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ASSESSMENT OF GROUNDWATER QUALITY USING HYDROGEOCHEMICAL INDICES AND STATISTICAL ANALYSIS IN THE TARKWA MINING AREA OF GHANA

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An assessment of groundwater quality using a multi criteria approach has been carried out in the Tarkwa mining area. The criteria includes hydrogeochemical indices, statistical analysis and water quality index to characterise the physico-chemical parameters of groundwater in the study area. A total of 39 samples were used for the study. Piper plot and Gibbs diagrams were constructed to determine the hydrogeochemical facies, water types and the mechanism that control groundwater quality in the study area. Correlation matrix, cluster analysis and factor analysis were used to determine relationships that exist between the parameters. Results from the Piper diagram revealed that two major hydrogeochemical facies exist in the study area and the two most dominant water types in the area are the CaHCO_3 and Mixed CaMgCl type. The Gibbs diagram also revealed that rock weathering controls the groundwater chemistry. The statistical analysis revealed the relationship that exist between the various physico-chemical parameters. Results from the water quality index showed that 82 % of the samples were classified in the region of excellent and very good water category. Groundwater in the Tarkwa area is suitable for drinking purposes.

INTRODUCTION

Water and sanitation are among the basic requirements for life on earth (Mara and Evans, 2011). According to the United Nations Sustainable Development goals on water and sanitation, about 2 billion people in the world are living in areas classified as water stress. The availability of water resources in quantity and quality is a prerequisite in dealing with the sustainability of the resource. Rapid population increase across the globe has resulted in an increase in food production, thereby putting a lot of stress on water resources (Kalaivanan *et al.*, 2017). In recent times, people have resorted to groundwater for their potable use especially in developing countries (Massally *et al.*, 2017). Observations show that the reliance on groundwater resources has risen because of quality issues associated with the use of surface water. The quality of groundwater, however, varies spatially in response to geogenic and anthropogenic factors (Annapoorna and Janardhana, 2015) which warrants an assessment of the water quality to serve the purpose for which it is used.

In the Tarkwa area, the quality of groundwater is of great concern because of the presence of both large and small scale gold mining companies. Hydrogeochemical studies have been conducted in the Tarkwa area to determine the trend of water quality over the years (Yankey *et al.*, 2011; Kuma and Ewusi, 2009; Kuma and Younger 2004; Kortatsi, 2004). Due to the irregular supply of water from the Bonsa Treatment Plant, people have resorted to the use of groundwater for their potable use in the Tarkwa area (Seidu, 2017). This increase is also as a result of higher water tariffs which makes drilling boreholes for use as a cheaper option. It has therefore become important to understand how the quality of the groundwater in the area is responding to the population growth and increasing anthropogenic activities. This study aims at assessing the groundwater quality in the Tarkwa area using hydrogeochemical indices and statistical tools and the water quality index.

STUDY AREA

Tarkwa, the capital of the Tarkwa-Nsuaem Municipality is a mining town located in the Western Region of Ghana. It is accessible by road about 85 km from Takoradi the regional capital, about 233 km from Kumasi and 316 km from the national capital, Accra (Seidu, 2017).

Tarkwa area is dominated by series of ridges and valleys which are parallel to one another with a general strike of northeast-southwest (NE-SW) of the underlying geology. Whitelaw, (1929) reported that transverse to the ridges and valleys are smaller valleys and gaps determined by faulting and jointing. Elevation in Tarkwa ranges from approximately 45 m to 330 m above mean sea level. The study area falls within the Ankobra River Basin which is an extensive drainage basin. The area is drained by a large number of streams including Huni and Bonsa Rivers. These rivers are perennial even though during dry months their flows decrease significantly (Kuma and Ewusi, 2009). Also, flooding during the rainy season is very common.

The Tarkwa area falls within the south-western equatorial climate zone with season's primary influenced by moist south-west monsoon winds from the South Atlantic Ocean and dry dust-laden north-east trade winds known as the Harmattan which blows over the Sahara desert from the northern sub-tropical high pressure zone. The Inter Tropical Convergence Zone (ITCZ) crosses over the Tarkwa area two times in a year which results in two peaks in the rainfall figures. The two wet seasons stretch from April to July (with a peak in June) and October to November.

