

Geostatistics and Spatial Analysis of Groundwater Hydrochemistry near Leliefontein in the Northern Cape, South Africa

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ABSTRACT

The fractured groundwater aquifers, predominantly found in South Africa, show varying groundwater chemical characteristics in various locations. The hydrochemistry of groundwater is affected by the weathering of rock formations in contact and anthropogenic activities. Determination of groundwater chemistry is important for aquifer protection and overall groundwater management. A hydrochemical analysis is a useful tool for identification of water types, chemical composition, its suitability for specified purposes, and an important requirement for water use licensing applications. The hydrochemical data of groundwater from 79 boreholes near Leliefontein, Kamiesberg local municipality of South Africa, were analysed, using integrated statistical, geostatistics and spatial interpolation methods. The result shows Na⁺ and Cl⁻ to be the abundant cation and anion. The mean concentration of Na at Leliefontein was 267.39 mg/l, and that of Cl was 574.81 mg/l. The ionic concentrations in groundwater was in sequence of Cl⁻ > Na⁺ > HCO₃⁻ > SO₄²⁻ > Ca²⁺ > Mg²⁺ > NO₃⁻ > Si > K⁺ > F⁻. The analysis indicated that the cation exchanges in groundwater are influenced by limited silicate weathering, with calcite and dolomite dissolution. Geostatistical and spatial analysis interpolation for the major cation (Na) and major anion (Cl), Sodium Adsorption Ratio (SAR), Electrical Conductivity (EC) and Water Quality Index (WQI) was performed using Inverse Distance Weighing method. The hydrochemical data for the Leliefontein groundwater were analysed to classify water for domestic use (drinking) and agriculture (irrigation) purposes, based on the recommended guidelines of the South African National Standard (SANS). The study area was characterised by high salinity of three water types, viz, Na-Cl seawater type, Ca-Cl reverse ion-exchange water type, and Na-HCO₃ base ion-exchange water types. About 70–80% of the boreholes in Leliefontein met the requirement for irrigation application for Sodium Adsorption Ratio (SAR) and salinity hazard analysis, while the groundwater generally required further treatment before domestic use.

Keywords: groundwater, hydrochemistry, geostatistics, spatial analysis, water quality

INTRODUCTION

The groundwater resources are an intrinsic part of the water resources of South Africa. It provides a substantially more significant portion of the water requirements for household consumption and agricultural activities: Agriculture – 62%, Rural and urban household use – 27%, Mining and industrial use – 6%, Afforestation – 3%, Power generation – 2% (SSA, 2016). In South Africa, domestic, industrial, and agricultural demands for water is unsustainable without the groundwater resources. It is, therefore, necessary to classify groundwater in terms of suitability for various

purposes for equitable utilisation. The South Africa's surface water resources are unequally distributed and incapable of sustaining the demand for all sectors on the economy (Bredenhann & Braune, 2000). For decision-makers on policy, uses, and protection of groundwater resources to equitably manage groundwater, the prerequisite is to comprehend the quality and the quantity of the groundwater resources available. The groundwater quality analysis and interpretation in a necessary scientific tool for ensuring sustainable management without compromising future demands.

The observed variations in the hydrochemical profile of groundwater from one location to

another are attributed to climatic, seasonal, geological, and anthropogenic variabilities (Jonch-Clausen, 2004). Groundwater chemistry changes from one place to the other and is controlled by the geological formations through which it flows. The chemistry of water determines the quality of all water resources including groundwater and therefore, the analysis and assessment of groundwater chemistry are essential for quality assessment and pollution control. Population increases have placed increasing demands on the surface water and groundwater resources in South Africa and throughout the world. The hydrochemical data analysis reveals the appropriateness of groundwater resources different purposes (Sardashivaiah et al., 2008).

Groundwater at specific locations is also influenced by such factors as climate, soil and land use, lithology, geological structures, and surface water bodies [Stallard & Edmond, 1983; Subba Rao, 2002]. Water type and geochemical evaluation are beneficial as a preliminary assessment tool for understanding the complex subsurface hydrogeochemical processes. Over the years, scientists have used various theories and techniques in the pursuit of water chemistry, groundwater chemistry, and hydrogeochemical processes (Hill, 1940; Piper, 1944; Durov, 1948; Stiff, 1951; Garrel, 1967; Miller, 1991, Kimblin, 1995; Mayo & Loucks, 1995; Hudson & Golding, 1997).

The application of statistical methods to groundwater hydrochemistry data is influenced by the type of data and the data characteristics. Statistical methods should be based on the scientific process of inductive and deductive modeling. Many studies in which the application of statistical analysis are based on wrong assumptions of data characteristics, result in the production of incorrect and inconclusive interpretations. Geostatistical methods are a subcategory, which is uniquely applicable to geographical data analysis and interpretation (Goovaerts, 1997). It is a scientific method used mainly for spatial data analysis (Cressie, 1993; Bolstad, 2008). Currently, the integration of geostatistics and GIS data is a useful method to explore spatial data analysis, ground data, remote sensing, improving DEM generation and for simulations (Hengl et al., 1983; Kyriakidis et al., 1999; Atkinson & Quattrochi, 2000; Brus & Heuvelink, 2007; Atkinson & Quattrochi, 2000). The geostatistical methods are widely applied in the fields of water resources, geosciences, environmental sciences, meteorology, mathematics

and statistics, agriculture and soil sciences, civil engineering, ecology, and petroleum engineering (Zhou et al., 2007; Hengl et al., 2009a). Spatial interpolation is aimed at the prediction of unknown values of a parameter over an area of concern which is then used for generating an image map (Lam, 1983; Mitas & Mitasova, 1999; Dubois & Galmarini, 2004). The geostatistical application mapping involves prediction based on the quantitative and statistical methods.

The use of groundwater resources requires a thorough investigation to ensure that it is free from contamination and conforms to the standard requirements for specified utilisation. The integrated application of statistical, geostatistics and spatial analysis methods essentially helps to understand and interpret the water types and composition similarities. The integrated assessment approach to hydrogeochemical analysis is an effective groundwater resource management technique.

DATA AND METHODOLOGY

Location of study area

Leliefontein is located in the Namakwa District Municipality in the Northern Cape of South Africa (Figure 1), east of Namaqua National Park and Skilpad Nature Reserve and between longitude 17°52'38.42"–18°29'47.31" E and latitude 30°18.40'74"–30°18'56.45" S with altitudes of 700 to 1195m a.s.l. The study area is within the Bushmanland subprovince with topography slopes is mostly of uniform elevation. The arid climatic condition of intense heat produces high evaporative rates within the region. The mean annual temperature is 17.4°C, mean annual precipitation is between 20 mm to 300 mm, and mean yearly evaporation is between 2000 mm to 2350 mm. The land in the study area is predominantly used for the crop, horticulture, and animal production. The Buffels River in the Northern cape flows through the Kamies mountain and discharges into the Atlantic Ocean.

The Leliefontein basement aquifers are made of fractured bedrocks and weathered regolith, with linear system structurally controlled by faults. The groundwater in the region is relatively saline, with high salt contents. The high salt concentration in groundwater is also attributed to the aquifer system lithology and the high evaporation rates of the region (Pietersen et al., 2009; Benito et al., 2010; Adams et al., 2010; Titus et al., 2002;

