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Multivariate Statistical and Geochemical Assessment of Groundwater Quality within Challawa and Sharada Industrial areas, Kano Metropolis, Northwestern Nigeria

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Abstract
Groundwater quality evaluation and characterization was carried out to determine the domestic and irrigation suitability of the groundwater occurrence within the Sharada and Challawa industrial estates. Hydrogeochemical field survey and sampling were undertaken with subsequent physico-chemical assessment and multivariate evaluation carried out to determine the water quality. This study revealed the area to consist of weakly acidic, low mineralized groundwater with pH of 6.0 and of Ca+Mg-HCO_3 type, which is characteristic of shallow, fresh and hard-water. Parametric contributions to the groundwater are from sub-surface geochemical water-rock interactions and anthropogenic activities. Drinking water quality index (DWQI) revealed excellent to good drinking water quality within both Nigerian Standard for drinking water quality (NSDWQ) and World Health Organization (WHO) standards. Similarly, irrigation water quality indices (IWQI) of % Na, SSP, RSBC, RBC, KR, and PS were 100% indicating excellent groundwater for such purpose. Multivariate statistical evaluation revealed strong to moderate relationship between most of the chemical variables which were formed under the same geochemical processes and environmental conditions. Though the groundwater was found to be safe for drinking (potable) and irrigation uses, intermittent evaluation of geogenic and anthropogenic contaminants is recommended for effective monitoring of the groundwater in study area.
Keywords: *Groundwater, hydrogeochemistry, WQI, factor analysis, base ion exchange, hard water, Kano*

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I. Introduction

The increasing interest in the geochemistry of groundwater and its quality assessment has underscored the importance of subsurface water occurrence and applications in regional hydrogeochemical studies (Hem 1985; Tay et al 2017). Changes in the major ion chemistry of groundwater indicate the geochemical processes that control its quality (Sadashivaiah et al., 2008; Ravikumar et al., 2011; Srinivas et al., 2013), hence, knowledge of such changes and processes are important aspects of assessing the quality of groundwater and its suitability for domestic, irrigation, and industrial uses. (Adimalla and Venkatayogi 2018).

Foster and Chilton, (2003) and Belkhiri et al. (2010) pointed out that quality of groundwater is controlled by both natural processes and anthropogenic activities with water-rock interactions, chemical weathering groundwater time of residence, flow paths, degree of fluid mixing and human exploitation constitute the main deterioration factors of groundwater quality. According to Zaman et al.,(2018) Salinity, Sodicity and ion toxicity are major problems in irrigation waters

According to Raju et al. (2001) global fresh water demand is rapidly increasing due to rapid population increase, urbanization, industrialization and heightened irrigation farming practices. These have profound impact on groundwater yield, quality and suitability for domestic and industrial utilization, leading to depletion and contamination of fresh water reserves. It is obvious that the quality of both the surface and groundwater resources is impacted significantly by anthropogenic activities and climate change (Arian et al. 2008; Bu et al 2010). These anthropogenic activities are in the increase resulting in increase in point source pollutants such as leachates from dumpsites, seepage from septic tanks, and municipal sewage plants, also pollutants from agro-based activities that include nitrate, pesticides, and other heavy metals and some persistent (recalcitrant) organic products (Kumazawa 2002; Balogun and Adegun 2013; Salami and Susu 2013, Adimalla and Venkatayogi 2017; Narsimha and Sudarshan 2017a, Islam and Singhal 2004).

The water quality index (WQI) which is a mathematical equation used to transform large numbers of water quality data into a single number (Stambuk-Giljanovic, 1999).This also assists in the understanding of water quality problems, the integration of many complex data and generating a score that describes water quality status of a water source and hence it has been applied for both surface and ground water quality assessment globally since the last few decades (Reza and Singh 2010, Bora1 and Goswami 2017).

As attested by Locsey and Cox, (2003), Corniello and Ducci (2014) Multivariate statistical analysis like the factor analysis (FA), principal component analysis (PCA), analysis of variance (ANOVA) and the cluster analysis (CA), are sound tools employed for detecting and explaining hydrogeochemical factors controlling the chemical composition of groundwater These statistical tools can be used to differentiate between anthropogenic and geogenic sources (Cuoco et al., 2015b; Kim et al. ,2009a; Pereira et al., 2003).Multivariate statistical technique for hydrogeochemical assessment of groundwater has been applied successfully in recent years as a tool in the study of groundwater chemistry. The utilization of multivariate statistical methods to geo-environmental data sets have helped in revealing hidden structures in the data sets and aided in resolving key geo-environmental issues at various scales (Sandaw et al. 2012). Fetter (1994) and Suk and Lee (1999) pointed out that Multivariate analysis of geochemical data operated on the concept that each aquifer zone is characterized by its own unique groundwater quality characteristics, depending on the chemical composition of the sediments that the aquifer is made of.

Globally a lot of researches have been carried out to assess the quality and suitability of groundwater of industrial areas for drinking and irrigation: these include the works of Manzoor et al., (2001), Stuart and Milne, (2001), Mondal et al., (2005), Nangare et al., (2008), Saadia K. Tariq et al.,(2009) , Deepali, and Gangwar (2010) , Muhammad Afzal et al., (2012), Brindha and Elango (2012) , Bhadra et al., (2013) , Oludare et al., (2015) , Kanagaraj and Elango (2016). In the area of present study Dan'azumi and Bichi, (2010) studied the industrial pollution and heavy metals profile of Challawa River in Kano, while J.C. Akan et al., (2007) determined the pollutants level in water of river Challawa. Egwuonwu et al., (2011) revealed that high porosity of the sandy soil in Challawa area enhances the easy and fast downward access of effluents into the groundwater iın the area. Mustapha et al (2019) in press studied the Geochemical evolution and quality assessment of groundwater resources at the downstream section of the Kano-Challawa River System.

Of all the above studies carried out by different researches on the area of present study, none has made an attempt to investigate on the drinking and irrigation water quality indices and their multivariate statistical evaluation of the groundwater resources in these industrial areas of Challawa and Sharada, these are the objectives of the study and the gaps to be addressed.