GEOLOGY AND HYDROGEOLOGY

Tarkwa is hosted on the unconformable contact between the younger Tarkwaian rocks to the west and Birimian rocks to the east. The Tarkwaian Group comprises a sequence of coarse, clastic, fluviatile meta-sedimentary rocks consisting of the Kawere conglomerates, Banket Series (host of gold mineralisation), Tarkwa Phyllite, and Huni Sandstones and Dompim Phyllite in the direction of younging (Fig. 1). About 20 % of the total Tarkwaian within the Tarkwa area is made up of intrusive igneous rocks (Kuma and Younger, 2001). These rocks range from hypabyssal felsic to basic igneous rocks, which form conformable to slightly transgressive sills with small number of dykes. The Tarkwa area is faulted and jointed with the most prominent joints trending in an east-southeast-west-northwest direction (Hirdes and Nunoo, 1994).

In the Tarkwa area, groundwater occurrence is associated with the development of secondary porosity through fissuring and weathering. The rock underlying the area lack primary porosity since they are consolidated. Kuma, (2002) stated that aquifers in the Tarkwa area possess dual and variable porosity and heterogeneous permeability with limited storage properties. Within an aquifer, folding of the whole area with the widespread presence of fractures, faults, fissures and dykes enhances this variability (Kuma and Younger, 2000). Two types of aquifers occur in the study area: the weathered and fractured zone aquifer. The weathered aquifer occurs mainly above the transition zone between fresh and weathered rocks. Due to the presence of clay and silt, these aquifers have high porosity and storage but relatively low permeability. The fractured zone aquifer occurs below the transition zone. They have high transmissivity but low storativity (Kortatsi, 2004).

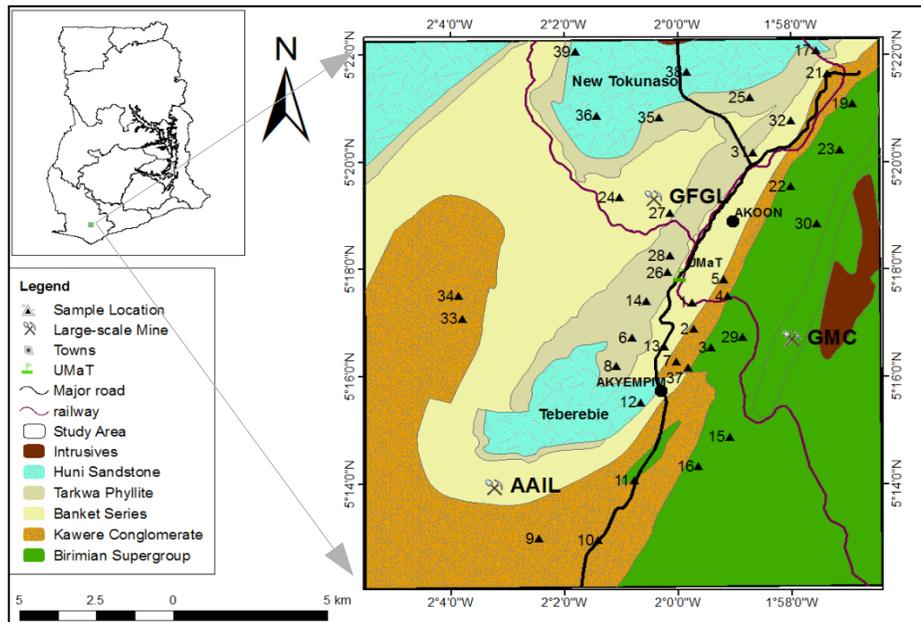


Figure 1. Simplified Geological Map of the Tarkwa Mining Area with Sample Locations.