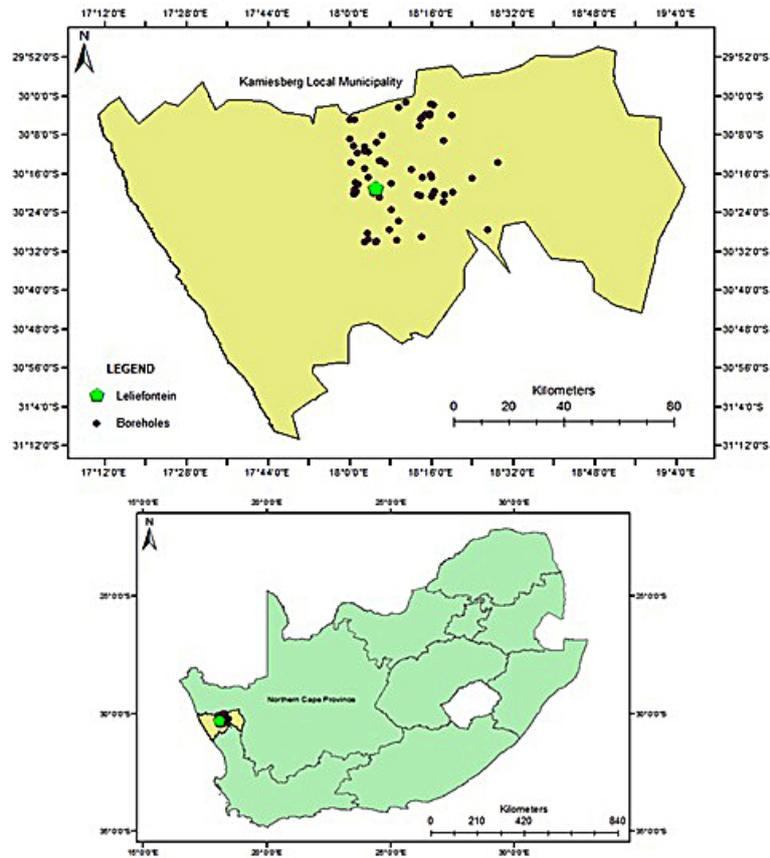


Figure 1. Map showing the location of Leliefontein and sampling boreholes

Leshomo, 2011). The distribution of boreholes and borehole identification numbers at the study location are shown on the map in Figure 2.

Geology and hydrogeology of Kamiesberg

A simplified geological map the study area presented in Figure 3. The geology of Kamiesberg consists of quaternary unconsolidated to

cemented sand overlaying Kamieskroon leucocratic gneisses (Zirco, 2012). The relief of the area is flat to moderate with a general east-southeast slope toward the Atlantic Ocean. On the basis of the structural, lithological, and geochronological differences, Kamiesberg is located within the Namaqua Metamorphic Province, which is divided into four subprovinces (Kroner, 1976): the Kheis subprovince, the Namaqua

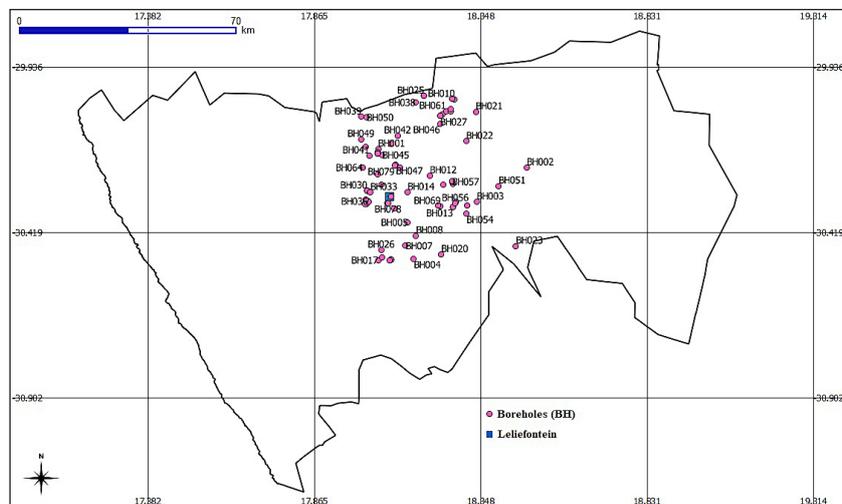


Figure 2. Map of borehole locations within the study catchment of Leliefontein

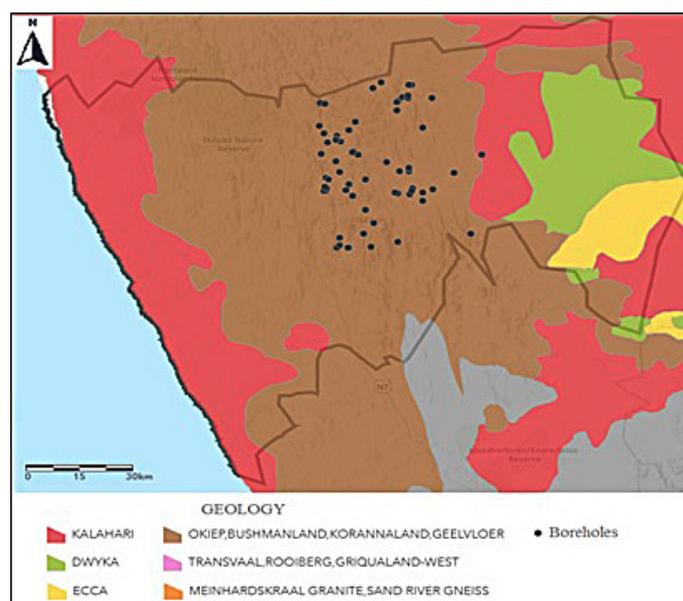


Figure 3. Geology of study location in the Northern Cape of South Africa

subprovince, the Richtersveld subprovince, and the Bushmanland subprovince. Leliefontein is located within the Bushmanland subprovince. Northern Cape, according to Slabbert et al., 1999, is characterised by an intricate pattern of folding and faulting and complicated by a large number of granite intrusions.

Leliefontein is located in a region popularly called Namaqualand in the arid to the semi-arid western part of South Africa. The area is characterised by low rainfalls, which significantly impact the net recharge of its local aquifers. The groundwater in the Leliefontein exists in three aquifer systems, which are sandy alluvial aquifers, fractured bedrocks, and weathered zones. The fractured bedrocks and weathered zones form the basement aquifer systems in the region. The underlying geology of igneous and metamorphic rocks (granite and gneisses) influence the geometry of aquifer systems in the area (Pietersen et al., 2009). The recharge in the regions with no direct infiltration is presumably a result of regional flow from other neighbouring catchments.

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Groundwater sample analysis

The groundwater samples from 79 boreholes were collected and analysed for various water quality parameters. The accuracy of chemical analysis of groundwater samples is essential to the assessment and interpretation of hydrochemical data, and therefore, require the accuracy checks and verifications to ascertain the data quality integrity. The electroneutrality principle is an excellent method of water chemistry data verification. The electroneutrality principle states that the sum of positive and negative charges of the water must be balanced or be equal to zero. The acceptance criteria for the percentage difference is <5%, which is calculated with the equation:

$$N. [\%] = \left| \frac{\sum \text{Cations}[\text{meq/l}] + \sum \text{Anions}[\text{meq/l}]}{\sum \text{Cations}[\text{meq/l}] - \sum \text{Anions}[\text{meq/l}]} * 100\% \right| < 5\% \quad (1)$$

The calculations of electroneutrality (EN%) for each sample, indicate that 76 out of the 79 samples have an electroneutrality lesser than 5%, implying 96.2% of the samples were within the acceptable limit. The plausibility of a chemical analysis is a comparison of chemical values for process variables (cations and anions) for determination of the errors in measurements. It is determined by the calculated total cation, total anion and the EC of the water samples with the equation:

$$\begin{aligned} \sum \text{Anions}[\text{meq/l}] &\approx \sum \text{Cations}[\text{meq/l}] \approx \\ &\approx \frac{\text{EC}[\mu\text{S/cm}]}{100} \pm 10\% \text{ for EC} < 2000 \mu\text{S/cm} \end{aligned} \quad (2)$$

Groundwater or water generally is electrically neutral, and therefore, calculating charge balance is useful for verifying the accuracy of chemical analysis (Cogho et al., 1989). For a given water sample, the sum in milliequivalents per litre (meq/l) of the positively-charged and negatively-charged species must be equal (Younger, 2007).

Statistical analysis

The choice of statistical methods involves the scientific process of a model building using both inductive and deductive reasoning. Selection of the right statistical method requires the knowledge of the characteristics of the data. The hydrochemical data was subjected to Pearson's correlation matrices, cluster analysis by agglomerative hierarchical clustering and principal component analysis for statistical interpretation, to determine the relationship between groundwater parameters and influencing factors (Usunoff & Guzman-Guzman, 1989; Schot & Van der Wal, 1992; Swan, 1995). Piper diagram and Chadha diagrams were also used for water type classification (Piper, 1944; Chadha; 1999).

Water quality index

The use of Water Quality Index (WQI) is a valuable method for classifying the levels of contamination for surface water and groundwater resources (Backman et al., 1998; Stambuk-Giljanovic, 1999). The purpose is a classification based on a grading scale of 0 to 300. The lower values on the grading scale are excellent while the increasing ones indicate increasing contamination levels. WQI calculation is derived from the following procedures:

1) Calculate the relative weight by using the equation:

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (3)$$

where: W_i – relative weight of each parameter, w_i – weight of each parameter, and n is the total number of parameters.

