A Case Study of Soutpansberg Region, Limpopo Province, South Africa

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Abstract: Groundwater is often the main or only source of fresh water supply in arid to semi-arid rural areas owing to decreasing rainfall patterns, reduced availability of surface water and socioeconomic activities. It is important to understand the hydro-geochemical processes influencing groundwater quality for improved management and sustainability of resources and to improve rural livelihoods. To understand the hydro-geochemical process influencing the hydro-geochemistry of the Soutpansberg region, this study assessed groundwater quality data from 12 boreholes and 2 geothermal springs collected between 1995 and 2017. This study indicated that the majority of the samples were classified as fresh groundwater dominated by Ca-HCO₃ and mixed Ca-Mg-Cl types. Gibbs diagrams, Pearson correlations, bivariate plots and saturation indexes suggested that rock dominance processes, such as weathering of silicates, dissolution of carbonates and halite minerals and ion exchange processes, were the main hydro-geochemical processes influencing the groundwater quality in the Soutpansberg region. The high concentration of F⁻ in the geothermal spring was attributed to the dissolution of fluorite mineral. Point source anthropogenic inputs from fertilisers were attributed to the high concentration of NO₃⁻ in the groundwater. This study recommends that research outputs should be used to influence and support policy change and groundwater allocation in arid to semi-arid rural environments for improved management of resources and livelihoods. This study further recommends that suitable defluoridation and denitrification techniques be applied to improve the quality of groundwater for drinking purposes.

Keywords: hydro-geochemical processes; hydro-geochemistry; groundwater protection policy; remediation



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1. Introduction

Groundwater has emerged as the major or only source of fresh water in many arid and semi-arid parts of the world for domestic use resulting from decreasing rainfall patterns, reduced availability of surface water and socioeconomic activities [1–3], and this is the case in the rural, semi-arid region of Soutpansberg. Groundwater interacts with aquifer materials resulting in variation of hydro-geochemical processes that may change the chemical components of groundwater during the hydrological process of recharge and transport [4]. Over the past few years, many countries across the world have been trying to improve drinking water accessibility and quality in relation to United Nation's Sustainable Development Goals (SDGs) [5,6]. For instance, a study conducted in Greece suggested ways of improving the quality of nitrate (NO₃⁻)-contaminated groundwater [7]. To limit the excessive usage of nitrogen fertilisers, the study suggested that engaging farmers, managed aquifer recharge (MAR) and installation of a monitoring network can assist in improving groundwater quality and achieving the Sustainable Development

Goals [7]. To improve access to clean drinkable groundwater, there is a need to understand the hydro-geochemical processes influencing groundwater quality and determine or develop baseline/standards or reference points so that we can assess the improvement in the deterioration of ambient groundwater quality instead of comparisons to tap water standards, e.g., [8] globally and [9] in South Africa. Several studies have been carried out to assess these hydro-geochemical processes influencing groundwater to understand various aquifers and improve water resource management. For instance, one study [10] determined that simple mixing, weathering and dissolution of silicates, carbonates and ion exchange are among the hydro-geochemical processes controlling groundwater quality in semi-arid Delhi, India. In the arid city of Sohag (Egypt), Abdelshafy et al. [11] used various methods to determine that precipitation processes and dissolution of halite minerals influenced groundwater quality. One study [12] classified groundwater as a Na-SO₄ type and determined that the major processes responsible for hydro-geochemistry were weathering of silicates and carbonates minerals, return flow from irrigation, domestic wastewater and ion exchange in the Jordan Valley. Another study [13] determined that weathering of rock forming minerals and contributions from anthropogenic activities were the main processes influencing the groundwater quality in semi-arid China. Various studies in semi-arid regions concur with these findings [14–17]. Varying techniques were applied in various studies to understand hydro-geochemical processes influencing groundwater quality across the world in the last decade [18–23]. Factors such as the local lithology, leaching, climatic conditions and anthropogenic activities (pit-latrines and irrigation) influence groundwater quality [24,25]. The purpose of this study was to identify hydro-geochemical processes influencing groundwater quality in rural areas within the Soutpansberg region. Identifying these processes will lead to a better understanding of the aquifers and assist in determining groundwater quality baseline/standards or reference points for various parameters. This is important as ambient groundwater quality is being compared to tap water standards, such as in [8,9], to determine the level of pollution in groundwater. Achieving the Sustainable Development Goals will not be possible if ambient groundwater quality continues to be compared with tap water standards, as groundwater is mainly controlled by lithology associated with host aquifer materials. This study argues that without understanding the hydro-geochemical processes and developing groundwater standards, it will be a challenge to manage and protect groundwater resources and determine the best possible groundwater remediation techniques for rural areas.

2. Description of the Study Area

The Soutpansberg region is located in the Vhembe District of the northern part of Limpopo Province, South Africa (Figure 1). The area lies between 250 and 1719 m above mean sea level and covers approximately 3099.6 km². In terms of climatic settings, Soutpansberg is in an arid region of South Africa with an average rainfall of 497.7 mm/a based on South African Weather Services (SAWS) data from 1980 to 2020. In terms of geological and lithological conditions, the volcanic-sedimentary Soutpansberg Group deposits from approximately 1800 million years ago dominate the area [26]. The Soutpansberg Group consists of the Tshifhefhe, Sibasa, Fundudzi, Wyllies Poort and Nzhelele formations [27]. The Sibasa Formation consists of approximately 3300 m of tholeiitic basalts, while the Fundudzi, Wyllies Poort and Nzhelele formations consist of arenaceous and minor argillaceous with volcanic materials [28]. A lithological map of Soutpansberg is presented in Figure 2, where ZQMPMA1, ZQMTVU1, ZQMGGG1, ZQMDMI1, ZQMHVE1 and ZQMWRT1 are situated in meta-arenaceous rocks such as quartzite, gneiss, migmatite and granulite. ZQMLV11 and ZQMKNW2 are hosted by arenaceous rocks such as sandstone, feldspathic sandstone and arkose. Mafic/ultramafic extrusive rocks, such as basalt and andesite, host ZQMMW11, ZQMTSU1, ZQMLRT1 and ZQMMBI1. The geothermal spring ZQMSOU1 is hosted by alluvium materials and ZQMTPS2 is hosted by various mixed lithologies (Figure 2). The 12 boreholes and 2 springs are within a shallow aquifer (1.5 to 36 m below ground level), where 148.3 Mm³/a of groundwater has been allocated for water supply, domestic use

and irrigation purposes. Soutpansberg region is dominated by a fractured aquifer type with an average yield ranging from 0.5–5 L/s. The majority of the groundwater quality monitoring sites are in this fractured aquifer type, while others are hosted by inter-granular and fractured aquifers with an average yield between 0.5 and 5 L/s.