MATERIALS AND METHODS

A total of 54 data points were initially gathered for this study. Out of the total number of samples gathered, 30 were collected from the archives of the Department of Geological Engineering, University of Mines and Technology and 24 samples were collected from field data. Physico-chemical parameters

were analysed using the standard method suggested by APHA (1995). Physical parameters like pH, TDS, EC, turbidity and temperature were taken in situ using pH meters and multiprobe meter. Chemical parameters were analysed in the laboratory. A reliability check was conducted on the 54 sample points using the charge balance equation (CBE). A total of 39 samples passed the reliability check using ± 10 in the local context (Seidu *et al.*, 2016). These samples were used for further Hydrogeochemical analysis. A Piper diagram (Piper, 1944) after constructed to determine the hydrogeochemical facies and water types in the area using aq.QA software.

Hydrogeochemistry

The samples which satisfied the reliability check were used for hydrogeochemical analysis to determine the water types in the study area and also determine the mechanism that influence water chemistry in the study area.

Piper Diagram

A Piper Diagram (Piper 1944) was constructed to determine the water types in the area using RockWare's aq.QA software. In Piper diagram, major ions are plotted in a two base triangles as cations and anions in equivalent weights. The respective cation and anion locations for analysis are projected into a diamond field, which represents the total ion relationship (Chadha, 1999).

Gibbs Diagram

A Gibbs diagram (Gibbs, 1970) was plotted using Microsoft Excel to determine the mechanism that controls water chemistry in the study area. In this diagram, TDS (mg/L) was plotted on the y-axis in a log scale and $(\text{Na}+\text{K})/(\text{Na}+\text{K}+\text{Ca})$ for cation and $\text{Cl}/(\text{Cl}+\text{HCO}_3)$ for anion was plotted on the x-axis with a normal scale with values in meq/L. The Gibbs diagram has three distinct fields which show the mechanism that controls the water chemistry: evaporation, rock–water interaction and precipitation dominance.

Statistical Analysis

Pairwise correlation matrix was constructed using Microsoft Excel to determine the linear relationship that exist between the physico-chemical parameters of the samples.

Hierarchical Cluster Analysis (HCA) was performed on the data using SPSS software to determine the relationship and differences from the categories of data sets (Kalaivanan *et al.*, 2017; Yidana *et al.*, 2012). Squared Euclidean distances were used to measure the degree of similarity among the parameters and the Ward's agglomeration technique was used to link the initial clusters.

Factor analysis was conducted on the samples to reduce the correlated variables to a small part independent composite variables using principal component as the method and the Kaiser (1960) normalization (Yidana *et al.*, 2012). An orthogonal rotation (Varimax) was applied on the factor matrix to enhance the differences among the resulting factors for easy interpretation of the results. Three factors were selected based on two dissimilar recommended principles known as cumulative variance and eigenvalue greater than 1.

Water Quality Index

WQI was computed after Asadi *et al.*, (2007). The parameters (TDS, HCO_3^- , Cl^- , SO_4^{2-} , PO_4^{3-} , NO_3^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and pH) in groundwater were given weight based on their relative importance in drinking water standards. Parameters like TDS, Cl^- , NO_3^- and SO_4^{2-} were given the maximum weight of 5. HCO_3^- and PO_4^{3-} were assigned the least value of 1 as they play insignificant role in water quality assessment.

The relative weight was computed using equation 1.

$$W_i = \frac{w_i}{\sum_{i=0}^n w_i} \quad (1)$$

where, W_i is the relative weight, w_i = weight of individual parameters and n = number of parameters.

Quality rating scale q_i for each parameter was assigned using equation 2.

$$q_i = \frac{C_i}{S_i} \times 100 \quad (2)$$

where, q_i = the quality rating, C_i is concentration of each chemical parameter in each sample of groundwater in mg/L and S_i is WHO drinking water standard for each chemical parameter in mg/L

The WQI was then computed using equation 3.

$$WQI = \sum SI_i \quad (3)$$

$$SI_i = q_i \times W_i \quad (4)$$

where, SI_i = the sub-index of the i th parameter.