2) Calculate Q value using the equation:

$$Q_i = \frac{C_i \times 100}{S_i} \quad (4)$$

where: Q_i – quality rating,
 C_i – concentration of each parameter (mg/l),
 S_i – SANS214(2015) water quality standard.

3) WQI is then calculated using the equation:

$$WQI = \sum W_i \times Q_i \quad (5)$$

Groundwater quality spatial distribution

The geostatistical method of Inverse Distance Weighting (IDW), is useful for spatial analysis to predict the groundwater quality over and area to produce image maps (Shepard, 1968; Bartier & Keller, 1996). The method also accurately checks the influence distances of all the points (Bartier & Keller, 1996). The IDW spatial analysis in ArcGIS 10.8 was used to interpolate and predict the distribution of ions in groundwater at Leliefontein to generate a pollution map (ESRI, 2019). IDW is a mechanical spatial prediction model which is flexible, empirical, and constitutes a widely used mechanical spatial prediction model (Lam, 1983; Myers, 1995; Mitas & Mitasova, 1999). Mechanical prediction models sometimes perform well or better compared to statistical models, and one such spatial prediction technique is the IDW (Shepard, 1968). For IDW interpolation, the value of the targeted parameters at a new point was derived as an average weight using the equation:

$$\hat{z}(s_0) = \sum_{i=1}^n \lambda_i(s_0) * z(s_i) \quad (6)$$

where: λ_i – weight for neighbour i , and the sum of weights must equal 1 to achieve unbiased interpolator. Equation, (6) is then changed to matrix form to the equation:

$$\hat{z}(s_0) = \lambda_0^T * z \quad (7)$$

The inverse distance from known points to unknown points is used to determine the weights using the equation:

$$\lambda_i(s_0) = \frac{1}{\sum_{i=0}^n \frac{1}{d^\beta(s_0, s_i)}} ; \beta > 1 \quad (8)$$

where: $d(s_0, s_i)$ – distance from the new point to a known sampled point;
 β – coefficient used to adjust the weights. The IDW method is based on Waldo Tobler's first law which stipulates the relation of everything to one another, with near things relating more to each other than the distant ones (Tobler, 1970).

RESULTS AND DISCUSSION

Statistical analysis

Descriptive statistics

The statistical overview of the hydrochemical data of Leliefontein is presented in Table 1. The major groundwater components with minimum, maximum, average, and South African National Standards (SANS241, 2015) are shown for the study location. The groundwater pH ranges from 5.97 to 8.7, and EC is between 19.3 to 920 mg/l (mean: 217.28). The bicarbonate (HCO_3^-) concentration ranges from 26.47 to 367.37 mg/l (mean: 155.75), while the mean Cl and SO_4 levels are 574.81 and 131.73 mg/l, respectively. The mean Na^+ and K^+ concentrations are 267.39 and 6.88 mg/l, respectively. The calcium concentration varies from 5.70 to 441.90 mg/l, higher than magnesium concentration which varies between 3.30 to 315.50 mg/l. High fluoride concentration (0.14 to 10.18 mg/l with mean: 2.48) was observed, with 71% of the groundwater samples exceeding the SANS241 recommended limits. The NO_3 concentration was between 0.09 and 695.26 mg/l, and 25% of the groundwater samples exceed the SANS241 recommended limits.

Correlation matrix

Pearson's correlation matrix was used to determine the relationships between the parameter of the hydrochemistry data (Swan, 1995), and the

results presented in Table 2 for correlations > 0.4 . The groundwater samples with correlations > 0.7 were classified as strongly correlated and those with correlations between 0.5 to 0.7 were classified as moderately correlated at < 0.05 significant level. A strong correlation was observed for the major elements, Ca, Mg, Na, Cl, SO_4 , Dissolved Major Salts (DMS) and SAR, and EC with correlations > 0.7 , which indicates their contribution to the groundwater salinity. Moderate correlations between 0.5 to 0.7 were observed between HCO_3^- with pH, which indicates a trend of ion concentration increasing along with pH. The salinity of groundwater usually is a result of increasing ion concentration, recharge water evaporation, and geological formations. Positive correlations between Ca, Na, Mg, SO_4 , and DMS are an indication of contributions by evaporative salts.

Factor analysis

The application of factor analysis is a useful method for the interpretation of geohydrological data (Schot & Van der Wal, 1992; Usunoff & Guzman-Guzman, 1989; Ashley, 1978; Dawdy & Feth, 1967). Factor analysis rearranges the data and presents it in a form that clearly explains the composition of the rudimentary system that produced the data (Dawdy & Feth, 1967). The hydrochemical parameters were created into a set of factors, using varimax rotation factor analysis to determine the main factors responsible for the groundwater chemistry in Leliefontein. Five

Table 1. A statistical overview of groundwater hydrochemical data (values in mg/l)

Groundwater (n = 79)						
Parameter	Mean	Median	Min	Max	Std Dev.	Acceptable limits (SANS241:2015)
EC (mS/m)	217.28	165.60	19.30	920	202.26	170
pH	7.50	7.52	5.97	8.70	0.55	$\geq 5.0 - \leq 9.7$
Ca^{2+}	90.35	66	5.70	441.90	77.99	≤ 150
Mg^{2+}	67.17	43.60	3.30	315.50	68.87	≤ 70
Na^+	267.39	157.40	18	1568.50	323.13	≤ 200
K^+	6.88	3.30	0.56	111.31	13.94	≤ 50
Cl	574.81	374.06	28.71	3022.70	675.01	≤ 300
SO_4^{2-}	131.73	92.80	4.50	563.90	128.08	≤ 250
F	2.48	2.37	0.14	10.18	1.65	≤ 1.5
Si	14.68	14.58	3.15	36.14	5.22	-
$\text{PO}_4\text{-P}$	0.02	0.01	0.003	0.49	0.06	-
HCO_3^-	155.75	149.94	26.47	367.37	82.03	-
NO_3^-	23.77	2.04	0.09	695.26	87.68	≤ 11
$\text{NO}_4\text{-N}$	0.09	0.05	0.02	1.66	0.19	≤ 1.5
DMS	1321.41	967.98	99	5892	1289.62	-
SAR	4.87	3.86	0.97	17.37	3.80	-

Table 2. Pearson's correlation matrices for groundwater hydrochemical data (values in mg/l)

Parameter	EC	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	F	Si	PO ₄	HCO ₃	NO ₃	NO ₄	DMS	SAR
EC	1															
pH		1														
Ca ²⁺	0.78		1													
Mg ²⁺	0.95		0.85	1												
Na ⁺	0.96		0.60	0.84	1											
K ⁺	0.62			0.48	0.68	1										
Cl ⁻	0.99		0.77	0.95	0.96	0.62	1									
SO ₄ ²⁻	0.96		0.82	0.89	0.91	0.57	0.94	1								
F		0.46							1							
Si									0.04	1						
PO ₄ -P									0.05		1					
HCO ₃		0.55			0.43				0.41			1				
NO ₃													1			
NO ₄ -N														1		
DMS	1.00		0.79	0.94		0.62	0.99	0.96				0.40			1	
SAR	0.79			0.58		0.63	0.77	0.76	0.41			0.50			0.79	1

factors were found to be responsible for 83.12% of the variance in the data set, as shown in Table 3. Factor 1 indicated a strong relationship contributing to the groundwater salinity at Leliefontein. The main contributing parameters to the salinity of groundwater are EC, Ca, Mg, Na, K, Cl, SO₄, HCO₃, DMS and SAR. The principal cations Na, Ca, Mg, and K correlated positively indicating the influence of the geological formations. The positive correlations between Ca, Mg and SO₄ are an indication of possible dissolution or precipitation of sulphide minerals. Factor 2 shows the positive effect of pH on F, HCO₃ and SAR, and

the negative correlation of NO₃ (unknown relationship). The factor 2 parameters are the determinants of the mobility and solubility of the trace elements such as fluoride found in the groundwater samples. Factor 3 gives the correlation of NO₄-N of the groundwater, while Factor 4 and Factor 5 relate the correlation of NO₃ and PO₄-P respectively for the groundwater samples, an indication of the anthropogenic processes.