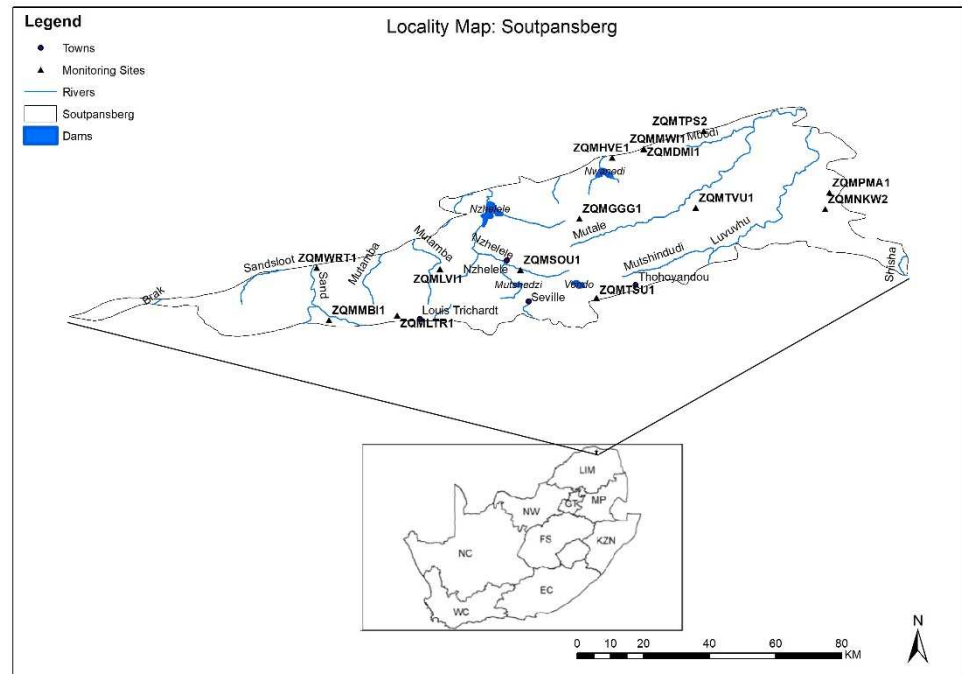


Figure 1. Locality map of the Soutpansberg region with the existing groundwater monitoring stations.

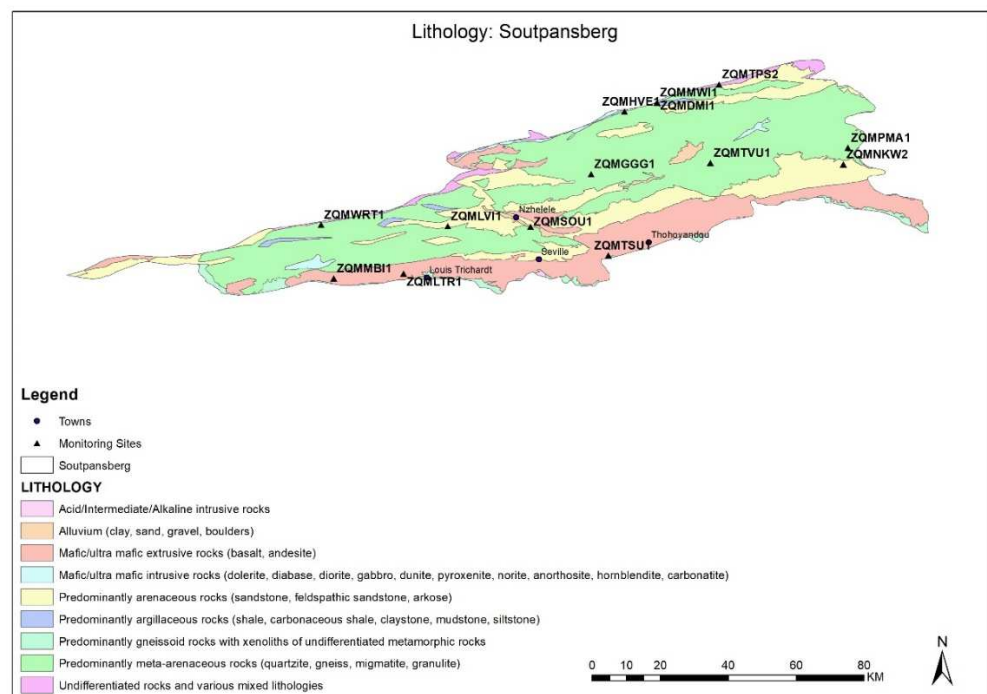


Figure 2. Lithological settings of the Soutpansberg region.

3. Material and Methods

3.1. Sampling

Physio-chemical parameters, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), bicarbonate (HCO_3^-), chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-),

silica (SiO₂), sulphate (SO₄²⁻), total dissolved solids (TDS), pH and electrical conductivity (EC), were determined from 1995 to 2017 twice a year (i.e., wet and dry seasons) from 12 boreholes and 2 springs (124 samples). EC, T, pH and TDS were measured using a YSI Professional Multi-parameter probe. These groundwater samples were collected as part of an active national groundwater quality monitoring network using sampling methods derived from [29]. Boreholes were purged until temperature, EC and pH stabilised to obtain a representative sample from the aquifer. The groundwater was collected using 500 mL polyethylene sampling bottles. The samples were analysed at the Department of Water and Sanitation's (DWS) laboratory. Cations were analysed using inductively coupled plasma mass spectrometry (ICP-MS), while anions were analysed using ion chromatography. Historical data were available from the DWS's water management system (WMS) as record reviews. To determine the precision, accuracy and reliability of the data, the ion balance error (IBE) was calculated for all samples and determined to be between 0 and 9%, lower than 10% [30].

3.2. Determination of Hydro-Geochemical Processes Influencing Groundwater Quality

Mean values for each parameter per site were used to assess the hydro-geochemical process influencing groundwater quality. Microsoft Excel was used for statistical analysis of the groundwater quality data. A Piper trilinear diagram [31] was used to understand the water type and hydro-geochemical facies for the 14 groundwater monitoring sites in the Soutpansberg region. A Gibbs diagram [32] was used to understand water–rock interaction using Equations (1) and (2) in milliequivalent per litre (meq/L). Schoeller's [33] chloro-alkaline indices (CAIs) method was used to understand interactions between groundwater and host rocks. The CAI was calculated in milliequivalent per litre (meq/L) using Equations (3) and (4). Geochemical modelling was conducted using PHREEQC (version 2) [34]. PHREEQC was used to understand the groundwater saturation state based on the saturation index (SI) in [35]. The saturation index indicates the tendency of minerals to precipitate (SI = positive), dissolve (SI = negative) and achieve equilibrium (SI = 0) in water. Ionic concentration ratios, such as Na⁺ vs. Cl⁻, Ca²⁺ + Mg²⁺ vs. Na⁺, Ca²⁺ + Mg²⁺/(HCO₃⁻ + SO₄²⁻), Na⁺/Cl⁻ vs. EC, Ca²⁺ vs. HCO₃⁻ and Ca²⁺ vs. SO₄²⁻, were calculated to understand hydro-geochemical processes.

$$\text{Gibbs ratio - I} = \frac{\text{Cl}^-}{\text{Cl}^- + \text{HCO}_3^-} \quad (1)$$

$$\text{Gibbs ratio - II} = \frac{\text{Na}^+ + \text{K}^+}{\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+}} \quad (2)$$

$$\text{CAI - I} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{\text{Cl}^-} \quad (3)$$

$$\text{CAI - II} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{\text{SO}_4^{2-} + \text{HCO}_3^- + \text{NO}_3^{2-}} \quad (4)$$