The WQI was computed based on the standard of WHO (2011), the assigned weight (w_i) and relative weights (W_i) for the parameters are presented in Table 1. The general water quality of the study area was rated after Asadi *et al.*, (2007) illustrated in Table 2.

Table 1. Relative Weights of Physicochemical Parameters used for WQI.

Parameter (mg/L)	WHO standard	Weight (w_i)	Relative weight
TDS	1000	5	0.147
HCO₃	500	1	0.029
Cl	250	5	0.147
SO₄²⁻	250	5	0.147
PO₄⁻	0.5	1	0.029
NO₃	45	5	0.147
Ca	75	3	0.088
Mg	50	3	0.088
Na	200	4	0.118
K	30	2	0.059
pH	6.5-8.5	2	0.059
		$\sum w_i = 34$	$\sum W_i = 1.00$

Table 2. Water Quality Index Categories (Asadi *et al*, 2007).

WQI	Description
0-25	Excellent
26-50	Good
51-75	Poor
76-100	Very poor
>100	Unfit for drinking

RESULTS AND DISCUSSION

Hydrogeochemistry

A summary statistics of physico-chemical parameters in the Tarkwa area is presented in Table 3. It is observed that pH ranges from 5.19 to 7.23 with a mean value of 6.23. Electrical conductivity has a minimum, mean and maximum values of 52.00 mg/L, 297.05 mg/L and 1152.00 mg/L. Na⁺ and Ca²⁺ are observed to be the most dominant cations whereas Cl⁻ and HCO₃⁻ are the most dominant anions. This supports earlier work conducted by Kuma and Younger (2004).

Table 3. Summary Statistics of Physicochemical Parameters for Groundwater Samples.

Parameter	Min	Max	Mean	Standard deviation
pH	5.19	7.23	6.23	0.52
EC	52.00	1152.00	297.05	215.85
TDS	34.00	771.00	194.82	141.91
Turbidity	0.00	47.00	5.63	9.29
Na	2.89	108.12	13.02	17.18
K	0.13	36.71	2.12	5.87
Ca	1.65	90.51	21.49	25.64
Mg	0.14	22.98	6.84	6.14
Cl ⁻	2.15	156.00	14.10	25.82
SO ₄ ²⁻	0.61	51.00	6.77	10.55
HCO ₃ ⁻	2.00	278.40	80.82	80.27
NO ₃ ⁻	0.00	7.00	1.67	1.73
PO ₄ ³⁻	0.00	3.24	0.83	0.83

*All values in mg/L except EC (μS/cm) and pH

Piper Diagram

Piper's trilinear diagram showing chemical relationship between groundwater constituents is shown in Fig. 2. Two main hydrogeochemical facies are observed in the diagram in the order Ca²⁺-Mg²⁺-Cl⁻-SO₄²⁻ > Ca²⁺-Mg²⁺-HCO₃⁻. The two facies collectively constitute 92 % of the total samples. Six

different water types are observed on the plot with Ca-HCO₃ being the most dominant water type. The results from the Piper plot is summarised in Table 4.