Description of the study area

Sharada and Challawa industrial areas fall within latitudes 11°52'29.2″ N to 11°57'44.9″ N and longitude 08° 20' 01.6″ to 08° 31' 04.2″ E. Highest elevation above sea level is recorded in Sharada area with 476 meters and lowest elevation is recorded at Challawa area with 426 meters. The area is characterized with flat topographically except for few undulations and low lying areas around river channels. Few outcrops of granitic intrusions can be seen around Challawa area. There is a considerable distance of about 4 kilometers between these two industrial areas. The climate of Kano state is tropical with wet and dry seasons and falls within the savannah belt of West African Savannah. Temperatures are generally high all year round gradual increase in temperature from January to mid-April and this gets as high as 40 ^{0}c. Three distinct seasons are recorded each year: a dry season starting from November to February during which the mean monthly temperature is between 21 – 23 ^{0}c, the harmattan northeast trade dust- laden winds blow at this time carrying dust from the Sahara desert and obscuring visibility. Secondly, there is the hot season which starts around March and lasts till May with mean monthly temperature of between 34-37 ^{0}c this is followed by the rainy season characterized by warm and humid weather with monthly mean temperature of about 26 ^{0}c. The mean annual rainfall is about 800 mm in Kano metropolis and about 1000 mm to the southern part of the state (Mustapha et al., 2014). Kano Metropolis is one of the fastest growing regions in the whole of the West African sub-continent. It is the single most populous urban centre in Nigeria and is ranked first in the Nigerian Federation. At present, the projected population of the region is over 12 million people at a growth rate of 2.9% (Olofin et al. 2008).

Geology of the Area

Geologically, Kano Metropolitan is underlain by the pre-Cambrian rock of the basement complex covering 80% which comprises of Granite, Gneisses, Amphibolites, Schists, Ignimbrite, and Quarzt Porphyry. Older granites which underlie large part of Challawa- Sharada industrial area of the Kano with different varieties encountered that includes medium to Coarse grained Biotite Granites, Coarse porphyritic biotite and Biotite hornblende Granite and Granite gneiss (Figure 1)

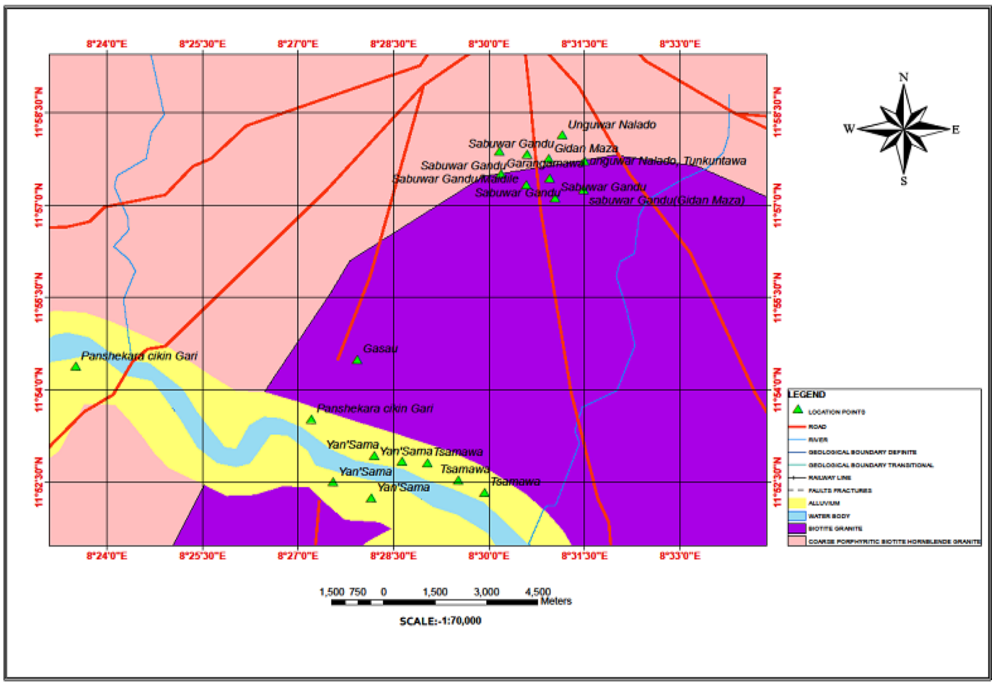


Figure 1: Geology Map of the Study area with sampling locations

II. Materials and Methods

Sampling exercise was conducted at the peaks of dry season in the month of April. Twenty (20) representative water samples were collected from different sources that include boreholes, tube wells and hand-dug wells. The coordinates and height above sea level in meters of the groundwater sampling points were taken using Global Positioning System (GPS) etrex garmin model. Before the commencement of sampling process the boreholes and tube wells were purged and flushed for 10-15 minutes for purpose of collecting samples that are true representative and flowing directly from the aquifers. Two samples were collected as separate aliquots in a ½ liter (500ml) and 300 ml high density polyethylene (HDPE) bottles in which anions and cations will be analyzed respectively. Prior to the collection of water samples, the polythene bottles were rinsed thoroughly with the water to be sampled, the sample bottles were them filled with the water and covered. Few drops of concentrated HNO_3 were added to the aliquot to be used for cations analysis to prevent precipitation of metal ions on the walls of the container and the lower the PH to 4 and to also prevent bacteriological activity (APHA, 1998). Physical parameters of water quality such as pH, temperature, total dissolved solids (TDS), electrical conductivity (EC) were measured in-situ. pH was determined using a handheld pen-type digital pH meter (SetnumdTechs) while Temperature, TDS, and Electrical conductivity were measured using a 3 in 1 hand held digital meter (SetnumdTechs). Measurement was achieved by immersing the instrument into the water, the values are read directly from the display screen on the meter. Collected water samples were transported immediately in ice-packed coolers to the laboratory to avoid bacteriological degradation (APHA, 1985). Table 1 contained the different methods, reagents and equipments used for the analysis of the different physicochemical parameters both in the field and in the laboratory.

Drinking water quality index (DWQI)

The groundwater quality and its suitability for drinking were assessed by using water quality index. This widely used method for drinking water quality index evaluation was first invented by Brown et al (1970) and then modified by Backman et al (1998). WQI can assist in the clarification of the combined effect of all detected chemical parameters in the analysed groundwater. In computing this index, each parameter was considered based on its WHO or National standard values. A relative weight based on its relative importance was assigned for each of the parameter considered. All relative weights were computed using the following formula.

$$W_i = \sum \frac{Wi}{\sum_{i=1}^{n} Wi} \qquad (1)$$

Where W_i represent the relative weight of each chemical parameter considered, and n is the number of parameters used in this study (Table 4). Computing of the rating scale q_i is the next stage, this was obtained by dividing the concentration of each of the chemical parameter considered by the WHO (2011) standard for each parameter and then multiplying that by 100 as given below, table 2.

$$q_i = (\frac{Ci}{Si}) \times 100 \quad (2)$$

q_i is the quality rating; C_i is the concentration in milligram per liter of the different chemical parameters in the groundwater sample and S_i represents the WHO (2011) standard for each of the chemical parameters in milligram per liter.