4. Results and Discussions

4.1. Hydro-Geochemistry

Table 1 shows the mean results of the major ions and physical parameters in this study area for each groundwater monitoring sites. pH is one the main parameter used to determine if water is acidic (pH < 7), neutral (pH = 7) or alkaline (pH > 7) [36]. In the study area, the average pH ranged from 7.7 to 9.3, which indicated that the groundwater was alkaline. The nature of the alkalinity can be attributed to the high concentrations of Na⁺, Mg²⁺, Ca²⁺ and HCO₃⁻ from the lithological settings in the Soutpansberg such as mafic–ultramafic igneous rocks. TDS classification by Freeze and Cherry [37] indicated that 85.7% of the monitoring sites were classified as fresh (TDS < 1000 mg/L), and 14.3% of the sites were classified as brackish. ZQMMB11 (Mafic–ultramafic extrusive rocks),

hosted by an intergranular-fractured aquifer (0.5–2 L/s), and ZQMPMA1 (meta-arenaceous rocks), hosted by a fractured aquifer (0.5–2 L/s), were the two monitoring sites that were classified as brackish (TDS > 1000–10,000 mg/L). The major cation dominance order in Soutpansberg was $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$, and for major anions it was $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$. Sodium (Na^+), as a dominant cation, ranged from 12 (ZQMWR1) to 424 mg/L (ZQMPMA1). Calcium (Ca^{2+}) ranged from 2 (ZQMTPS2) to 86 mg/L (ZQMPMA1), while Mg^{2+} ion ranged from 1 (ZQMTPS2) to 118 mg/L (ZQMMBI1). In terms of major anions, the dominant HCO_3^- ranged from 28 (ZQMTVU1) to 455 mg/L at ZQMMBI1 (Table 1). Concentration of Cl^- ranged from 5 (ZQMDMI1) to 664 mg/L (ZQMMBI1), while the NO_3^- concentration ranged from 0 to 22 mg/L (ZQMMBI1). Fluoride (F^-) was highly concentrated in the geothermal spring ZQMSOU1 with an average of 2.5 mg/L. The high F^- concurs with a previous study in ZQMSOU1 and the surrounding area of Siloam that showed the high concentration resulted from fluorite mineral associated with igneous and sedimentary rocks in the area [38]. Dental fluorosis resulting from a high F^- concentration in groundwater already poses health risks in the Siloam area where ZQMSOU1 is located [38]. The geothermal spring (ZQMTPS2) mineralisation with respect to Ca^{2+} and Mg^{2+} was very low, owing to association with deep ancient groundwater. The groundwater from ZQMPMA1 was highly mineralised in relation to Na^+ , Cl^- , HCO_3^- and Ca^{2+} , which could indicate a strong water–rock interaction, and the groundwater is expected to be saline, as the TDS was >1000 mg/L (brackish). High NO_3^- in groundwater is associated with leachate from landfill, the application of fertilisers and leakage from septic tanks/sewage, and this can pose health risks in infants such as baby blue syndrome [17]. Fertilisers are not only responsible for depositing NO_3^- in groundwater but also for Mg^{2+} , Ca^{2+} , Cl^- and K^+ , and this may alter groundwater quality [39]. Application of various types of fertilisers and usage of pit latrines is common in the Soutpansberg region.

Table 1. Physico-chemical results used for various analyses.

Site ID	pH	T	EC	TDS	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	HCO_3^-	NO_3^-	SiO_2	F^-	SO_4^{2-}
ZQMPMA1	7.9	27	279	1810	86	61	424	2	664	452	0	30	0.5	22
ZQMSOU1	8.2	39	36	262	12	10	45	2	33	119	1	22	2.5	10
ZQMTPS2	9.3	45	34	231	2	1	66	2	39	84	0	34	0.7	19
ZQMLRT1	8.3	22	88	697	43	47	76	4	76	335	7	21	0.4	14
ZQMINKW2	7.7	24	20	125	8	7	16	1	25	50	1	17	0.1	4
ZQMDMI1	8.4	22	89	633	53	40	68	3	146	227	5	11	0.4	25
ZQMHVE1	8.2	26	48	328	15	9	64	2	55	122	2	19	0.8	26
ZQMMBI1	8.3	26	202	1418	64	118	175	8	334	455	22	30	0.3	65
ZQMMWI1	8.5	24	70	494	41	29	59	3	109	183	2	10	0.7	20
ZQMGGG1	8.1	24	123	905	50	77	97	4	192	322	15	26	0.4	24
ZQMWR1	8.4	23	22	155	12	11	12	1	20	74	1	11	0.1	5
ZQMTSU1	8.2	25	25	180	16	12	13	1	15	87	3	25	0.3	2
ZQMTVU1	7.8	26	28	179	13	10	22	1	29	28	15	7	0.2	2
ZQMLVI1	8.3	25	50	360	30	25	32	1	62	156	2	18	0.3	12
Min	6.7	13	5	33	1	1	3	0	5	5	0	2	0	1
Max	9.6	47	287	1869	99	154	460	10	755	612	37	58	3	71
Mean	8.4	31	59	372	22	23	65	2	75	170	4	23	1	14
Median	8.3	28	36	248	13	10	59	2	34	109	1	22.0	0	11
Detection limit	2	0	1	1	1	1	2	0.1	3	4	0.01	0.4	0.1	0.8

4.2. Hydro-Geochemical Processes

In the study area, a variety of water types were determined (Figure 3), where the dominant water types were Ca- HCO_3 (35.7%) and mixed Ca-Mg-Cl (35.7%) water types. Ca- HCO_3 is classified as typical shallow, fresh and recently recharged groundwater. The majority of samples (besides ZQMLRT1) in the Ca- HCO_3^- class were in the shallow aquifer with a depth-to-water level of <15 m below ground level (mbgl), and this supports that this is shallow, fresh and recently recharged water. In the mixed Ca-Mg-Cl water type, alkaline earth cations (i.e., Mg^{2+} and Ca^{2+}) were dominant over the HCO_3^- . Samples in the mixed Ca-Mg-Cl water type were situated between 16 and 37 mbgl. The least dominant water types were Na-Cl (14.3%) and mixed Ca-Na- HCO_3 (14.3%). ZQMPMA1 and ZQMHVE1 were classified as a Na-Cl water type, which is typical of deep ancient groundwater where alkali cations ($\text{Na}^+ + \text{K}^+$) dominate over Mg^{2+} and Ca^{2+} . The Na-Cl water type in Soutpans-

berg was hosted in shallow aquifers with groundwater depths <15 mbgl, and this may indicate other factors, such as shallow weathering of host rocks, than deep ancient groundwater. Mafic–ultramafic extrusive hosted groundwater was classified as more Ca-HCO₃ than others. The geothermal springs (i.e., ZQMSOU1 and ZQMTPS2) in Soutpansberg were classified as a mixed Ca-Na-HCO₃ water, which is typical of deep groundwater influenced by ion exchange. Minerals rich in Mg²⁺, Ca²⁺, Na⁺, Cl⁻ and HCO₃⁻ influence groundwater quality in the Soutpansberg region. It is therefore clear that ion exchange and water–rock interactions between fresh groundwater, deep ancient groundwater and deep geothermal springs influence the groundwater quality in the Soutpansberg region. Studies conducted in arid regions, such as in [10], also determined that alkali earth minerals influence groundwater quality. ZQMTSU1 was classified as Ca-HCO₃ (typical of fresh and recently recharged water) with a mean NO₃⁻ of 15 mg/L. This could indicate that a high concentration of NO₃⁻ is associated with anthropogenic activities such as pit latrines, animal waste and irrigation leaching from the topsoil during recharge processes. Boreholes classified as Ca-HCO₃ contained very low mineralisation in terms of major ions, further indicating that this was fresh and recently recharged groundwater. The majority of samples were dominated by alkali earth mineral HCO₃⁻, which suggests the possibility of carbonate and silicate weathering and ion exchange processes in groundwater [40,41]. Previous studies in parts of the Soutpansberg Basin [21] indicated that Na-Cl was the major groundwater facies and, in this study, only 14.3% of the samples were classified as Na-Cl. The difference in Na-Cl can be attributed to the fact that this study covered a larger area of Soutpansberg compared to the study in [21]. A study carried out in similar climatic conditions in China [42] also determined that the groundwater type in a shallow aquifer was Ca-HCO₃⁻. Various researchers across the world have used a Piper diagram to understand and determine the hydro-geochemical processes influencing groundwater quality [43–45].