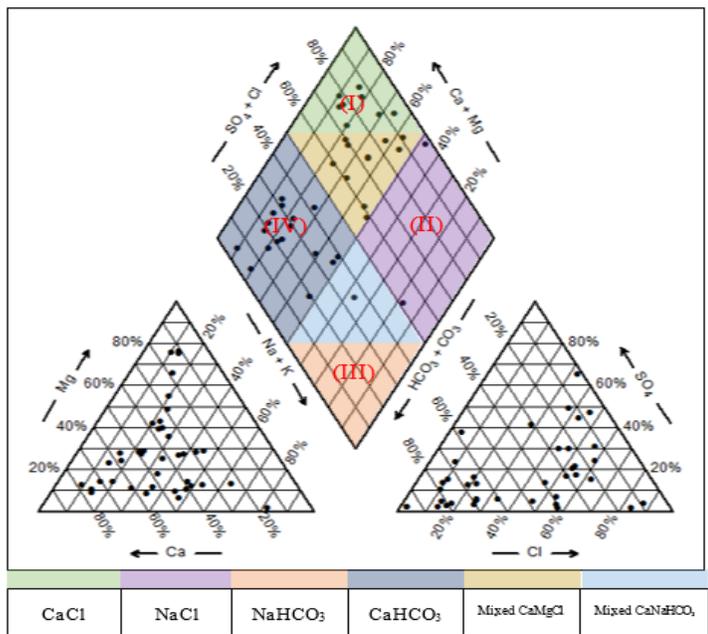


Figure 2. Piper Plot of Groundwater Samples.

Table 4. Classification of Groundwater Samples.

Class	Groundwater Types	Sample Statistics	
		No. of samples	%
Hydrogeochemical facies			
I	Ca ²⁺ - Mg ²⁺ -Cl ⁻ -SO ₄ ²⁻	19	48.72
II	Na ⁺ -K ⁺ -Cl ⁻ -SO ₄ ²⁻	2	5.12
III	Na ⁺ -K ⁺ -HCO ₃ ⁻	1	2.56
IV	Ca ²⁺ -Mg ²⁺ -HCO ₃ ⁻	17	43.59
Water types			
	Ca-HCO ₃	18	46.15
	Mixed CaMgCl	10	25.64
	CaCl	8	20.51
	NaCl	2	5.13
	Mixed CaNaHCO ₃	1	2.56

Gibbs Diagram

Results from the Gibbs plot show that 72 % of the groundwater samples are influenced by the geology and 28 % of the samples are influenced by the rainfall (Fig. 3). It is therefore observed that the

mechanism controlling most of the groundwater chemistry in the area is rock weathering. Samples 2, 4, 7, 8, 24, 25, 26, 28, 32, 33 and 35 fall within the precipitation dominance region. These samples are distributed among the Tarkwa Phyllite (5 samples), Kawere Conglomerate (4 samples) and Banket Series (2 samples). The samples whose chemistry are influenced by rainfall is attributed to younger and shallow groundwater which are in contact with precipitation.

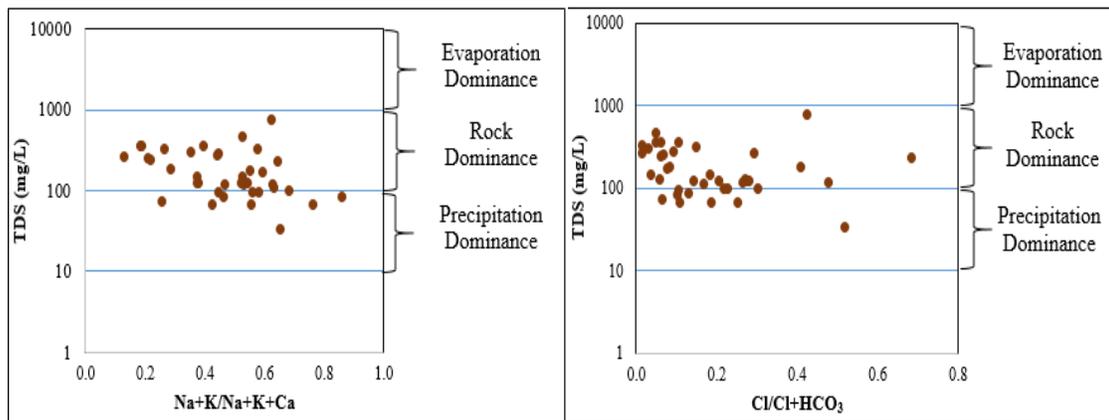


Figure 3. Anions and Cations Mechanism controlling the Groundwater Chemistry (Gibbs 1970)

Statistical analysis

Correlation Matrix

A correlation matrix was constructed to determine how the samples correlate with one another. It was observed that Na correlates well with TDS, EC, K and Cl. Ca correlates well with HCO₃. This supports the results obtained from the Piper plot which suggest that the most dominant water type in the study area is CaHCO₃ type. Na⁺ and Cl⁻ are also observed to have a good correlation. The source of Cl⁻ can be attributed to the presence of Phyllite in the Tarkwa area which is likely to dissolve to influence the water chemistry (Yidana *et al.*, 2012). Results from the correlation matrix is summarised in Table 5.