Agglomerate hierarchical clustering (AHC)

The application of cluster analysis results in the identification of different chemical facies

Table 3. Factor analysis of groundwater hydrochemical data (values in mg/l)

Parameter	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
EC	0.992				
pH		0.737			
Ca ²⁺	0.771				
Mg ²⁺	0.921				
Na ⁺	0.963				
K ⁺	0.657				
Cl ⁻	0.981				
SO ₄ ²⁻	0.965				
F		0.674			-0.495
Si			-0.593		
PO ₄ -P		0.419		0.492	0.656
HCO ₃	0.446	0.704			
NO ₃		-0.452	-0.490	0.582	
NO ₄ -N			0.612		
DMS	0.993				
SAR	0.822	0.403			
Explained Variance	7.691	2.204	1.377	1.081	0.946
Cum. % of Variance	48.065	61.843	70.449	77.208	83.119

of the groundwater by means of the Q-mode AHC method. From the AHC analysis, the result shows that the determining factor the grouping of the groundwater hydrochemistry data into three groups are the sodium and chloride ion concentrations, an indication of the salinity associated with the groundwater samples (Figure 4). In Group 1 there are 57 groundwater samples from boreholes (BH001, BH002, BH004, BH006 – BH011, BH014 – BH019, BH022, BH023, BH026, BH029 – BH035, BH037 – BH043, BH045 – BH047, BH049 – BH050, BH053, BH056 – BH058, BH061 – BH067, BH069, BH071 – BH076, BH078, and BH079). These 57 wells have a mean concentration of 269.88 mg/l for Cl, 146.02 mg/l for HCO₃, and 129 mg/l for Na, representing the lowest salinity water group of the three groups. The order of concentration of the major ions in Group 1 water samples is as follows Na⁺ > Ca²⁺ > Mg²⁺ > K⁺ and Cl⁻ > HCO₃ > SO₄ > NO₃. The hydrochemical water type is characterized by sodium chloride with Na (min = 18 mg/l, max = 225.5 mg/l, and mean = 129 mg/l), and sodium (min = 28.71 mg/l, max = 586.1 mg/l, and mean = 269.88 mg/l). HCO₃ also exist (min = 26.47 mg/l, max = 341.53 mg/l, and mean = 146.02 mg/l) with calcium. 19.3% of Group 1 boreholes samples exceeded the recommended Na limit in drinking water, and 35.1% of boreholes exceeded the Cl concentration stipulated by SANS241:2015.

Group 2 is comprised of 19 boreholes (BH003, BH005, BH012, BH013, BH020, BH021, BH024, BH025, BH027, BH028, BH036, BH044, BH048,

BH051, BH052, BH054, BH055, BH059, and BH068) with a mean concentration of 1487.85 mg/l for Cl, 648.07 mg/l for Na, and 306.46 mg/l for SO₄. The order of concentration of the major ions is Na⁺ > Ca²⁺ > Mg²⁺ > K⁺, and Cl⁻ > SO₄ > HCO₃ > NO₃, and the hydrochemical characteristics are the same as in Group 1. The hydrochemical water type is sodium chloride with Na (min = 234.67 mg/l, max = 1568.5 mg/l, and mean = 648.07 mg/l), and chloride (min = 567.91 mg/l, max = 3022.7 mg/l, and mean = 1487.85 mg/l). SO₄ also exist (min = 135.9 mg/l, max = 563.9 mg/l, and mean = 306.46 mg/l) with calcium. All the boreholes in the group 2 water samples exceeded the recommended Na and Cl limit for drinking water, and 52.6% of the boreholes have the water samples with SO₄ above the limit guideline recommended by SANS241:2015. The SO₄ concentration is a likely contributing factor for the average lowest pH in Group 2.

Group 3 is made up of three boreholes (BH060, BH070, and BH077) with a mean concentration of 485.86 mg/l for Na, 585.95 mg/l for Cl, and 277.59 mg/l for HCO₃. The order of concentration of the major ions is Na⁺ > Ca²⁺ > Mg²⁺ > K⁺ and Cl⁻ > HCO₃ > SO₄ > NO₃. The water type is also sodium chloride with Na (min = 466.77 mg/l, max = 508.02 mg/l, mean = 485.86 mg/l), Cl (min = 495.86 mg/l, max = 677.3 mg/l, and mean = 585.95 mg/l), and HCO₃ (min = 166.04 mg/l, max = 367.37 mg/l, and mean = 277.59 mg/l). All the boreholes in Group 3 exceeded Na and Cl SANS241:2015 guideline limit for drinking water.

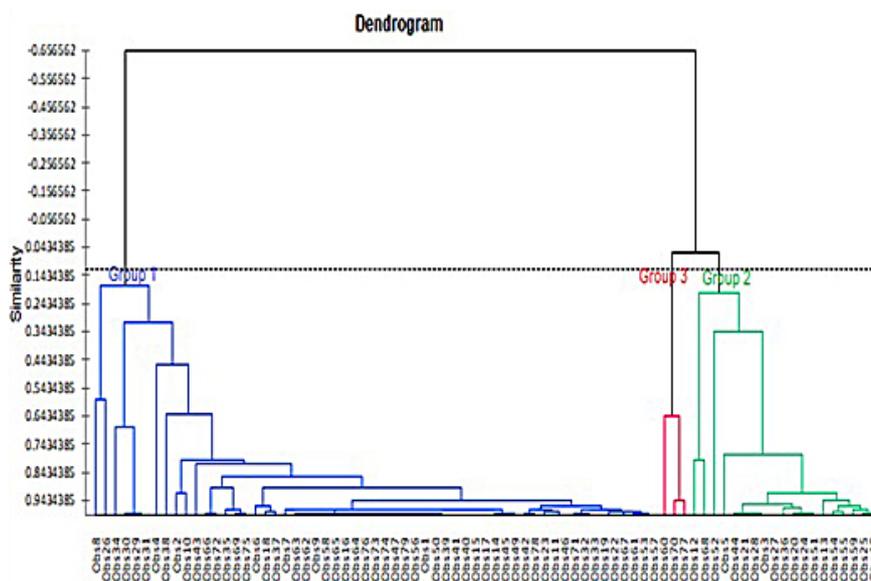


Figure 4. Dendrogram of Q mode cluster analysis of water samples

Groundwater types

The Piper and Chadha diagrams for the chemistry of Leliefontein hydrochemical data are presented in Figure 5. The water types in piper plots are generally classified into six groups, which are Ca-HCO₃ type, Na-Cl type, Ca-Mg-Cl type, Ca-Na-HCO₃ type, Ca-Cl type, and Na-HCO₃ type. The piper plot by WISH shows the water types falling into three groups of Na-Cl type, Ca-Cl type, and Na-HCO₃ type. Group 1 has Na-Cl, Ca-Cl and Na-HCO₃ water types, Group 2 water was classified as Na-Cl and Ca-Cl water type, and Group 3 is Na-Cl water type. The Chadha diagram is a modified version of the Piper diagram, is useful for the verification of water type classification. The Chadha plots show that Na and Cl characterised most of the groundwater at Leliefontein. Most of the boreholes indicated seawater Na-Cl water type and

reverse ion-exchange Ca-Mg-Cl/SO₄ water type. Only two of the boreholes showed base ion-exchange Na-HCO₃ water type. The Chadha diagram affirms the classification by Piper plot groundwater type analysis.