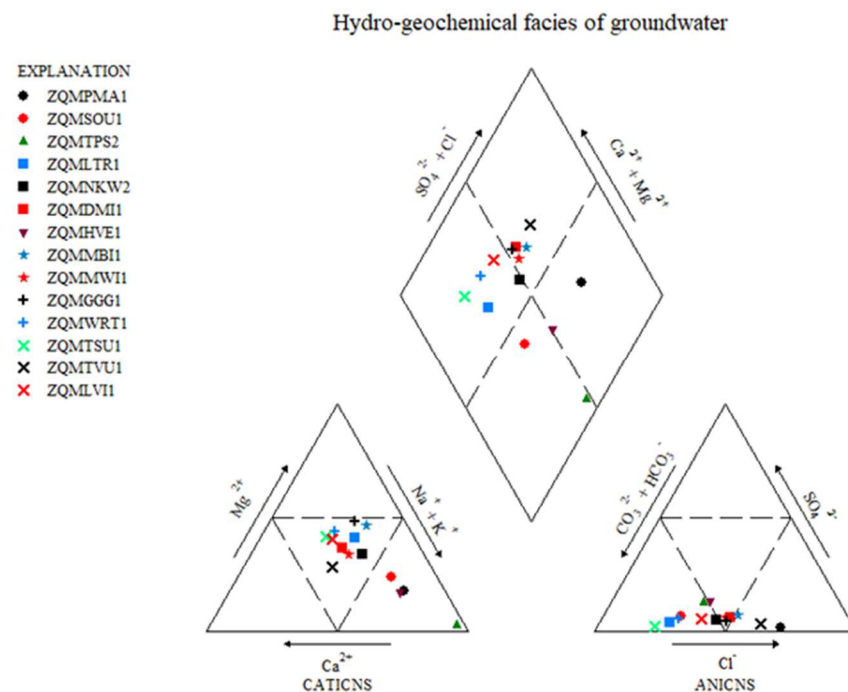


Figure 3. Piper diagram indicating the water types in the Soutpansberg region.

A Gibbs diagram [32] is based on two diagrams (Figure 4a,b) and Equations (1) and (2) where the relationships between TDS and the ratio of cations $(\text{Na}^+ + \text{K}^+)/(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ and the ratio of anions $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ are evaluated to determine the main factors controlling groundwater quality. Samples in the Soutpansberg region lie in the rock dominance zone (Figure 4a,b). This indicates that the primary factor controlling

groundwater quality in Soutpansberg was the weathering of host rock and aquifer minerals. This finding also concurs with other studies in similar climatic conditions, such as in [42,46], that determined that weathering of aquifer minerals influenced groundwater quality. All samples had a $\text{Na}^+ + \text{Cl}^- / (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ ratio >0.5 , and this suggest ion exchange also controls groundwater quality [41]. This finding is similar to those in Tshikondeni, which is part of the Soutpansberg Basin, that indicated that the $\text{Na}^+ + \text{Cl}^- / (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ ratio was greater than >0.5 (ion exchange) and the weathering of rocks influenced the groundwater chemistry [21].

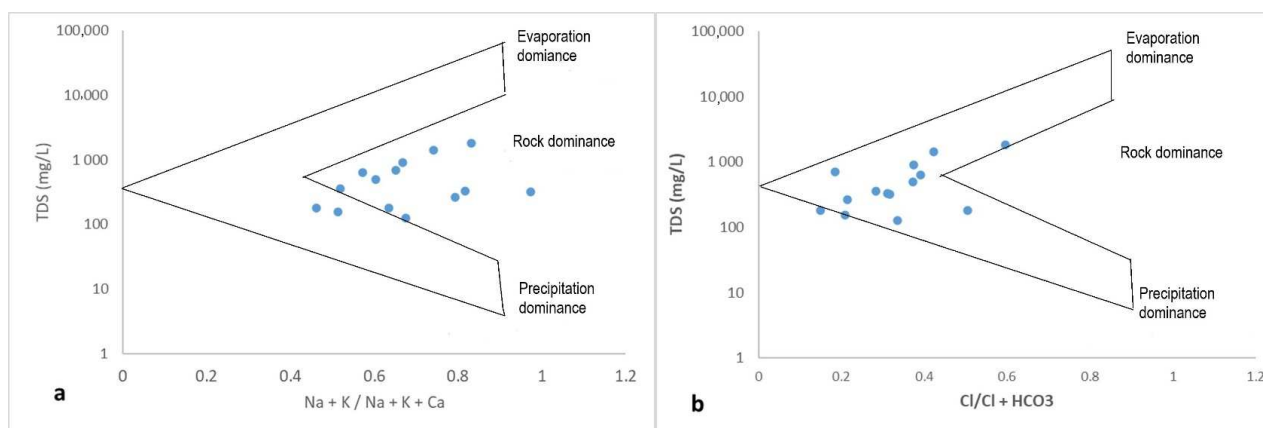


Figure 4. Gibbs diagram of the water samples collected in the Soutpansberg region where (a,b) are based on Equations (1) and (2) respectively.

In this study, the classification used in [47] was adopted, where parameters with a correlation coefficient >0.7 were considered to be strongly correlated. Parameters with correlation coefficient >0.5 to <0.7 were considered to have a moderate correlation and a correlation coefficient less than 0.5 indicated that there was no relationship between the parameters. The correlation coefficients and p -values determined in the Soutpansberg region are tabulated in Table 2 and Table S1 (Supplementary Materials), where Na^+ was strongly correlated with Cl^- (1.0), HCO_3^- (0.9) and Ca^{2+} (0.8) and moderately correlated with Mg^{2+} (0.6); this indicates the deduction of Na^+ from silicate weathering, except for the dissolution of halite [48]. HCO_3^- is highly correlated with Ca^{2+} (0.9) and Mg^{2+} (0.9) indicating that dissolution of carbonate minerals (calcite) influenced groundwater quality in the Soutpansberg region. A strong correlation ($r = 1$) between Na^+ and Cl^- indicates that these parameters originated from the same source. The correlation coefficient between TDS and EC was determined to be one (strong correlation), which suggests that the TDS can be predicted from the EC with an accuracy of 100%. Ca^{2+} was strongly correlated with EC (0.9), TDS (0.9), Mg^{2+} (0.8), Na^+ (0.8), Cl^- (0.9) and HCO_3^- (0.9), suggesting that it is a major parameter influencing groundwater quality. HCO_3^- was strongly correlated with all parameters (except pH), indicating that it plays a significant role in the hydro-geochemistry of the Soutpansberg region. If silicate weathering is the main source of Na^+ in groundwater, HCO_3^- should be the main abundant anion in groundwater [49]. In the Soutpansberg region, HCO_3^- was the most abundant anion in groundwater, indicating silicate weathering influences the groundwater quality. TDS and EC had strong relationships with all parameters, indicating that they contributed to the mineralisation of groundwater [50]. The majority of parameters (Table 2) were correlated to each other in the Soutpansberg region, and this concurs with other studies in semi-arid to arid environments [50,51] where correlation between these parameters resulted in the mineralisation of groundwater. The other sources of Mg^{2+} , Ca^{2+} , Na^+ , Cl^- , SO_4^{2-} and HCO_3^- in groundwater may be from anthropogenic activities such as irrigation [52]. A strong correlation between NO_3^- and Cl^- suggests anthropogenic inputs in groundwater [53]; however, there was a weak correlation ($r = 0.2$), indicating minimal impact of anthropogenic inputs. A correlation of TDS with

SO_4^{2-} , Cl^- , NO_3^- and Na^+ can be used to assess the impact of anthropogenic activities on the chemistry of the aquifer [54]. TDS was strongly correlated with Cl^- (1) and Na^+ (0.9), and it had a significant correlation with SO_4^{2-} (0.6), suggesting a fair contribution of anthropogenic activities and the weathering of silicates elevated Na^+ in the groundwater [55]. The concentration levels of NO_3^- was high in three samples (Table 1) and could be due to the fact of anthropogenic inputs as suggested by strong correlations with K^+ (0.8), Mg^{2+} (0.7) and SO_4^{2-} (0.6) [56]. These correlations suggest a significant contribution of livestock waste, irrigation returns and extensive use of fertilisers [57]. Insignificant correlations between Ca^{2+} (0.3), HCO_3^- (0.4) and F^- (−0.3) indicate that natural geochemical contributions to high NO_3^- in groundwater was low [58]. A negative correlation between F^- and Ca^{2+} (−0.2) was attributed to the dissolution of fluorite (CaF_2) mineral in the groundwater of a geothermal spring (i.e., ZQMSOU1) and the removal of Ca^+ through precipitation [53]. Removal of Ca^{2+} and the elevation of Na^+ in groundwater leads to F^- enrichment, as was the case with the geothermal spring [59].