Table 5. Correlation Matrix of Groundwater Samples.

	pH	EC	TDS	Na	K	Ca	Mg	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	NO ₃ ⁻
pH	1.00										
EC	0.51	1.00									
TDS	0.52	0.97	1.00								
Na ⁺	0.51	0.80	0.80	1.00							
K ⁺	0.21	0.68	0.69	0.86	1.00						
Ca ²⁺	0.71	0.77	0.74	0.59	0.37	1.00					
Mg ²⁺	0.13	0.39	0.38	0.29	0.34	0.20	1.00				
Cl ⁻	0.38	0.73	0.72	0.92	0.86	0.49	0.36	1.00			
SO ₄ ²⁻	0.23	0.25	0.21	0.14	-0.07	0.46	-0.01	-0.02	1.00		
HCO ₃ ⁻	0.76	0.72	0.71	0.50	0.22	0.94	0.21	0.34	0.39	1.00	
NO ₃ ⁻	-0.21	-0.22	-0.24	-0.20	-0.12	-0.13	0.16	-0.15	0.31	-0.18	1.00

Hierarchical Cluster Analysis

The Hierarchical Cluster Analysis is presented as a dendrogram (Fig. 4). Results from the cluster analysis divide the study area into three clusters with most of the samples within clusters 1 and 2. There is a good correlation between Na^+ , Cl^- , Ca^{2+} and HCO_3^- as depicted in cluster 2.

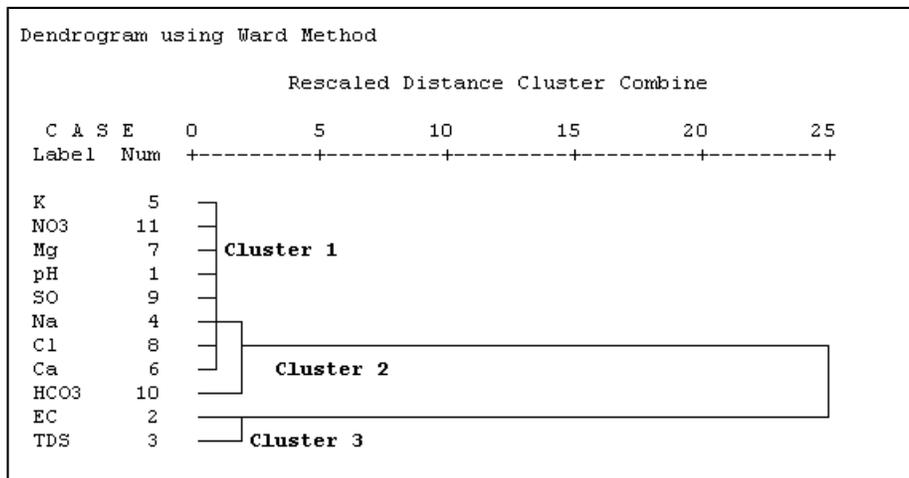


Figure 4. Dendrogram for the Groundwater Grouping for Physico-chemical Parameter

Factor Analysis

Results of factor analysis, including factor loading matrix, eigenvalue, and variances of the various factors are summarised in Table 6a and 6b. According Liu, (2003), absolute factor loadings which are greater than 0.75 are classified as having a strong factor loading. The analysis show that EC, TDS, Na^+ , K^+ , Ca^{2+} , Cl^- and HCO_3^- have high positive factor loadings in factor 1. Factor 3 has high positive loading for NO_3^- (Table 6a). Factor 1 show sources which are attributed to geogenic activity whereas factor 2 and 3 represents anthropogenic phenomenon (Kalaivanan *et al.*, 2017). The three factors account for 81 % of the total variance in the hydrochemistry of the area (Table 6b).