The computation of the sub-index for the *i*th parameter SI is the final step in computing the WQI which is evaluated using the formula

$$SI_i = W_i \times q_i \quad (3)$$

Where SI_i is the sub-index for the *i*th parameter, q_i is the rating whose value depends on the concentration of the *i*th parameter

The final WQI was then calculated using the equation

$$WQI = \sum_{i=1}^{n} SIi \quad (4)$$

n represent the number of parameters that were considered.

Table 1: Analytical methods reagents and equipment used for groundwater analysis

S/N	Physicochemical Parameter	Analytical Methods	Chemical reagent/ Equipment used
1	PH	Measurement	2 in 1 Digital PH and Temperature meter
2	Temperature	Measurement	2 in 1 Digital portable PH and Temperature meter
3	Electrical conductivity (EC)	Measurement	3 in 1 Digital Portable EC TDS and Temperature meter
4	Total dissolved solid (TDS) DO	Measurement	3 in 1 Digital Portable EC TDS and Temperature meter
5	Turbidity	Titrimetry	$MnSO_4$, 2 ml Conc H_3PO_4,0.025M thiosulfate
6		Measurement	HACH 2100P Turbidimeter.
7	Ca^{2+}	EDTA	0.1 M HCl and EDTA
8	Mg^{2+}	EDTA	5 M HCl and Eriochrome black T
9	Na^+	Photometry	Flame Photometer
10	K^+	Photometry	Flame Photometer
11	HCO_3^-	Titrimetry	0.05 M H_2SO_4 and Phenolphthalein indicator
12	CO_3^{2-}	Titrimetry	0.05 M H_2SO_4 and methyl orange indicator
13	H_2SO_4	Titrimetry	1.1 M HCl, and $BaCl_2$
14	NO_3^-	Titrimetry	MgO, Devarda's alloy and 5 M Boric acid
15	Cl^-	Titrimetry	KCr and 0.05 M $AgNO_3$

Table 2: Standard used for Drinking water quality index

Parameter	WHO Standard	Assign weight (Aw_i)	Weight (W_i)	NSDWQ (2015)
pH	7.5	2	0.048	65.5-8.5
EC	1000	4	0.098	1000
TDS	500	5	0.122	500
TH	150	3	0.0732	150
Na	200	2	0.048	200
K	12	3	0.0732	12
Ca	200	4	0.098	200
Mg	150	3	0.0732	20
SO_4	250	4	0.098	100
HCO_3	120	1	0.0244	100
Cl	250	5	0.122	250
NO_3	50	5	0.122	50
		$\sum Aw_i=41$	$\sum W_i=1.00$	

Irrigation Water Quality Indices (IWQI)

Different equations were used for computing the irrigation water quality indices used in this study. All concentrations of the parameters were given in meq/l.

Multivariate Statistical analysis

The acquired hydrogeochemical Data set was subjected to statistical evaluation by employing the statistical tool components of Correlation matrix (CM), Principal components analysis (PCA), and Cluster analysis (CA) using the SPSS Statistical version 21 soft ware package of IBM. These statistical tools were used to bring out the relationship, origin and similarities that existed between the hydrogeochemical components present in the analyzed groundwater samples from the study area.

Table 3: Equations adopted and used for computing the different Irrigation water quality indices

S/N	INDICES	EQUATION	Reference
1	Sodium Absorption Ratio(SAR)	$\frac{(Na)}{\sqrt{[(Ca+Mg)/2]}}$	Richards (1954)
2	Residual Sodium Carbonate (RSC)	$(HCO3+CO3)-(Ca+Mg)$	Eaton (1950)
3	Soluble Sodium Percentage (SSP)	$[(Na+K)/(K+Na+Ca+Mg)]\times 100$	Wilcox (1955)
4	%Na	$\frac{Na}{Ca+Mg+Na+K}\times 100$	Wilcox (1955)
5	Permeability Index	$[\![Na+\sqrt{HCO3}\,]/[Ca+Mg+Na]]\times 100$	Szabolcs and Darab (1964)
6	Magnesium Hazard	$\left[\frac{(Mg)}{(Ca+Mg)}\right]\times 100$	Wilcox (1955))
7	Kelly's Ratio	$[(Na)/(Ca+Mg)]$	Kelly (1940)
8	Potential Salinity (PS)	Cl $\sqrt{SO4}$	Doneen (1964)
9	Residual Sodium Bicarbonate	$HCO_3^{-}Ca^{2+}$	Eaton (1950)

III. Results and Discussions

The concentrations of the analyzed and measured physicochemical parameters of groundwater obtained in the study area are presented in table 4 while the statistical summary is given table 5.

Based on results in tables 4 and 5, all the analysed metals Na, K, Ca and Mg, with the exception of Mg which had concentrations above the accepted limits of 20 mg/l of the Nigerian Standard for Drinking Water Quality NSDWQ (2015), in 9 of the samples, this account for 45% out of the 20 samples analyzed. The other metals had concentrations that are within the set limits of NSDWQ and the WHO, (table 2). The result revealed calcium (Ca) to be dominant over other metallic ions detected in the analyzed groundwater samples in the order Ca > Mg >Na >K, this also shows the concentrations of the alkaline earth metals to be higher than those of the alkali metals in the groundwater from the area. The anions concentrations indicated all analyzed non metallic ions in the collected sampled water to be within the maximum permissible limits of the NSDWQ with HCO_3 concentration exceeding the other analyzed anions. HCO_3 concentrations exceeded the NSDWQ standard in 5 samples (25 %). This indicates the dominance of weak acids over strong acids as given in the order HCO_3 > CO_3 > SO_4 > Cl. The measured Electrical conductivity EC and the Total dissolved solids TDS showed only two samples had values that were above the NSDWQ values of 1000 µS/cm and 500 mg/l respectively. All the two samples were located at the Sharada industrial area. Groundwater $_{P}$H gives a range of between 5.4 and 6.3 with an average of 6 indicating the groundwater to be weakly acidic. Calculated total hardness TH in this study revealed 6 samples (30 %) out of the total samples had TH values less than 150 which were between 120 and 150 making them to be of moderate hardness, while the remaining 15 samples 75% had total hardness above 150 placing them in the class of hard water based on the classification range given by Sawyer and Mc Carty (1967). From the results in table 4, higher readings of Turbidity above the Standard value of 5 NTU was recorded in 4 out of the total analyzed samples, these are for groundwater samples that were collected from a Hand Dug Well and three Tube Wells in the area. Dissolved Oxygen DO ranges between 2- 9.2 with an average of 5.75 which is within the accepted range of 4-10 of the WHO, all values that are below 6 indicate pollution.