Table 2. Correlation coefficients of major physiochemical parameters determined in the water samples collected from boreholes and springs located in the Soutpansberg region.

	pH	EC	TDS	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	F^-	NO_3^-
pH	1											
EC	−0.2	1										
TDS	−0.1	1.0	1									
Ca^{2+}	−0.2	0.9	0.9	1								
Mg^{2+}	−0.1	0.8	0.8	0.8	1							
Na^+	−0.2	0.9	0.9	0.8	0.6	1						
K^+	0.0	0.6	0.6	0.6	0.9	0.3	1					
Cl^-	−0.2	1.0	1.0	0.9	0.7	1.0	0.4	1				
SO_4^{2-}	0.2	0.6	0.7	0.6	0.8	0.4	0.9	0.5	1			
HCO_3^-	−0.1	0.9	0.9	0.9	0.9	0.8	0.8	0.8	0.7	1		
F^-	0.2	−0.1	−0.1	−0.2	−0.2	0.01	0.05	−0.1	0.03	−0.1	1	
NO_3^-	−0.2	0.3	0.4	0.3	0.7	0.1	0.8	0.2	0.6	0.4	−0.3	1

Bold = strong correlation ($r > 0.7$), $n = 124$.

Highly mobile Cl^- and NO_3^- ions concentration levels in groundwater are usually elevated because of agricultural activities and they are usually correlated [60]. NO_3^- can naturally occur in groundwater but at low concentration levels, and any concentration >3 mg/L can be attributed to anthropogenic inputs [61]. A strong correlation between Cl^- and NO_3^- can also suggest that the ions were derived from animals and human waste [62,63]. There was a weak correlation (0.2) between NO_3^- and Cl^- based on the Pearson correlation (Table 2), indicating that irrigation, animal and human waste were not influencing the groundwater in most parts of Soutpansberg. However, the NO_3^- vs. Cl^- correlation in ZQMTVU1 indicated a moderate correlation (0.5), suggesting agricultural inputs, animals and human waste had an impact on the high concentration of NO_3^- (15.2 mg/L). The findings were further supported by strong correlations between NO_3^- and K^+ (0.8) and Mg^{2+} (0.7), which further suggest that potassium nitrate and magnesium nitrate fertilisers used in agricultural activities to enhance plant nutrients had an impact on the hydro-geochemistry. A moderate correlation (0.6) between NO_3^- and SO_4^{2-} (Table 2) suggested that the enrichment of NO_3^- was from point source pollution [64]. All the samples with a high concentration of NO_3^- were classified as a mixed Ca-Mg-Cl type (Figure 3), and they were probably fresh and recently recharged water contaminated by nutrients in the soil during the recharge process in a shallow sedimentary aquifer. These results suggest that the input of fertilisers and, in some part, animal and human waste due to the fact of poor sanitation infrastructure in rural areas were responsible for the enrichment of NO_3^- in the groundwater of Soutpansberg, and these findings are similar to other studies in similar environments [65,66].

Bivariate plots were used to determine the main hydro-geochemical processes controlling the hydro-geochemistry of the Soutpansberg region. Hydro-geochemical reactions in aquifers control groundwater quality [67]. Cations, such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} , in groundwater are derived from water–rock interaction processes such as dissolution of carbonates and silicates minerals (i.e., anhydrite, calcite, gypsum, pyrite and evaporates of dolomites) [68]. Scatter plots and ionic ratios are used to understand hydro-geochemical processes such as reverse and forward ion exchange [67]. In the reverse ion exchange process, Na^+ ions replace Ca^{2+} and Mg^{2+} in groundwater. Na^+ ions are replaced by Ca^{2+} and Mg^{2+} in groundwater during forward ion exchange [69]. The Na^+ vs. Cl^- scatter plot of the Soutpansberg region is presented in Figure 5a. If halite dissolution was the main source of Na^+ in the groundwater, the samples should plot in a 1:1 equiline (Na^+ vs. Cl^-), and deviation from this equiline indicates that ion exchange or silicate weathering influenced the hydro-geochemistry [70]. There was a strong correlation ($R^2 = 0.9573$) between Na^+ and Cl^- (Figure 5a). Fifty percent of the sample plots on the 1:1 line indicated that dissolution of halite influenced the majority of the sites. Samples from ZQMPMA1, ZQMKNW2, ZQMWRT1, ZQMTSU1, ZQMMWI1, ZQMLVI1 and ZQMTVU1 were influenced by the dissolution of halite. Eighty percent of the Ca-HCO_3 water types and shallow aquifers were influenced by halite dissolution. Other samples deviated from 1:1, indicating other processes such as reverse ion exchange in 21.4% of the samples (ZQMDMI1, ZQMGGG1 and ZQMMBI1), where Na^+ ions replaced Ca^{2+} and Mg^{2+} in the groundwater. The dominant cation in the groundwater influenced by reverse ion exchange in the Soutpansberg region was Na^+ , and it was classified as saline. Groundwater from 28.6% (i.e., ZQMLRT1, ZQMHVE1, ZQMTPS2 and ZQMSOU1) of the plots above the 1:1 line (Figure 5a) indicate the influence from silicate weathering or forward ion exchange, where Na^+ ions were replaced by Ca^{2+} and Mg^{2+} in the groundwater. A Na^+/Cl^- ratio greater than one indicates a contribution of Na^+ in the groundwater by hydrolysis of silicates [52]. The two geothermal springs in the study were influenced by silicate weathering or forward ion exchange. The dominant ion in the samples influenced by silicate weathering was HCO_3^- , and this concurs with [49] in that HCO_3^- will be the dominant ion if weathering of silicate is the main source of Na^+ in the groundwater. Figure 5b (Na^+/Cl^- vs. EC) also indicates that the geothermal springs as well as ZQMHVE1 were influenced by weathering of silicate minerals. In Figure 5b, the ZQMLRT1 plot on the 1:1 line suggested the dissolution of halite minerals influenced the hydro-geochemistry, in contrast to Figure 5a, which suggested processes of forward ion exchange and silicate weathering; however, HCO_3^- was the dominant ion indicating that the weathering of silicate was responsible for Na^+ ions in the groundwater [49]. The remaining 10 samples (71.5%) plotted below 1, and this suggests that there was a reduction of Na^+ in the groundwater resulting from reverse ion exchange processes [69]. Seventy-five percent of the mixed Ca-Na-HCO_3 groundwater type was influenced by silicate weathering or forward ion exchange. The geothermal springs were expected to plot on the Na-HCO_3 water type (Figure 3); however, processes of forward ion exchange, where Na^+ ions were replaced by Ca^{2+} and Mg^{2+} , possibly changed the water type to Ca-Na-HCO_3 . The concentration levels of Ca^{2+} and Mg^{2+} were very low in the samples that were influenced by forward ion exchange. A Ca^{2+} against HCO_3^- scatter plot is shown in Figure 5c, where the samples that plotted on the 1:1 equiline indicate dissolution of calcite. Three samples (i.e., ZQMKNW2, ZQMWRT1 and ZQMTSU1) plotted on the 1:1 equiline, indicating dissolution of calcite. Carbonic acid (silicates) weathering seemed to influence the groundwater in five samples. There were six samples, including the geothermal springs, that plotted below the 1:1 line, indicating weathering of carbonates minerals (Figure 5c). The remaining five samples plotted above the 1:1 line, suggesting weathering of carbonic acid (silicates) minerals. If the samples plotted on the 1:1 line of Ca^{2+} vs. SO_4^{2-} (Figure 5d), this indicated gypsum/anhydrite dissolution. In the Soutpansberg region, the majority of the samples plotted above the 1:1 line, suggesting the weathering of silicate or reverse cation exchange processes influenced the groundwater quality.