Hydrogeochemical processes

The scatter plots of dissolved major salts (DMS) versus the major cations (Na⁺, Ca²⁺, Mg²⁺), and DMS versus major anions (Cl⁻, HCO₃⁻, SO₄²⁻) are presented in Figure 6. A consistent relationship between DMS and cations/anions was observed. All ion concentrations increased along with the concentration of DMS. The major cations concentration increases in the sequence of Na⁺ > Ca²⁺ > Mg²⁺, and major anions concentration also increases in the sequence of Cl⁻ > HCO₃⁻ > SO₄²⁻. The possible explanation of the trend

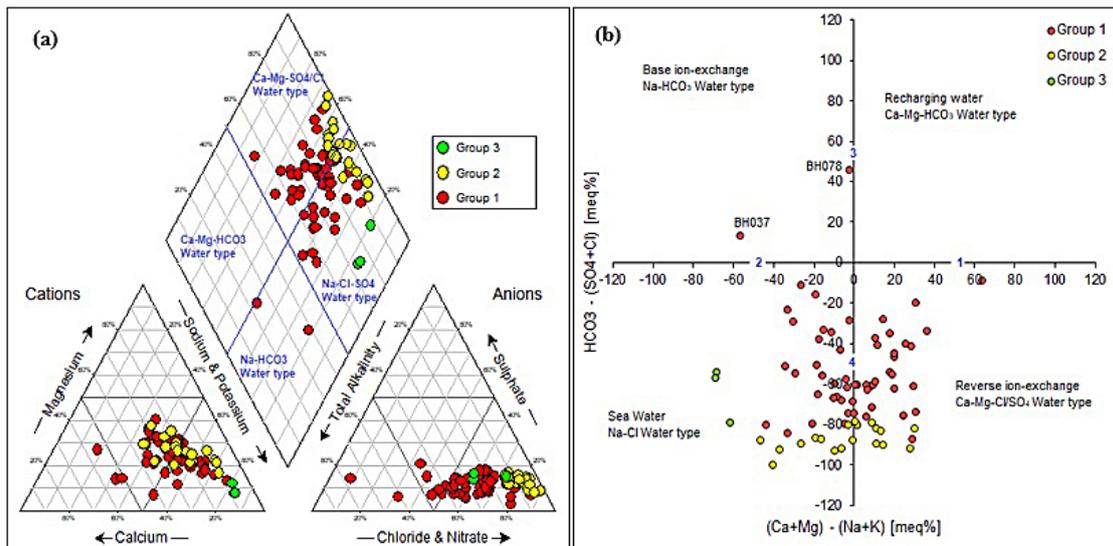


Figure 5. (a) Piper diagram (b) Chadha diagram for the chemistry of water at Leliefontein

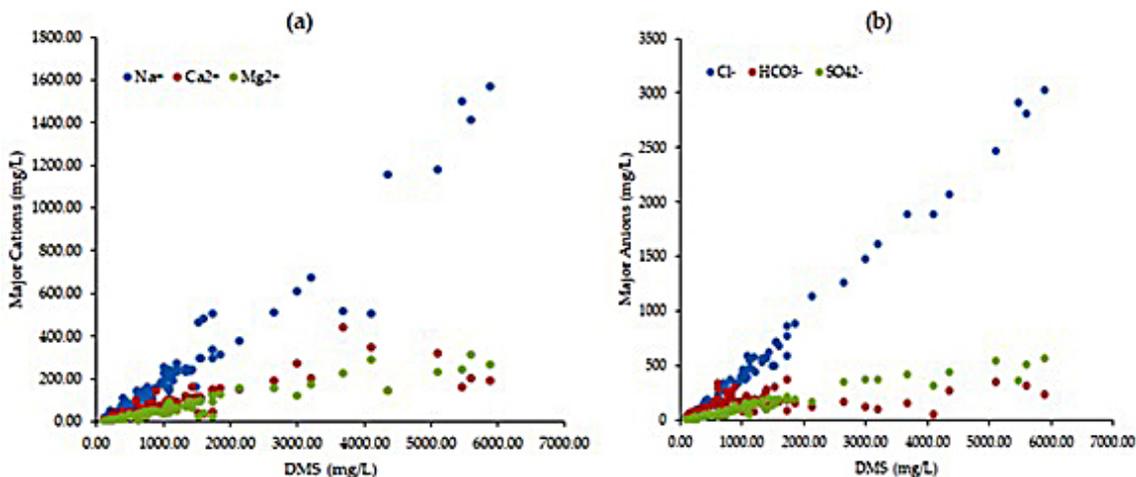


Figure 6. Scatter plots of (a) main cations vrs. DMS, (b) main anions vrs. DMS

between DMS and the major ions, is the dissolution of the minerals containing Na^+ and Cl^- was responsible for major hydrochemical processes in the groundwater.

The weathering of silicates

The weathering of silicate is one crucial geological process that dominates the chemical interaction of major ions in groundwater (Mackenzie & Garrells, 1965). The ratio of $\text{Na}:\text{Cl}$, when approximately equal to one is an indication of halite dissolution and responsible for sodium concentrations, and when the proportion is higher than one it is interpreted as silicate weathering leading to the release of sodium (Mayback, 1987; Li et al., 2016). The water samples from the boreholes in Leliefontein as seen on the scatter plot in Figure 7(a) shows the ions cluster above the $\text{Na}:\text{Cl}$ 1:1 line, an indication of sodium release as a result of silicate weathering. Studies have shown that the

weathering of silicate as a sodium source produces HCO_3^- as the predominant anion (Rogers, 1987; Rajmohan & Elango, 2004). In this study, HCO_3^- is not the dominant anion; it is chloride which is the dominant anion, as seen in Figure 7(b).

The weathering of silicate can further be probed by estimating the Na^+ to total cation (TC^+) ratio in groundwater. In this study, the groundwater samples are reclining about 0.57 CT^+ below 1:1 $\text{Na}^+:\text{CT}^+$ line, an indication of limited silicate weathering (Figure 7b). The plot of $\text{TA}:\text{Cl}^-$ reclining below the equiline (Figure 7c) indicates the abundance or formation of chlorides in the limited silicate weathering process. The scatter plot of $\text{Ca}^{2+}+\text{Mg}^{2+}$ against $\text{SO}_4^{2-}+\text{HCO}_3^-$ presented in Figure 7(d) clusters most groundwater samples below the equiline at the $\text{SO}_4^{2-}+\text{HCO}_3^-$ side of the $\text{Ca}^{2+}+\text{Mg}^{2+}:\text{SO}_4^{2-}+\text{HCO}_3^-$ 1:1 ratio, an indication of carbonate weathering and sulfuric acidity during hydrogeochemical processes. The scatter plot of $\text{Ca}^{2+}+\text{Mg}^{2+}$ against $\text{SO}_4^{2-}+\text{HCO}_3^-$ showing