From the result obtained 10 samples (50%) of the sampled water are considered polluted based on measured DO. From the above it is clear that the groundwater from the area is of low chemical concentration that is within the limit of the National standard (NSDWQ) this makes it safe for drinking and other household uses without any health implications.

Drinking water quality index

The quality of water for drinking for the groundwater in the studied area was assessed by computing the drinking water quality index (DWQI) table 6. Based on the classifications in table 7, the critical value of drinking water quality is taken as 100. The calculated quality indices for this study as contained in table 5 has a range of between 21.61 and 68.47, hence based on the classification given in table 6, 17 out of the 20 groundwater sampled in the area are of Excellent quality with quality index values below 50 which represent 85 % of the total samples considered, while the three remaining groundwater samples fall within the good water quality class of drinking water index, this showed the water to be of excellent to good quality for drinking purpose and very safe for human and livestock consumption the average value for the area is 35 8 which denote an overall excellent quality for groundwater in the study area.

Table 4: Result of the physicochemical analysis of groundwater from Sharada and Challawa areas

S/NO	Well ID	Ca^{2+} mg/l	Mg^{2+} mg/l	Na^{+} mg/l	K^{+} mg/l	TH mg/l	HCO_3^- mg/l	SO_4^{2+} mg/l	NO_3^{2-} mg/l	Cl^- mg/l	CO_3^{2-} mg/l	TDS mg/l	EC μS/cm	DO	Temp °C	PH	Turbidity NTU
1	SH1	20	30	2.3	0.7	170	120	55.14	1.6	1.4	0	111	230	5.9	31	5.82	1.52
2	SH2	52	15.6	3	1	194	100	50.61	1.4	3	0	235	448	8.3	29	6.24	2.86
3	SH3	30	39.6	1.7	0.5	237	100	51.44	1	1.4	0	75	147	6.2	31	6.05	1.03
4	SH4	88	15.6	7.5	6.3	284	150	50.61	1.6	9.4	20	880	1795	5.1	29	6.2	9.1
5	SH5	32	2.4	8	1.4	179	130	49.38	1	9.7	20	912	1801	6.8	29	6.35	0.8
6	SH6	34	34.8	3.5	1	228	100	53.91	1	4.1	0	257	509	6.1	30	6.01	1
7	SH7	54	2.4	2.9	2.8	145	100	51.03	1	4.8	0	280	555	5.9	29	5.4	1.6
8	SH8	86	0	4	1.5	215	110	50.2	1.6	5.8	0	384	762	5.2	29	6.07	2.6
9	SH9	36	46.8	1.7	1	282	110	48.97	1	1.5	10	74	142	8.8	30	5.6	1.04
10	SH10	68	0	3.5	1.1	170	160	50.2	1.2	5.1	0	272	540	9.2	29	5.68	1.6
11	CHL1	60	0	3.5	1.3	150	90	53.08	1.4	3.3	0	228	453	4.7	31	6.23	1.01
12	CHL2	60	0	4.1	3.5	150	90	48.97	1.4	4.5	0	378	790	4.4	29	5.74	2.01
13	CHL3	48	0	1.5	0.9	120	100	49.79	1.2	1.5	0	102	211	4.2	27	5.9	2.49
14	CHL4	30	39.6	0.9	0.3	238	170	48.97	1.4	0.9	20	47	97	2	28	6.35	0.96
15	CHL5	44	2.4	4.5	3.8	120	90	51.85	1.2	2.7	0	285	578	5.6	29	6.02	3.01
16	CHL6	44	30	2.5	2.3	233	90	49.79	1	1.5	0	102	200	5.6	30	5.78	9.18
17	CHL7	38	13.2	4.3	0.5	149	110	52.67	1.2	2.5	0	101	204	6	31	5.85	9.2
18	CHL8	30	49.2	8	2	277	170	53.5	1.4	4.7	20	405	799	6.3	28	6.23	1.56
19	CHL9	48	37.2	4.3	1	273	210	52.26	1	2.2	20	212	434	4	27	6.1	2.54
20	CHL10	28	66	9.8	1.5	334	140	53.08	1.2	3.9	0	429	853	4.6	27	6.38	7.37

Table 5: Statistical summary of concentrations of physicochemical parameters in groundwater of study area

Parameter	Minimum	Maximum	Mean	Std. Deviation	Variance
Ca^{2+}	20.0	88.0	46.5	18.7	348.6
Mg^{2+}	0	66.0	21.24	20.72	429.14
Na^{+}	0.9	9.8	4.075	2.44	5.94
K^{+}	.3	6.3	1.7	1.44	2.08
TH	120.0	334.0	207.4	61.8	3816.5
HCO_3^-	90.0	210.0	122	33.97	1153.7
SO_4^{2-}	48.97	55.14	51.3	1.83	3.5
NO_3-	1.0	1.6	1.24	.22	.05
Cl-	0.9	9.7	3.7	2.47	6.12
CO_3^{2-}	0	20.0	5.5	8.9	78.68
Ph	5.40	6.38	6	.273	.07
DO	2.0	9.2	5.75	1.69	2.85
Temp	27.0	31.0	29.2	1.31	1.7
EC	97.0	1801.0	577.4	480.45	230833.8
Turbidity	.80	9.20	3.12	2.97	8.8
TDS	47.0	912.0	288.5	239.4	57312.3

Table 6: SI and Drinking water quality indices for analyzed groundwater samples in the area of study