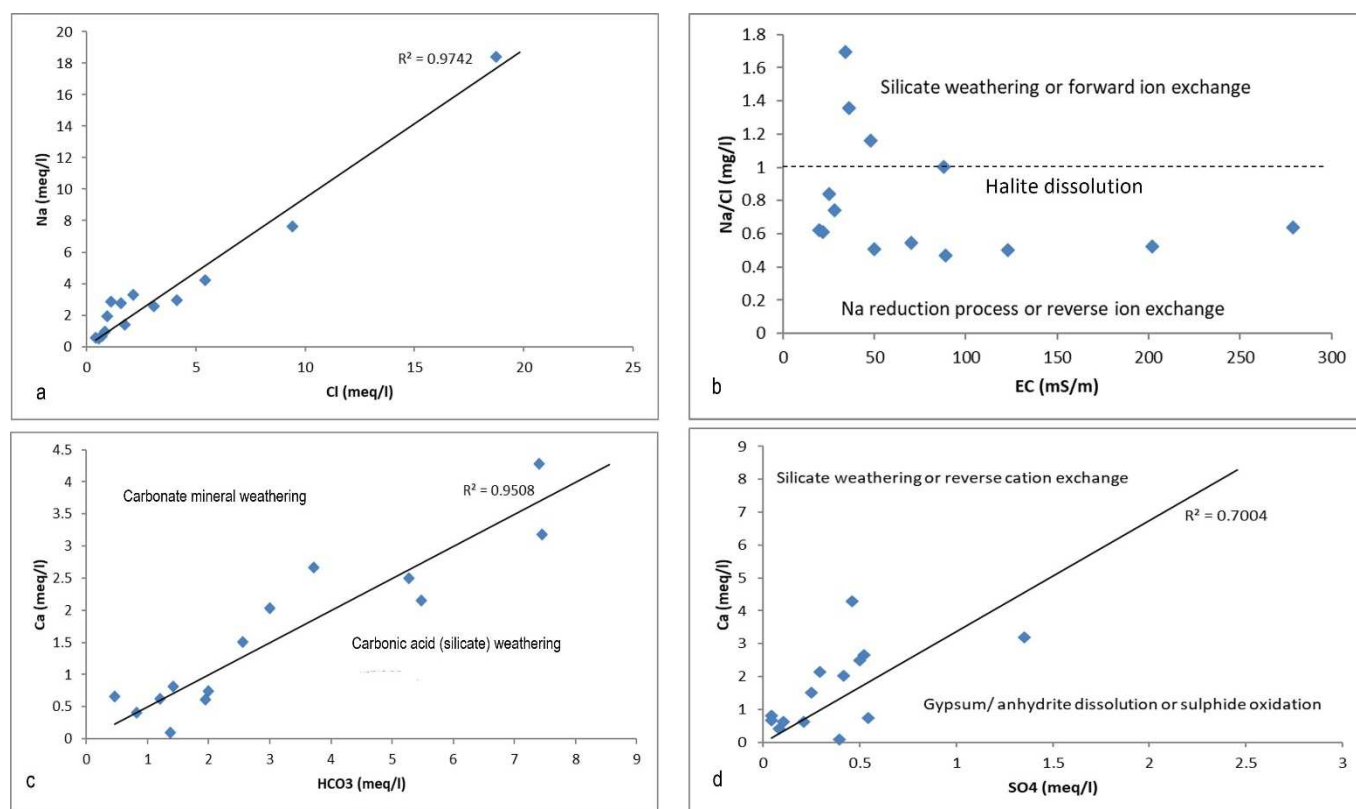


Figure 5. Scatter plots for (a) Na^+ vs. Cl^- ; (b) Na^+/Cl^- vs. EC; (c) Ca^{2+} vs. HCO_3^- ; (d) Ca^{2+} vs. SO_4^- of water collected in the Soutpansberg region.

The remaining few samples plotted on or below the 1:1 line, suggesting dissolution of gypsum/anhydrite processes controlled the hydro-geochemistry in a few samples from Soutpansberg. Figure 6a further indicates that in ZQMHVE1, ZQMTPS2 and ZQMPMA1, Na^+ ions in the groundwater were released during forward ion exchange and Ca^{2+} and Mg^{2+} ions were released during reverse ion exchange in the majority of the samples [64]. Furthermore, it is indicated in Figure 6b that Ca^{2+} and Mg^{2+} in the groundwater were not from carbonates weathering in the majority of samples but from silicate weathering. In 28.6% of the samples (i.e., ZQMTVU1, ZQMDMI1, ZQMGGG1 and ZQMMBI1), weathering of carbonate minerals was responsible for Ca^{2+} and Mg^{2+} in the groundwater. There was no obvious correlations between the hydro-geochemical processes, aquifer type and yield of aquifer in the Soutpansberg region. Schoeller [33] chloro-alkaline indices (CAI-I and CAI-II) were calculated to further authenticate the type and occurrence of ion exchange processes in groundwater regulating movements of pollutants and chemicals in soil and groundwater [4]. The CAI in the Soutpansberg region is presented in Figure 7a,b, where both CAI-I and CAI-II indicate that 50% of the samples were influenced by reverse ion exchange, and the other 50% were influenced by forward ion exchange (Table 2). These findings indicate that both reverse and forward ion exchange processes played an important role in influencing the groundwater. Ions, such as Na^+ , Ca^{2+} , Mg^{2+} and HCO_3^- , are important in controlling the hydro-geochemistry in the Soutpansberg region. The influence of anthropogenic activities were further indicated in Figure 8a,b, where correlation of NO_3^- against K^+ ($R^2 = 0.572$) and Mg^{2+} ($R^2 = 0.5123$) suggested that usage of fertilisers enriched the NO_3^- concentration in ZQMGGG1 (15.4 mg/L), ZQMMBI1 (22.3 mg/L) and ZQMTVU1 (15.2 mg/L).

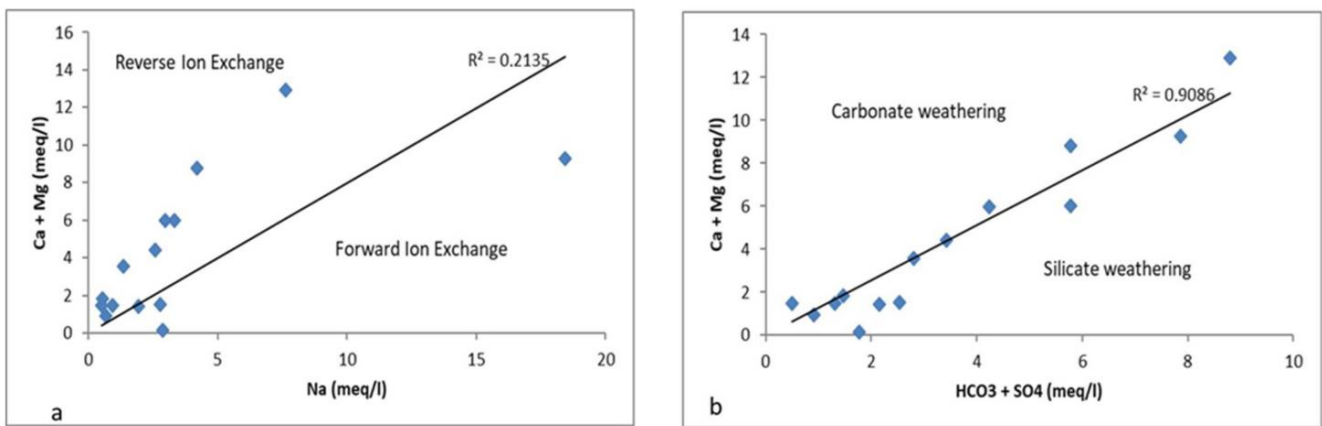


Figure 6. Scatter plots for (a) $Ca^{2+} + Mg^{2+}/Na^{+}$ and (b) $Ca^{2+} + Mg^{2+}/HCO_3^{-} + SO_4^{-}$ of water collected in the Soutpansberg region.