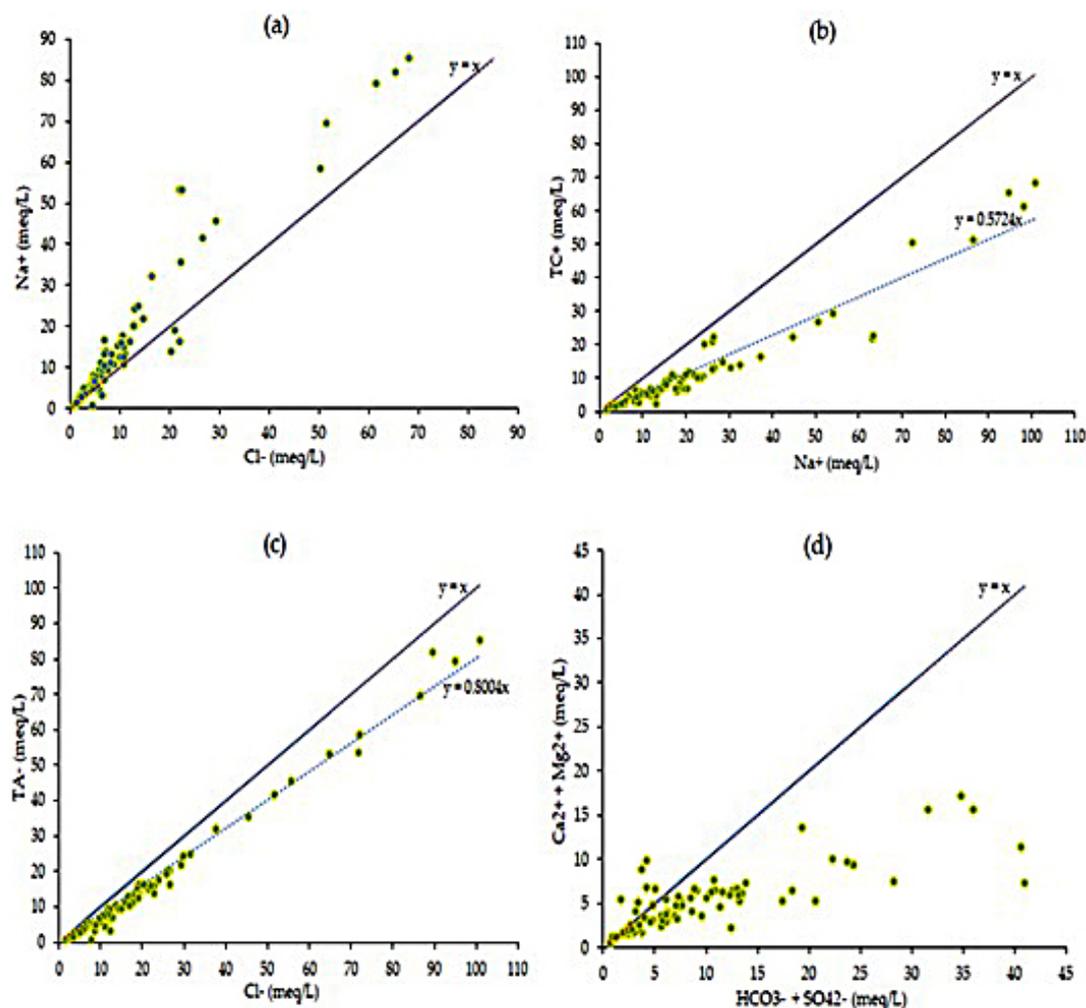


Figure 7. Scatter plots of (a) Na^+ vrs Cl^- , (b) Na^+ vrs TC^+ , (c) Cl^- vrs TA^- , and (d) $(\text{HCO}_3^- + \text{SO}_4^{2-})$ vrs $(\text{Ca}^{2+}+\text{Mg}^{2+})$

the groundwater samples clustering almost along the equipotential line, is an indication of possible carbonate and silicate origination of ions (Datta & Tyagi, 1996; Fisher & Mullican, 1997).

Carbonate weathering and dissolution

Studies have shown that when the ratio $\text{Ca}^{2+}/\text{Mg}^{2+}$ is equal to 1, the dissolution of dolomite is highly likely and the ratio greater than 1 (ratio >1), constitutes an indication of the calcite dissolution (Maya & Loucks, 1995). The scatter plot of Ca^{2+} against Mg^{2+} for the groundwater samples shows that the dissolution of dolomite dominates calcite dissolution (Figure 8e). Most groundwater samples (80%) are distributed near the $\text{Ca}^{2+}/\text{Mg}^{2+}$ equiline, which means a predominant dolomite dissolution. About 20% of the groundwater samples have ratio >1 , an indication of calcite dissolution in hydrogeochemical process; 11% of the groundwater from Leliefontein recline below the equiline of Mg^{2+} versus Ca^{2+} scatter plot, indicating less calcite dissolution. There is clustering at the $\text{Ca}^{2+}+\text{HCO}_3^-$ side of the 1:1 $\text{Ca}^{2+}+\text{HCO}_3^-:\text{Na}^++\text{Cl}^-$ equiline, an indication of calcium and bicarbonate solubility and formation of sodium chloride (Figure 8f). The solubility of calcium is limited compared to carbonate, and most of the calcium precipitates as calcium carbonated (Data & Tyagi, 1996).

General hydrochemistry

The EC of groundwater at Leliefontein varies and the recommended limit for drinking water by SANS241:2015 guideline of 170 mS/m at 300 °C. In this study, the EC ranges from 19.3

to 920 mS/cm at the study location. Out of the 79 boreholes sampled in the study area, 40 boreholes (50.6%) are within the guideline limit, and 39 boreholes (49.4%) are above the recommended guideline limit of SANS241:2015. The high electrical conductivity in some boreholes may be as a result of the high evapotranspiration rate contributing to the high salinity. High EC may be as a result of hydrogeological conditions and not necessarily an indication of the presence of pollution. The pH is one of the critical water quality parameters and in the study area it varies between 5.97 to 8.7. The drinking water quality guideline recommended a pH of 7.0 to 8.5 for freshwater (SANS241, 2015). The pH measurements at the study area, 81% of the boreholes sampled have the pH values within an acceptable range and 19% out of the recommended range values of SANS241.

Naturally, chloride is present in all water at various concentrations influenced by geochemical processes. Major salts like sodium chloride, potassium chloride, calcium chloride and magnesium chloride are highly soluble in water. Chloride in groundwater predominantly originates from igneous and metamorphic rocks such as granite-gneiss. Chloride can also accumulate in groundwater as a result of irrigation return flows, seawater intrusion, and other anthropogenic activities. Chloride in domestic water produces a salty taste of water and escalates the corrosion rate of metals. The SANS241:2015 guidelines for the Cl concentration in drinking water are ≤ 300 mg/l. Out of the 79 boreholes, 34 boreholes (43%) have the Cl concentrations within the guideline limit value, and 45 boreholes (57%) of have chloride concentration exceeding 300 mg/l acceptable limit value of SANS241.

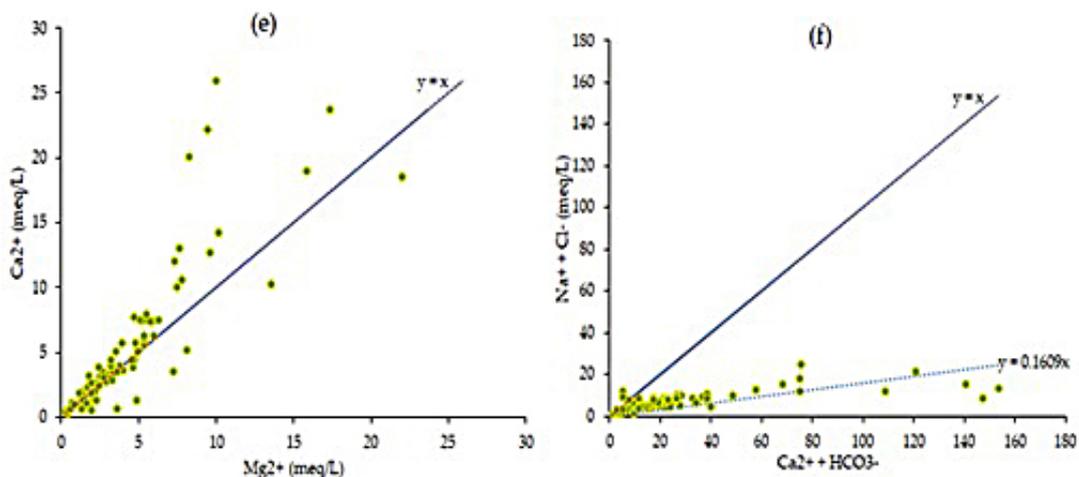


Figure 8. Scatter plots of (e) Ca^{2+} vrs. Mg^{2+} and (f) Na^++Cl^- vrs. $\text{Ca}^{2+}+\text{HCO}_3^-$

Sodium is a highly soluble natural chemical element and found in groundwater. An increase in the sodium concentration in groundwater above natural levels is an indicate pollution from a point or non-point. The SANS241 guideline value for sodium concentration is <200 mg/l. Out of the 79 boreholes, 36 boreholes (45.6%) have the sodium concentration >200 mg/l, and 43 boreholes (54.4%) are within acceptable limit of <200 mg/l for the study location.

Fluoride minerals mostly occur as fluor-spar, calcium fluoro-phosphate, and fluor-apatite, and associated with volcanic rocks. Hydrogen fluoride is a soluble gas in magmas emanating from volcanic eruptive activities. Phosphate fertilisers also contribute significantly to the fluoride content in soil and groundwater resources. The weathering of micaceous rock such as granite and gneisses also produces fluoride in groundwater, prevails as a result of rock-water interaction, long residence time and evapotranspiration. The SANS241 guidelines set out for drinking water for fluoride concentration is ≤ 1.5 mg/l (DWAF, 1996). The study shows that 72% of the boreholes in Leliefontein have the fluoride concentration above an acceptable range > 1.5 mg/l, while the remaining 28% are within an acceptable range of ≤ 1.5 mg/l. The high fluoride concentrations in the groundwater of Leliefontein are a significant problem to the quality of groundwater in the region. High levels of fluoride in drinking water are the cause of skeletal fluorosis with crippling, as well as the loss of teeth.

The nitrate and nitrite ions form part of the nitrogen cycle and occur naturally in many ecosystems, with nitrate ion (NO₃) is the stable form. The recommended DWAF guideline set out for drinking waters nitrate concentration not exceeding ≤ 11 mg/l-N, and high levels have adverse health effects on infants of less than two years old (DWAF, 1996). In Leliefontein, 74.7% of the boreholes show the nitrate concentrations lesser than 11 mg/l and are within the acceptable range, while 25.3% were above the guideline acceptable limit.