well ID	PH	TDS	EC	TH	Na	K	Ca	Mg	HCO_3	SO_4	CL	NO_3	WQI
SH1	3.73	2.71	2.25	8.3	0.06	0.43	0.98	1.5	2.44	2.2	0.07	0.4	**25.07**
SH2	4	5.7	4.4	9.5	0.07	0.61	2.55	0.76	2	2	0.15	0.34	**32.08**
SH3	3.9	1.83	1.44	11.6	0.041	0.31	1.5	1.9	2	2.02	0.07	0.24	**26.85**
SH4	4	21.5	17.6	13.9	0.18	0.23	4.3	0.76	3.1	2	0.5	0.4	**68.47**
SH5	4.1	22.3	17.65	8.74	0.2	0.85	1.6	0.12	2.6	1.94	0.5	0.24	**60.84**
SH6	3.85	6.3	4.91	11.13	0.08	0.61	1.7	1.7	2	2.1	0.2	0.24	**34.84**
SH7	3.5	6.8	5.44	7.1	0.07	1.71	2.65	0.76	2	2	0.23	0.24	**32.5**
SH8	3.9	9.4	7.44	10.5	0.1	0.92	4.2	0	2.24	2	0.28	0.4	**41.38**
SH9	3.6	1.81	1.4	13.8	0.041	0.61	1.8	2.3	2.24	1.92	0.07	0.24	**29.83**
SH10	3.64	6.64	5.3	8.3	0.08	0.67	3.3	0	3.3	2	0.25	0.3	**33.78**
CHL1	4	5.6	4.44	7.32	0.08	0.8	2.9	0	1.83	2.1	0.2	0.34	**29.61**
CHL2	3.7	9.2	7.7	7.32	0.1	2.14	2.9	0	1.83	1.92	0.22	0.34	**37.37**
CHL3	3.8	2.5	2.1	5.9	0.04	0.55	2.4	0	2	1.95	0.07	0.3	**21.61**
CHL4	4.1	1.15	0.96	11.6	0.022	0.18	1.5	1.9	3.5	1.92	0.44	0.34	**21.61**
CHL5	3.85	7	5.7	5.9	0.11	2.32	2.2	0.76	1.83	2	0.13	0.3	**32.1**
CHL6	4	2.5	1.96	11.4	0.06	1.4	2.2	1.5	1.83	1.95	0.07	0.24	**29.11**
CHL7	3.7	2.5	2	7.3	0.1	0.31	1.9	0.64	2.24	2.1	0.12	0.3	**23.21**
CHL8	4	10	7.8	13.5	0.2	1.22	1.5	2.4	3.5	2.1	0.23	0.34	**46.79**
CHL9	3.9	5.2	4.25	13.3	0.1	0.61	2.4	1.84	4.3	2.05	0.11	1	**39.1**
CHL10	4.1	10.5	8.4	16.3	0.24	0.92	1.4	3.2	2.85	2.1	0.2	0.3	**50.51**
											Total		**716.66**
											AVERAGE WQI		**35.8**

Table 7: Standard classes of Drinking water quality index

SN	WQI Class	WQI Category	No. of water samples	% of Samples
1	< 50	Excellent water	17	85
2	50-100	Good water	3	15
3	100-200	Poor water	0	0
4	200-300	Very poor water	0	0
5	>300	Unsuitable for drinking	0	0

Irrigation water quality

The suitability of the groundwater in the area for irrigation purpose was computed using the different equations given in table 3. Nine quality indices used in categorizing irrigation water quality were computed in these studies, (table 8). The calculated values of these indices were compared with the given standards presented in table 9.

Table 8: Calculated groundwater Irrigation water indices for the study area

well ID	SAR	SSP	%Na	PI	KR	MH	RSC	RBSC	PS
SH1	10	2.8	3.3	42	0.03	71	-1.49	1.01	1.1
SH2	13	3.2	3.9	36	0.03	13	-2.26	-0.96	1.1
SH3	6.4	6.7	1.7	28	0.06	6.4	-3.16	0.14	1.09
SH4	27.5	5.3	8.5	34	0.06	27.5	-3.2	-1.9	1.3
SH5	52.2	16	17.7	86	0.2	52.2	0.99	0.53	1.3
SH6	18.2	4.2	4.79	32	0.04	18.2	-2.26	-0.06	1.2
SH7	15.3	4.2	6.45	48	0.04	15.3	-1.26	-1.06	1.2
SH8	16	3.8	4.7	33.5	0.04	16	-2.5	-2.5	1.2
SH9	6.2	1.3	1.8	24	0.01	16.2	-3.85	0	1.04
SH10	16.3	4.2	5.03	49.7	0.04	16.3	-0.8	-0.8	1.16
CHL1	17	4.7	5.7	43.4	0.05	17	-1.5	-1.5	1.14
CHL2	20.7	5.5	8.3	45	0.06	20.7	-1.5	-1.5	1.14
CHL3	8.8	2.8	3.6	49.6	0.03	8.8	-0.76	0.76	1.06
CHL4	3.64	0.8	0.9	35	0.008	3.64	-1.34	1.3	1.04
CHL5	26	7.7	11	55.5	0.08	26	-0.9	-0.7	1.12
CHL6	10	2.2	3.5	31	0.02	10	-3.2	-0.7	1.06

CHL7	23	6.3	6.7	47	0.07	23	-1.2	-0.1	1.12
CHL8	29	5.9	6.8	35	0.06	29	-5.04	1.3	1.2
CHL9	16.7	3.5	4	34	0.04	16.7	-1.44	1	1.11
CHL10	33	5.9	6.5	27	0.06	33	-4.5	0.9	1.2

Table 9: Irrigation water quality indices Standards

Irrigation Index	Range/ Class interval	Classes of indices	Number of samples analyzed	% of samples in each class	Reference
SAR	<10 10-18 18-26 >26	Excellent Good Doubtful Unsuitable	4 8 4 4	20 40 20 20	Richards (1964)
SSP	<20 20-40 40-80 >80	Excellent Good Fair/permissible Poor	20	100	Wilcox (1955)
% Na	<20 20-40 40-60 60-80 >80	Excellent Good Permissible Doubtful Unsuitable	20	100	Eaton (1950)
RSBC	<5 mg/l 5-10 mg/l >10 mg/l	Safe Marginal Unsatisfactory	20	100	Eaton (1950)
RSC	< 1.25 1.25-2.5 >2.5	Good Doubtful Unsuitable	20	100	Eaton (1950)
PI	<80 80-100 100-120	Good Moderate Poor	19 1	95 5	Doneen (1961)
MH	<50 >50	Suitable Unsuitable	18 2	90 10	Szabolcs and Darab (1964)
KR	<1 >1	Suitable Unsuitable	20	100	Kelly (1940)
TDS	<1000 mg/l 1000-3000 mg/l 3000-10,000 mg/l 10,000-35,0000 mg/l	Fresh water Slightly saline Moderately saline High saline	20	100	US Geological survey (2000)
EC	<250 µS/cm 250-750 µS/cm 750-2250 µS/cm 2250-5000 µS/cm >5000	Excellent Good Permissible Doubtful Unsuitable	7 7 6	35 35 30	Wilcox (1955)
TH	0-75 mg/l 75-150 mg/l 150-300 mg/l	Soft Moderately hard Hard	 6 14	 30 70	Sawyer and Mc Carty (1967)
PS	(< 5) 5-10 (<10)	Excellent to Good Good to Injurious Injurious to Unsatisfactory	20	100	Doneen (1964)

Irrigation water quality indices interpretation

Water required for irrigating the land is normally selected based on its physicochemical properties and also on the concentration and quantity of dissolved salts in it. At the root zone plants will selectively take up nutrients while the excess are left to accumulate around the root of plants to cause toxicity and salinization of the soil. The general effects of excess salt on the soil is modifications of permeability, structures and air circulations that have direct bearing on the growth and yield of plants.