Table 6a. Factor Loadings Matrix from Factor Analysis.

Parameter	Component		
	1	2	3
pH	0.671	0.413	-0.257
EC	0.943	-0.023	0.023
TDS	0.937	-0.05	-0.003
Na^+	0.896	-0.291	0.024
K^+	0.733	-0.57	0.132
Ca^{2+}	0.842	0.453	-0.043
Mg^{2+}	0.396	-0.233	0.501
Cl^-	0.814	-0.462	0.08
SO_4^{2-}	0.262	0.676	0.43
HCO_3^-	0.783	0.535	-0.144
NO_3^-	-0.221	0.17	0.869

Table 6b. Variances explained by the various Factors.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.816	52.872	52.872	5.816	52.872	52.872	3.967	36.063	36.063
2	1.828	16.614	69.486	1.828	16.614	69.486	3.619	32.897	68.96
3	1.305	11.868	81.354	1.305	11.868	81.354	1.363	12.394	81.354
4	0.805	7.321	88.675						
5	0.527	4.791	93.466						
6	0.337	3.068	96.534						
7	0.176	1.6	98.134						
8	0.119	1.083	99.217						
9	0.061	0.553	99.77						
10	0.022	0.195	99.965						
11	0.004	0.035	100						

*Extraction method: Principal Component Analysis

Geology Based Water Quality Index

The calculated WQI ranges from 9.84-61.72 with a mean of 20.53. It is observed that excellent and very good water quality make up a cumulative sum of 84 %, whereas 13 % fall under good water quality and 3 % under poor water quality. The water quality rating of the study area is summarised in Table 7. A plot of the various sample points and their WQI is shown in Fig. 5. Generally the water quality index in the various lithology are classified as good-excellent. In the Birimian Supergroup, out of 9 samples, 2 were classified as excellent, 3 samples as very good and 4 samples in the good water quality categories. In the Kawere Conglomerate, 6 samples and 4 samples were recorded as having excellent and very good water quality respectively. In the Banket Series, out of 6 samples, 3 samples are classified as good, 2 samples were classified as very good and 1 sample was classified as excellent. 8 samples were recorded in the Tarkwa Phyllite: out of that, 3 samples are classified as excellent, 4 classified as very good and 1 classified as good water quality. Four (4) samples are in the very good water quality and 1 sample is in the excellent water quality in the Huni Sandstone. One sample (sample 21) is observed to be in the poor water quality category. Field observation show that the shallow groundwater has been affected by the illegal mining around it. This suggest that the quality might have been affected by anthropogenic activities.

CONCLUSIONS

According to the hydrogeochemical analysis, results from the Piper diagram revealed that there are two main hydrogeochemical facies in the Tarkwa area, namely: $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-\text{-SO}_4^{2-}$ and $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$, these two constitute 92 % of the total samples. The two most dominant water types in the area are CaHCO_3 and Mixed CaMgCl type, which gives an indication that fresh water types are available in the area. It is observed from the Gibbs plot that 72 % of the samples are controlled by rock weathering and 28 % are controlled by precipitation. This suggest that groundwater chemistry in the study area is controlled by natural factors (geology).

Table 7. Water Quality Index for Individual Parameters

Sample No.	WQI	Classification	Sample No.	WQI	Classification
1	15.96	Very Good	21	61.72	Poor
2	9.84	Excellent	22	24.73	Very Good
3	12.64	Excellent	23	14.96	Excellent
4	10.20	Excellent	24	24.82	Very Good
5	18.12	Very Good	25	19.22	Very Good
6	18.08	Very Good	26	12.68	Excellent
7	9.99	Excellent	27	28.89	Good
8	18.54	Very Good	28	11.72	Excellent
9	21.26	Very Good	29	33.67	Good
10	18.86	Very Good	30	24.04	Very Good
11	19.35	Very Good	31	24.99	Very Good
12	13.93	Excellent	32	10.64	Excellent
13	22.46	Very Good	33	10.87	Excellent
14	25.16	Very Good	34	14.80	Excellent
15	25.39	Very Good	35	10.96	Excellent
16	18.44	Very Good	36	21.19	Very Good
17	17.76	Very Good	37	13.88	Excellent
18	25.55	Good	38	22.60	Very Good
19	29.69	Good	39	23.20	Very Good
20	36.90	Good			