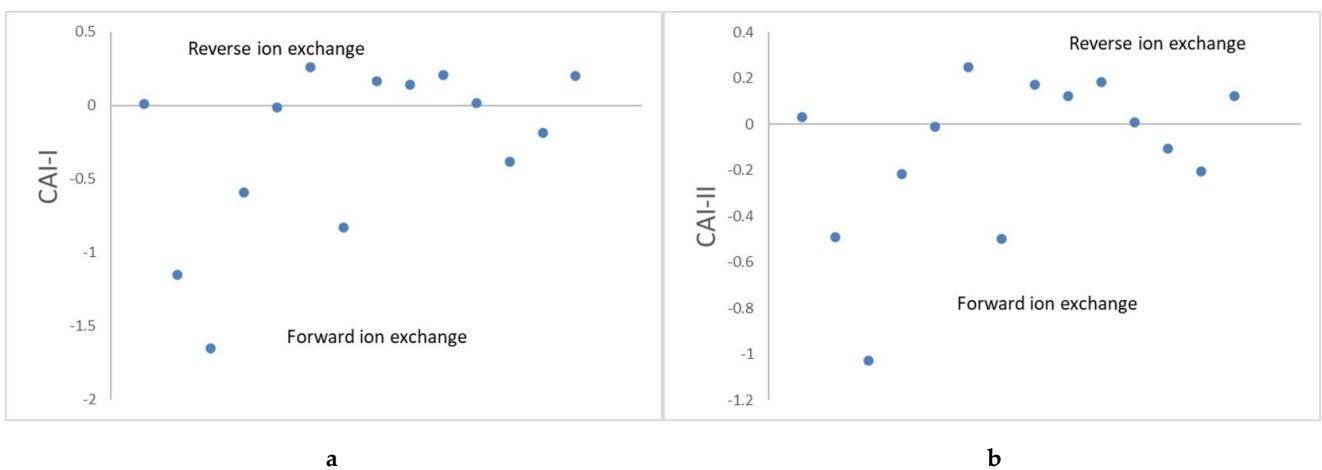


Figure 7. Schoeller [33] (a) CAI-I and (b) CAI-II plots of water collected in the Soutpansberg region.

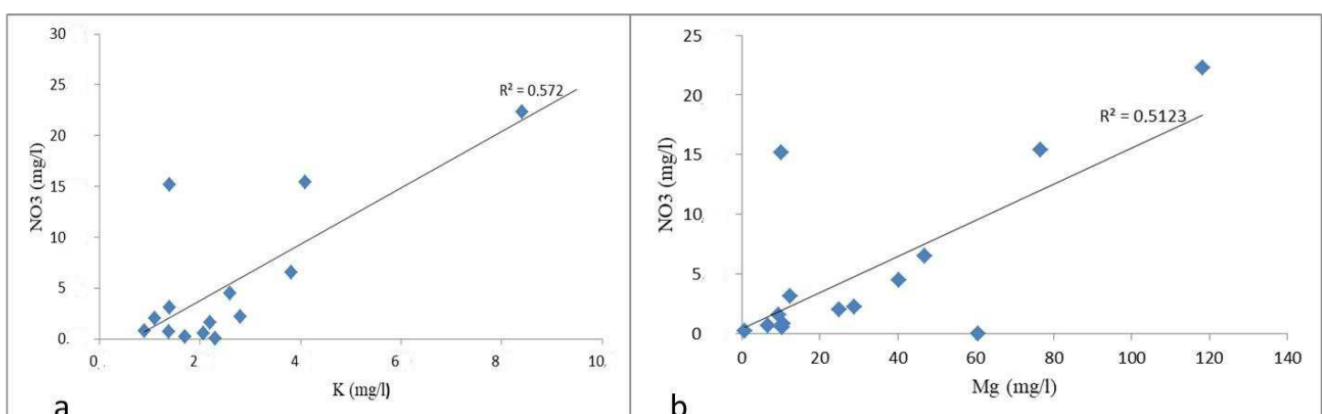


Figure 8. Scatter plots of NO_3^{-} vs. (a) K^{+} and (b) Mg^{2+} of water collected in the Soutpansberg region.

In the study area, the saturation indexes of calcite ($CaCO_3$), halite ($NaCl$), fluorite (CaF_2), quartz (SiO_2), aragonite ($CaCO_3$) and talc ($Mg_3Si_4O_{10}(OH)_2$) were determined using PHREEQC, and the results are presented in Figure 8 and Table 3. The SI values of calcite ($-1.89-0.84$) indicated that the groundwater in 57.1% of sites was undersaturated (dissolution) with respect to calcite. The SI values of calcite were negative in 42.7% of the sites, indicating precipitation processes. There was a strong correlation between calcite and aragonite (Figure 8), and this suggests that both dissolution and precipitation

of carbonate minerals influenced the groundwater quality in the Soutpansberg region. Dissolution of carbonate minerals was responsible for the enrichment of F^- (2.5 mg/L) in the groundwater of the geothermal spring (i.e., ZQMSOU1) through dissolution of fluorite (CaF_2) mineral [50,71]. When comparing the two geothermal springs' F^- enrichment in the groundwater, a F^- concentration of 0.8 mg/L was recorded in ZQMTP2, and this can be associated with a low concentration of Ca^{2+} (1.8 mg/L) compared to 12.2 mg/L in ZQMSOU1. This suggests that the dissolution of fluorite (CaF_2) depends on the concentration of Ca^{2+} in geothermal groundwater. This further indicates that high concentrations of F^- in groundwater is not associated with anthropogenic inputs but from water–rock interaction. TDS seemed to have a role in the saturation state of carbonates minerals (i.e., calcite and aragonite), as a TDS < 360 mg/L is associated with dissolution of carbonates minerals, and a TDS > 360–1418 mg/L is associated with precipitation of carbonates minerals (Figure 9). A TDS > 1418 is associated with slightly undersaturated (dissolution) of carbonates minerals in groundwater. The SI values for halite (−8.28 to −5.18) indicated undersaturation of halite in groundwater for all sites. This suggest that dissolution of halite influenced groundwater quality through enrichment of Na^+ in groundwater. Quartz SI values (0.05–0.67) were all positive (oversaturated), indicating that precipitation of silicate mineral (quartz) plays a significant role in the hydro-geochemistry. The SI values of another silicate mineral, talc (−5.6–5.6), indicated a dissolution state in 21.4% of the sites and precipitation in 78.6% of the sites. Dissolution of silicates minerals influenced groundwater quality in ZQMKNW2, ZQMPMA1 and ZQMTPVU1. Combined SI values for silicate minerals suggest that precipitation of these minerals influences groundwater quality in the Soutpansberg region. The major processes influencing groundwater quality in the Soutpansberg regions are ion exchange, dissolution and precipitation of carbonates and silicates and dissolution of fluorite and halite minerals. The impacts of anthropogenic inputs were only attributed to concentration levels of NO_3^- at a few sites.