Sodium adsorption ratio (SAR)

Excess Sodium (Na) accumulating in the soil can affect the physical property of soil which can lead to reduction of soil permeability. Excess salts especially sodium can affect the osmotic pressure in soil leading to reduction in the nutrient and water intake by plants roots and consequently slowing down the movement of water to the different parts of the plants especially the leaves, this will consequently result in the increase of soil alkalinity which is not good for the proper function of plants largely their growth and yield. The calculated SAR values range between 3.64 and 52.2 based on the Richards (1964) classification in table 9, where 20 % of the studied groundwater samples are of excellent irrigation water quality, eight of the samples (40%) fall in the class of good irrigation water quality while the doubtful and unsuitable constituted 20 % each of the analysed sampled groundwater. On the Wilcox diagram figure 2, SAR was used to plot the salinity diagram which is the Salinity hazard against Alkalinity hazard. All groundwater samples fall in the S1 class of low sodium hazard which is the safe class in terms of alkalinity. For Salinity hazard majority of the samples fall in the medium salinity hazard class of C2 followed by the C1 class of low salinity while the C3 class of high salinity hazard had only three of the sampled groundwater in it. However, groundwater in the area in terms of the computed SAR values obtained can be considered safe for use as irrigation water.

Soluble Sodium percentage (SSP) and Percentage Sodium (Na %)

These two indices are almost the same as their computed values are closely related and almost the same in magnitude. All values obtained for the analyzed water samples (100 %) fall into the excellent categories of irrigation water. The % Na was plotted against electrical conductivity (EC) values of groundwater to obtain the Wilcox plot figure 3. It is very clear from the plot that all the groundwater that is 100 % analyzed in this study belong to the excellent to good class of irrigation when considering the EC and % Na which is safe for land irrigation.

Electrical conductivity (E C)

EC can affect the yield of crops when it is high and also the quantity of water transported by plant, also the higher EC values in groundwater used in irrigating the land can affect the root zone and the soil fertility. Based on the classification on table 9 of Wilcox (1955) and the following classification given by Handa (1975) as low < 250, medium (250-750), high (750 -2250) showed that EC values above 750 µs/cm is not suitable for irrigation. Based on Wilcox classification, the excellent and good class of EC constituted 35 % each of the collected groundwater samples while the remaining 6 samples fall in the Permissible class, this revealed that 70 % which is 14 sampled groundwater are safe for irrigation based on EC values.

Permeability Index PI

When the soil is continuously exposed to high quantity of Ca, Na, Mg and HCO_3 through the use of water with high concentrations of these ions it will affect the soil permeability a lot. The permeability plot figure 4, of Doneen (1964) classified irrigation water into three categories. 80 % of the sampled groundwater (16 samples) belong to class II category of permeability index with 75 % maximum permeability while the remaining fall into the class I permeability domain. Based on Doneen (1961) classification in table 9. Out of the total samples, 95 % of the sampled water belongs to the good class with only a sample in the medium permeability class.

Residual sodium carbonate (RSC)

Higher content of HCO_3 and CO_3 over Ca and Mg lead to the precipitation of more Ca and Mg which increases the alkalinity of the soil with a resultant effect of decreasing the soil permeability. Eaton (1950) classified irrigation water on the bases of RSC into three classes, for this study 100 % of the sampled water fall into the good class of irrigation water.

Residual Sodium Bicarbonate (RSBC)

The high concentration of sodium bicarbonate and carbonate in irrigation water can affect the physical properties of the soil. RSBC is classified as safe, marginal and unsuitable by Eaton (1950). All the 20 groundwater samples fall in the safe class of irrigation.

Magnesium Hazard

When magnesium content of the soil is high it increases relative to that of sodium in the soil this leads to dispersion of clay particles and damage to the structure of the soil with a resultant reduction of soil hydraulic conductivity. This can slow the uptake and distribution of water and nutrients to the different parts of plant which can slow plant growth and therefore causing poor yield. The computed MH showed 90 % of the samples fall in the class of suitable irrigation water while the 10 % of the samples are unsuitable for irrigation purpose based on Szabolcs and Darab (1964) classification.

Potential Salinity (PS)

Salts with low solubility do accumulate in the soil these will increase the salinity of the soil. They normally precipitate out of solution and get accumulated in the root zone within the soil. Doneen develop the soil potential salinity to evaluate the suitability of groundwater for irrigation. The classification of Doneen in table 9 revealed that all the 20 samples are of excellent to good quality for irrigation.