Sodium adsorption ratio and EC

The related concentration of Na, Ca, and Mg is an essential indicative factor of the suitability of water for agricultural (irrigation application). elevated Na and low Ca and Mg in the water for irrigation results in cation exchange complex becoming saturated with Na. The high Na

concentration leads to soil structure deformation as a result of the dispersion of clay particles, decreased permeability and aeration, which affects the plant growth. SAR is used to assess the risk of Na anomalies in groundwater (Fetter, 1994):

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}} \tag{9}$$

The SAR measurements of the groundwater samples for Leliefontein with the hazard classification is presented in the SAR diagram using WISH (Lukas, 2012) in Figure 9.

The sodium hazard is also useful for the determination of water use of water for irrigation. According to Fipps (2003), there are two types of problems associated with salt in water for irrigation, salt associated with the total salinity (EC) and salt associated with sodium (SAR); or a combination of both. The classification of groundwater at the study site for irrigation purpose based on SAR is presented in Table 4. From the rating, all group 1 water samples have a low SAR, group 2 ranges from a low SAR to medium and high SAR, while all the group 3 water samples indicated high SAR. Therefore, according to Fipps (2003) and Aza-Gnandji et al., 2013, the water with low sodium hazard is suitable for irrigation. Generally, 91.1% of boreholes in Leliefontein are ideal for the irrigation purposes based on SAR values. The classification of groundwater from the boreholes at Leliefontein for the irrigation purposes based

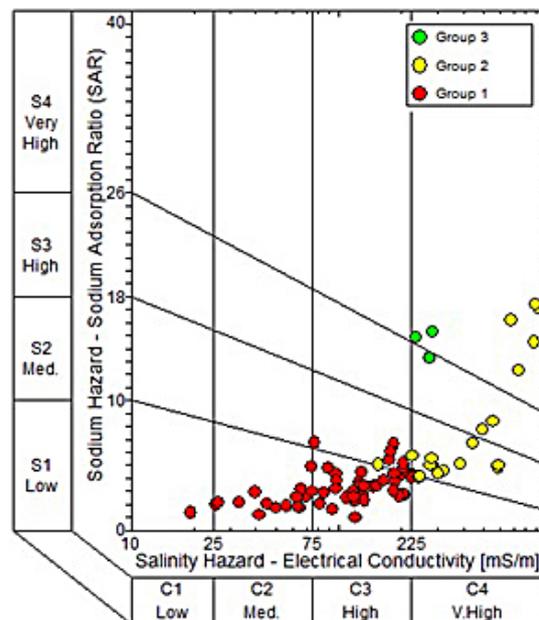


Figure 9. SAR and Salinity Hazard classification plot of groundwater samples

Table 4. Classification of groundwater based on SAR and EC for irrigation

Sodium hazard (SAR) (Class)	Water class	Number of Boreholes	% of Boreholes
0 – 10 (S1)	Low	69	87.3
10 – 18 (S2)	Medium	3	3.8
18 – 26 (S3)	High	7	8.9
> 26	Very High	0	0
Salinity hazard EC (mS/m) (Class)	Water class	Number of Boreholes	% of Boreholes
< 25 (C1)	Excellent	2	2.5
25 – 75 (C2)	Good	15	18.9
75 – 225 (C3)	Fair	38	48.1
> 225 (C4)	Poor	24	30.4

on salinity hazard (EC) is also shown in Table 4, with 70.6% of the boreholes suitable for irrigation application, and 30.4% are classified as poor and not appropriate for irrigation.

The deposits of salts in the groundwater at Leliefontein is likely due to the agricultural activities, natural groundwater movement through the geological formation and saltwater intrusion. Leliefontein is located about 100 km from the coast of the Northern Cape, and Kamiesberg local municipality as a whole is situated at the coastline of Northern Cape of South Africa.

Water quality index

Water quality index (WQI) is an acceptable method that offers a simplified expression of water quality for surface water and groundwater investigations. WQI is a numerical expression summarising the water quality data set into simple terms as excellent, good, poor, and unsuitable. Scientists around the world develop various WQI methods which are widely used by many authors (Amadi, 2011; Gebrehiwot et al., 2011; Desai & Desai, 2012; Aly et al., 2014; Amaliya & Kumar, 2015; Goher et al., 2015; Paul et al., 2015). The WQI analysis is vital to generate the maps of the groundwater quality coverage over regions of interest. WQI can be used to identify the factors and sources influencing the groundwater quality for

both management of water resources and monitoring of the groundwater quality. The classification of groundwater at Leliefontein based on WQI calculations is presented in Table 5. On the basis of the cluster analysis, group 1 of 57 samples shows 15 boreholes (26.3%) with excellent WQI, 14 boreholes (22.8%) with good WQI, 13 boreholes (24.6%) with poor WQI, 12 boreholes (21.1%) with very poor WQI, and three boreholes (5.3%) of unsuitable WQI. The group 2 groundwater 19 samples portray only one borehole (5.3%) with excellent WQI, five boreholes (26.3%) with poor WQI, five boreholes (26.3%) with very poor WQI, and eight boreholes (42.1%) with unsuitable WQI. The group 3 groundwater samples are made up of three boreholes, with one (15%) being poor and two (75%) very poor for WQI. The groups are in the order of Group 1 < Group 2 < Group 3 for WQI.

Water quality spatial distribution maps

Spatial distribution maps of WQI, Na, Cl, EC and SAR were generated for Kamiesberg local municipality by Inverse Distance Weighing (IDW) interpolation method with ArcGIS 10.8 (ESRI, 2019), are presented in Figures 10, 11, and 12. The spatial interpolation from all generated maps indicated the water quality for all parameters were best at the western portions of

Table 5. WQI classification of boreholes at the study location

QWI Range	Classification	Number of Boreholes	% of Borehole
0 – 25	Excellent	16	20.3
26 – 50	Good	13	16.5
51 – 75	Poor	20	25.3
76 – 100	Very Poor	19	24.1
> 100	Unsuitable	11	13.8