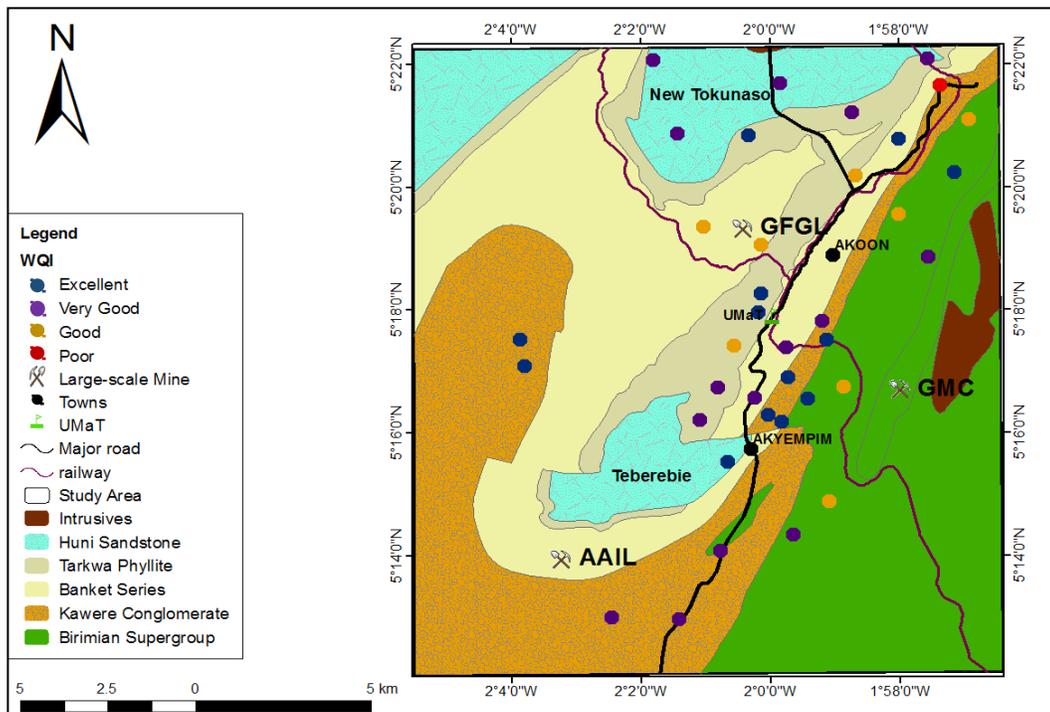


Figure 5. Distribution of WQI in the Tarkwa mining area

The cluster analysis revealed that the two most dominant cations are Na^{2+} and Ca^{2+} , and the two most dominant anions are HCO_3^- and Cl^- . The three factors extracted from the factor analysis accounted for 81 % of the total variance in the hydrochemistry of the area. The analysis showed that EC, TDS, Na^+ , K^+ , Ca^{2+} , Cl^- and HCO_3^- have high positive factor loadings in factor 1.

Results from the WQI reveal that excellent and very good water quality category sum up to a total of 86 % in the study area. Samples from the Kawere Conglomerate were observed to have the best water quality category (33 % for sum of excellent and very good water quality). Sum of excellent and very good water quality in the Huni Sandstone, Tarkwa Phyllite, Banket Series and Birimian Supergroup are 17 %, 23 %, 10 % and 17 % respectively. This suggests that the water quality in the Tarkwa area is potable.

Combining these three methods to understand the groundwater chemistry in the Tarkwa area has been good. These methods have established that Na^+ and Ca^{2+} are the most dominant cations and Cl^- and HCO_3^- are the most dominant anions.

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