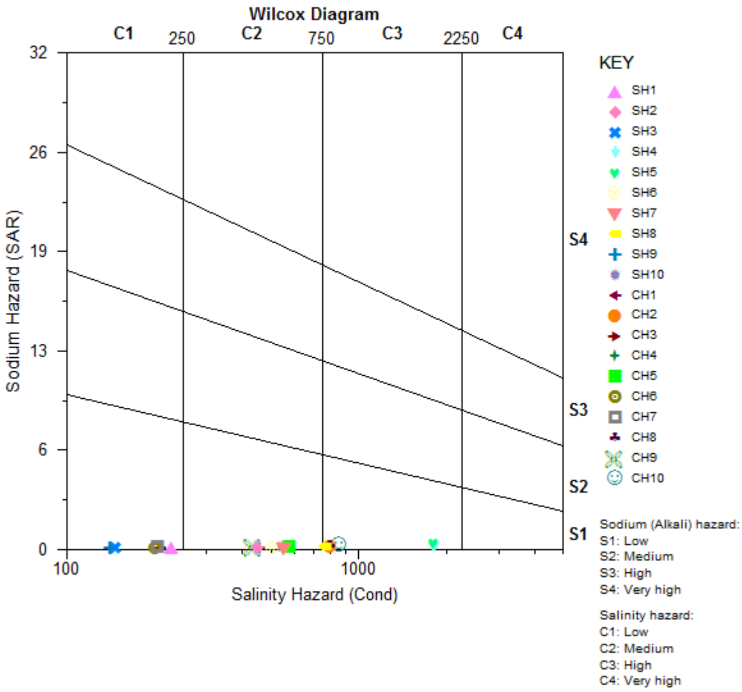


Figure 2: Wilcox Salinity diagram

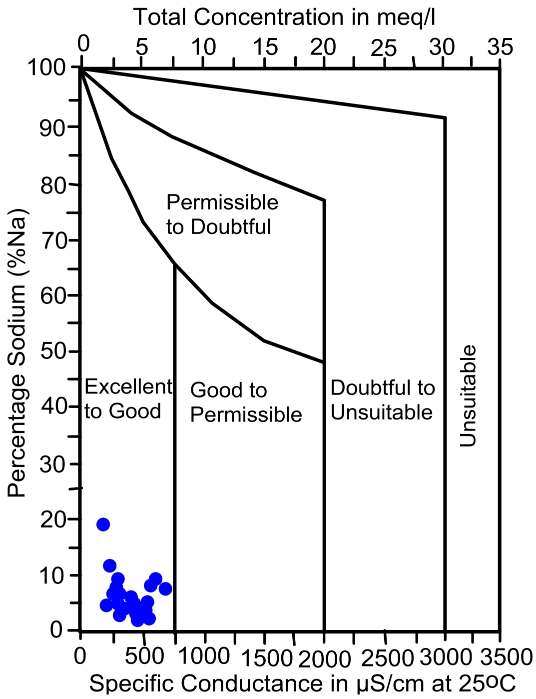


Figure 3: Wilcox diagram for Irrigation water

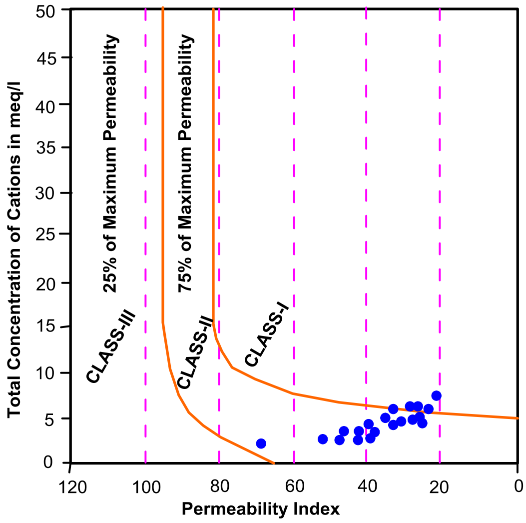


Figure 4: Doneen permeability index plot for irrigation water

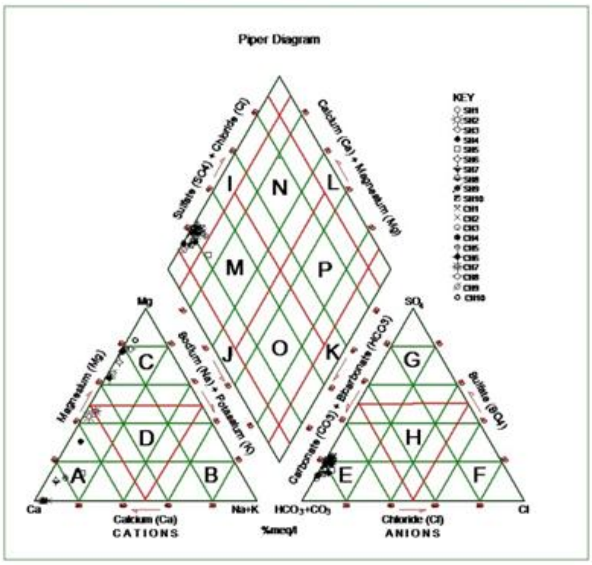


Figure 5: Piper Trilinear plot

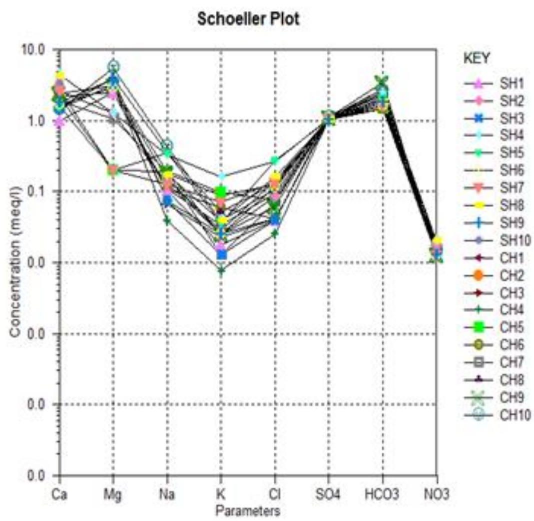


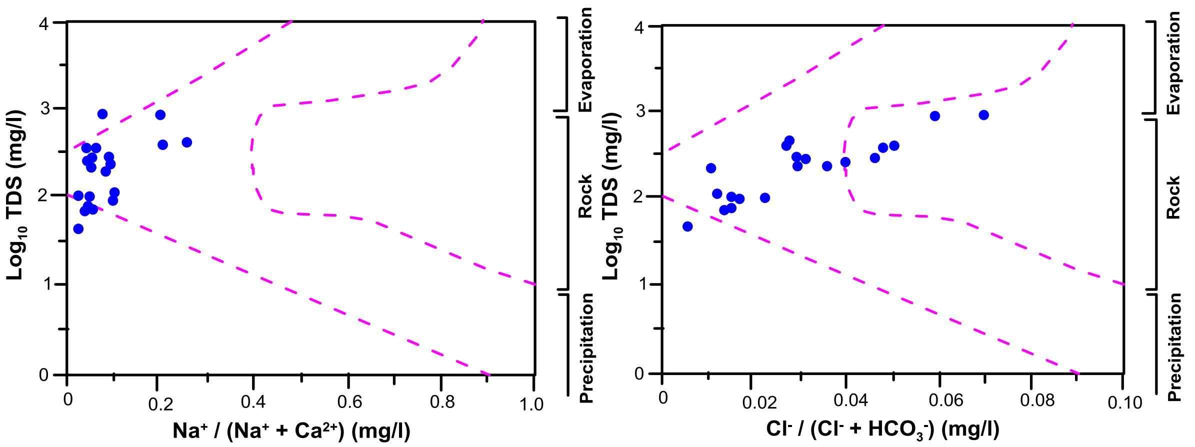
Figure 6: Schoeller plot for the groundwater in the study

Groundwater types

The groundwater species in the study area were classified using the Piper (1944) trilinear diagram figure 5 and 6 this was found to be predominantly Ca+ Mg-HCO_3 water type which is shallow, fresh and hard with less dissolved solutes.