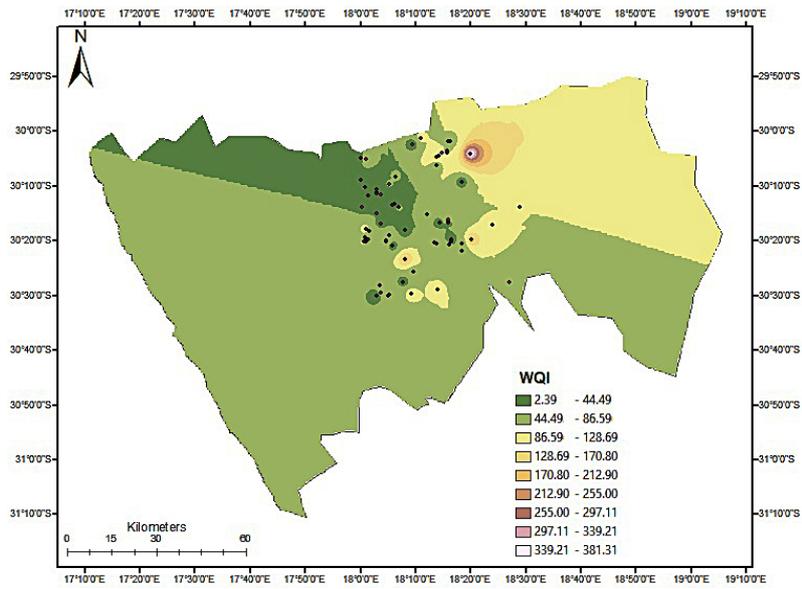


Figure 10. Spatial distribution map of groundwater for WQI in Kamiesberg

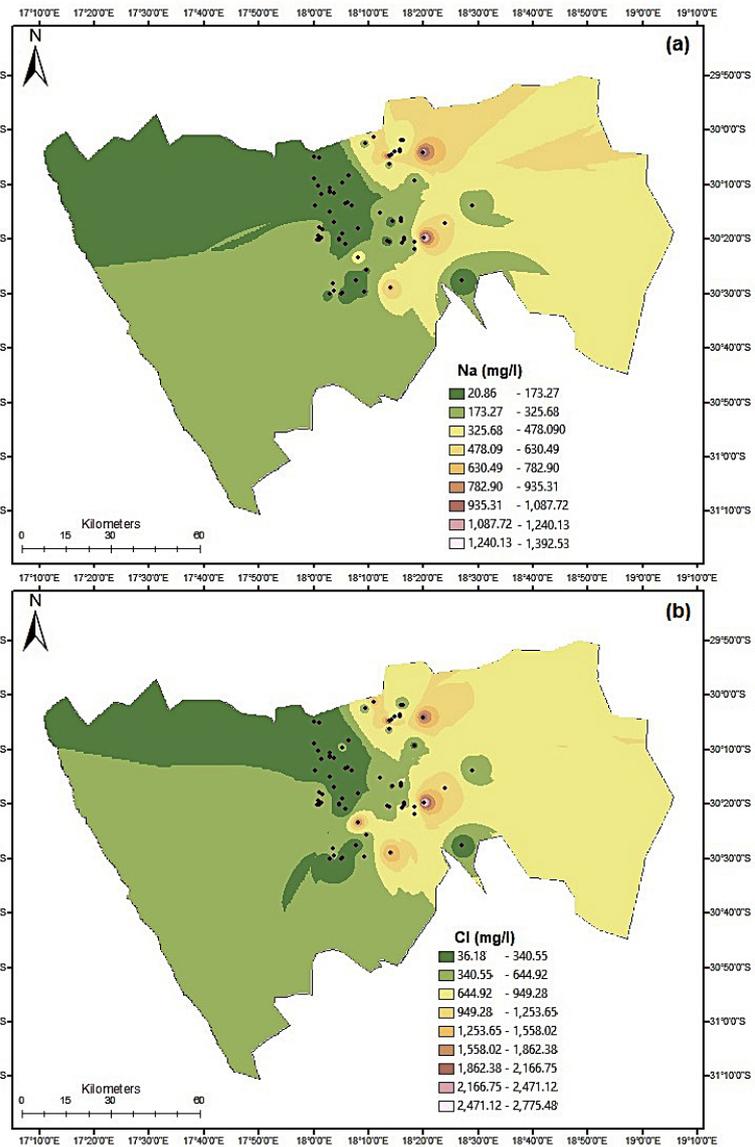


Figure 11. Spatial distribution map of groundwater for (a) Na and (b) Cl in Kamiesberg

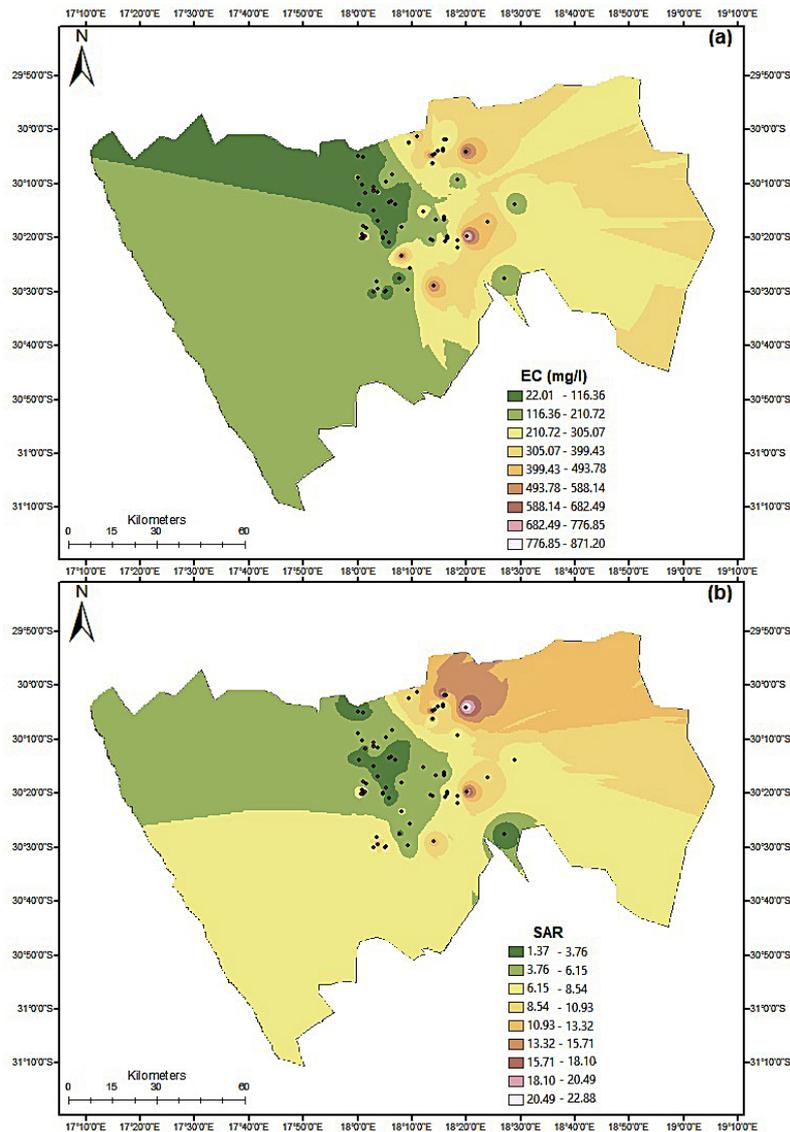


Figure 12. Spatial distribution map of groundwater for (a) EC and (b) SAR in Kamiesberg

Leliefontein, and deteriorated from the central portion towards the east. The poor groundwater quality predictions in the eastern part of Leliefontein could be as a result of ion leaching, agricultural impact, effluent discharge, geology, and anthropogenic sources.

The geology of Kamiesberg is a likely factor influencing the deteriorating groundwater quality towards the eastern portion of Kamiesberg, as shown in the geology map in Figure 3. The ECCA group geological formation located at the east part is known to exhibit high salinity in the Kalahari groundwater regions (Nell & van Huysteen, 2014). There are sedimentary deposits of the Eccca Group and Dwyka Formation, both of the Karoo Supergroup present at the eastern side of Kamiesberg (Figure 3). Dwyka groups at the eastern portions of Kamiesberg are known to

produce the groundwater with associated with high salt concentrations of major ions (Sherman, 1998), likely contributing to the enrichment of major ion concentrations towards the eastern side of Leliefontein.

CONCLUSIONS

The groundwater quality assessment is an essential step towards groundwater management, utilisation and pollution control. The groundwater hydrochemistry data for Leliefontein was analysed for the domestic and irrigation application. Major cations, anions, EC, pH, SAR, WQI, were analysed with geostatistical and spatial modelling to predict the groundwater quality in the region. Leliefontein is dominated by NaCl groundwater

type, and from the results, 94.7% indicated the NaCl type, 2.6% CaCl type and 2.6% NaHCO₃ type. SAR and salinity hazard (EC) classifications mainly considered groundwater in Leliefontein to be suitable for irrigated agricultural activities. The water types in Leliefontein are influenced by geological interaction and anthropogenic activities. The Northern Cape is a region associated with high temperatures resulting in high evaporation rates, which potentially contributes to the high chloride content of groundwater. The groundwater is generally suitable for irrigation, but domestic consumption requires further treatment as the groundwater has high contents of chloride, sodium, and fluoride above the SANS241 (SANS, 2015) recommended guidelines. In the study area, 60–100% of the boreholes show nitrate, sodium EC, pH, and SAR within acceptable standard values prescribed by SANS241 (SANS, 2015).

This study presents an integrated approach for hydrochemical data analysis with multiple validations. On the basis of WQI, 36.8% of the samples (29 boreholes) shows an excellent to good water quality, 49.4% (39 boreholes) exhibited poor to inferior water quality, and 13.8% (11 boreholes) were unsuitable water quality for Leliefontein. SAR, EC, and major ions Cl and Na show that SAR (8.9% 7 boreholes), EC (49.4% 39 boreholes), Cl (57% 45 boreholes), Na (45.6% 36 boreholes), were above the prescribed standards, an indication of moderate level of pollution in the Leliefontein. The spatial analysis map generated for the predicted groundwater parameters show that the western portion of Leliefontein gave generally good groundwater quality, and deteriorated from the middle towards the eastern side of Leliefontein. The results show the dominance of Cl and Na as the determining factors in differentiating the different water groups and contributing to the high salinity of groundwater in Leliefontein.

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