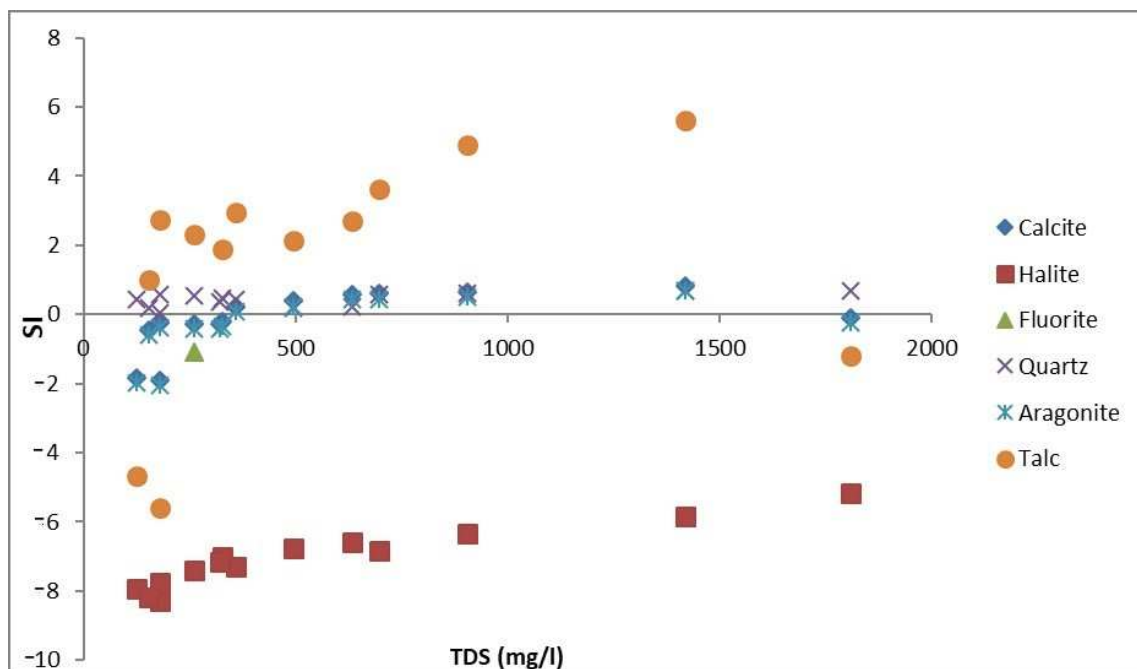


Figure 9. Saturation index of minerals of water collected in the Soutpansberg region.

Table 3. Chloro-alkaline indices (CAIs) and saturation indexes (SIs) for all sites.

Site ID	CAI-I	CAI-II	SI Calcite	SI Halite	SI Fluorite	SI Quartz	SI Aragonite	SI Talc
ZQMPMA1	0.013	0.032	−0.09	−5.18	*	0.65	−0.23	−1.2
ZQMSOU1	−1.150	−0.493	−0.26	−7.39	−1.08	0.54	−0.4	2.3
ZQMTPS2	−1.651	−1.029	−0.29	−7.15	*	0.35	−0.42	*
ZQMLRT1	−0.592	−0.216	0.6	−6.82	*	0.56	0.45	3.64
ZQMKNW2	−0.011	−0.009	−1.83	−7.95	*	0.43	−1.97	−4.67
ZQMDMI1	0.262	0.250	0.57	−6.58	*	0.24	0.43	2.69
ZQMHVE1	−0.828	−0.500	−0.19	−7.01	*	0.47	−0.33	1.89
ZQMMBI1	0.168	0.173	0.84	−5.85	*	0.67	0.69	5.6
ZQMMWI1	0.139	0.124	0.39	−6.76	*	0.2	0.24	2.13
ZQMGGG1	0.206	0.185	0.65	−6.33	*	0.61	0.5	4.9
ZQMVRT1	0.019	0.008	−0.44	−8.17	*	0.2	−0.58	1
ZQMTSU1	−0.380	−0.106	−0.25	−8.28	*	0.58	−0.39	2.73
ZQMTVU1	−0.187	−0.206	−1.89	−7.76	*	0.05	−2.04	−5.6
ZQMLVI1	0.200	0.124	0.22	−7.28	*	0.43	0.08	2.96

* not detected.

Understanding these processes is crucial in the rural areas and semi-arid environment where people have no other source of fresh water. Various studies conducted on hydro-geochemical processes in arid to semi-arid [48,53,67,72] areas determined water types and that weathering of rocks forming minerals and anthropogenic input are the main processes influencing groundwater quality. These studies recommended various actions such as controlling sources of anthropogenic inputs, increased monitoring frequency, sustainable development of groundwater resource and an improvement in groundwater quality to meet various drinking water standards. To increase the availability and access to safe groundwater in small rural communities, such as those around the Soutpansberg region, Verlicchi and Grillini [73] suggest that adequate and reliable groundwater treatment methods should be applied. Application of small-scale or community schemes groundwater remediation plants in rural communities have a high potential of eliminating the waterborne diseases discussed by Madilonga et al. [74] in the Mutangwi River, Limpopo Province, South Africa. There seems to be a gap between research outputs and policies related to protection and management of groundwater resource in most countries, as monitoring data and research outcomes are not being used to influence or support groundwater allocation policies. It is important that regulators of water resources use data, reports and outputs from national groundwater resource monitoring points to influence groundwater allocation and protection policies. In this study, the monitoring sites used are part of a national groundwater quality monitoring stations and there is a need to develop groundwater quality baseline and targets for each site and the aquifer in general. Even though it is important to compare ambient groundwater with treated or tap water standards, such as in [8,9], this practice tends to send out a misleading concept that groundwater is polluted, where it is the case that it is natural or ambient groundwater quality influenced by the weathering of rocks. In the study area, only NO_3^- concentration in groundwater was attributed to anthropogenic input during recharge process and it is important to remediate all parameters above certain drinking water limits in order to sustain good health and livelihood. A high concentration of F^- and salinity were attributed to rock–water interaction processes, and these are natural processes that can only be managed after the water has been pumped in rural settings. Remediation of groundwater quality to reduce concentration levels that are above drinking water standard [8,9] is important, and communities in rural and semi-arid environments rely on groundwater, mostly as the only source of fresh water.

5. Conclusions

High concentration of F^- in the geothermal spring (ZQMSOU1) resulted from the dissolution of fluorite, where the dissolution of carbonate minerals was also noted. Moderate to strong correlations between NO_3^- and Cl^- , K, Mg^{2+} and SO_4^{2-} suggested that high concentrations of NO_3^- in Maebane (ZQMMBI1), Gogogo (ZQMGGG1) and Tshitavha Sambandou (ZQMTVU1) were from anthropogenic inputs, resulting from the application

of fertilisers and leaching of human and animal waste as point sources of contamination. This study further concluded that research outputs on groundwater quality were not being used to support and improve groundwater allocation, protection and management policies. In cases where ambient groundwater is used for drinking and irrigation purposes, there is a need to develop a suitable groundwater quality remediation technique fit for rural settings, as the majority of groundwater users use groundwater without treatment. This study recommends that a groundwater remediation plan be considered when planning groundwater supply in rural areas. To protect groundwater resources in rural areas, there is a need to regulate the type of fertilisers used and raise awareness of the impact of certain activities that may pollute the much-needed fresh groundwater in areas where there is limited supply of surface water due to the presence of socioeconomic issues.

Supplementary Materials: The *p*-values of the correlation matrix can be downloaded at: <https://www.mdpi.com/article/10.3390/w14121972/s1>, Table S1.

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