The Origin of Hydrogeochemical parameters

The origin of both the cations and anions in the groundwater were predicted and demarcated using the Gibbs (1970) plots figure 7a and 7b. The three controlling factors of chemical precipitation, rock and evaporation domain were demarcated. In the diagram most of the cations fall in the rock domain (18 samples) with one sample each falling in the precipitation and evaporation. For the anions 19 samples out of the 20 samples were in the rock domain only one sampled groundwater was in the precipitation domain. The origin of the chemical parameter in the groundwater in the area showed that both the cations and anions originated from the interaction between the percolated groundwater and the rock/aquifer materials through the weathering and dissolution of the rocks and more importantly the aquifers in the sub surface.



Figures 7a and 7b: Gibbs diagram for the origin of chemical species in groundwater

Ion-exchange process

The ion-exchange process that could lead to the enrichment of Ca and Mg in groundwater was given by Schoeller (1977), the Chloro-Alkaline indices CAI-I and CAI-II were used to differentiate or evaluate between ion exchange process between groundwater and the aquiferous rock through water-rock interaction during residence and travel in the subsurface. The computed indices were obtained by using the following equations

$$\text{CAI-I} = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \qquad (5)$$

$$\text{CAI-II} = \frac{Cl^- - (Na^+ + K^+)}{(SO4^{2-} + HCO3^- + CO3^- + NO3^-)} \qquad (6)$$

When the value of CAI is positive it indicate no base ion exchange but when the value obtain is negative it implies base ion exchange occurrence between the Na and K in groundwater and the Ca and Mg in the rock matrix during which the Ca and Mg in the rock dissolve to take the position that was previously occupied by Na and K in the groundwater. In Table 10, all computed CAI-I and CAI-II values show all the groundwater had undergone base ion exchange which has led to the enrichment of Ca and Mg ions in the groundwater.

Table 10: Chloro-Alkaline indices of groundwater in the area

Well ID	CAI-1	CA1-II
SH1	-1.98668	-0.02498
SH2	-0.84426	-0.02631
SH3	-1.19628	-0.01733
SH4	-0.83805	-0.06281
SH5	-0.40263	-0.0347
SH6	-0.53751	-0.02238
SH7	-0.46058	-0.02295
SH8	-0.29796	-0.01696
SH9	-1.35212	-0.02016
SH10	-0.25382	-0.0099
CHL1	-0.99267	-0.0355
CHL2	-1.11021	-0.05599
CHL3	-1.08607	-0.01705
CHL4	-0.84426	-0.0056
CHL5	-2.84621	-0.08422
CHL6	-2.96039	-0.04956
CHL7	-1.83361	-0.0443
CHL8	-2.01055	-0.06796

CHL9	-2.42609	-0.03312
CHL10	-3.22354	-0.10373

Multivariate Statistical analysis

Pearson correlation

The Pearson correlation was performed on the 16 physico-chemical parameters data set, for the interpretation the 0.01 significant level at 99 % confidence was used, table 11. EC was strongly and positively correlated to TDS (*p* 1.00), Cl (*p* 0.954), Na (*P* 0.779), and gives a moderate correlation with K (*p* 0.625) this high correlations of EC with other parameters point to the dependency of EC on these ions and also the contribution of the groundwater salinity by these dissolved elements. The correlation between Total dissolved Solids (TDS) and some other elements ranges from strong to moderate, TDS and Cl was (*p* 0.956), TDS and Na (*p* 0.783) but it correlates moderately with K (*p* 0.609) this could probably be an indication of formation under the same geochemical condition. Chloride Cl was moderately correlated to Na (*p* 0.685) this indicates the origin of the two ions under the same hydrogeochemical environment as well as their contribution to the salinity of the groundwater, on the other hand Cl had almost the same strong and positive relationship with TDS (*P* 0.956) and EC (*P* 0.954) which showed that significant contribution made by Cl to the salinity and dissolved components in the groundwater. As expected HCO_3 and CO_3 were positively and strongly correlated which point to their same origin and formation under the same geochemical condition. The moderate and strong positive correlations between Ca and Mg (*p* 0.610) and between TH and Mg (*p* 0.833) can be attributed to the contribution made by these dissolved ions to the hardness of the groundwater and also show a common source for the ions in the water.

Factor Analysis

The mode factor analysis for the reduction and extraction of the hydrogeochemical data was employed in this analysis, also the Kaiser (1958) method was used in which only factors with Eigen values greater than 1 were retained after the varimax rotation which is considered significant. Factor loading of each variable in any of the components are classified based on the Liu et al (2003) classification into 'Strong', 'Moderate' and 'Weak' with corresponding values of > 0.75, 0.75-0.5 and 0.5-0.3 respectively. In table 12, the reduced and extracted factors for this study are 5, with to a total variance of 79.7 % contributed. Factor 1 which has Eigen value of 5.039 was positively and strongly loaded TDS (0.93), EC (0.933), Cl (0.855) and Na (0.826), while K, CO_3, and $_pH$ were moderately positively loaded with values of (0.621), (0.607) and (0.516) respectively. These ions loading in this factor can be considered to be those responsible for the salinization of the groundwater mostly derived from the rock- water interactions within the aquifer, which might have been controlled by the $_pH$ of the groundwater which had the lowest loading among its pears in this factor. This factor contributed 31.5 % out of the total variance. The second factor contributed 20.84 % of the variance and with an Eigen value of 3.334, it is strongly and positively loaded with Mg (0.893) and positively and moderately loaded with TH (0.707) and HCO_3 (0.630). Ca was negatively and moderately loaded in the second factor with (-0.644), CO_3 and pH had low values but were moderately loaded in the second factor by (0.469) and (0.457) respectively. From the composition of the second factor it can be said that these elements are responsible for the hardness of the groundwater and probably get into the water by weathering and dissolution of minerals from the rock. Factor 3 was moderately loaded with SO_4 (0.618), DO (0.463), and Temperature (0.542) and was responsible for10.19 % of the total variance and with an Eigen value of 1.630. The probable geochemical processes that led to the release of SO_4 into the groundwater were the oxidation-reduction process which was enhanced by the dissolved Oxygen DO which occurred alongside this ion in the third factor and also from the weathering of rock and leaching of minerals. The fourth factor was moderately positively loaded with NO_3 by (0.667) while DO was negatively moderately loaded with (-0.635) with 9.28 % of the variance and an Eigen value of 1.484. The oxidation –reduction process could be the probable source of the NO_3 in groundwater or from other anthropogenic sources like the dissolution of animal excreta into water and addition of organic contaminant. The Fifth value factor contributed 7.92 % out of the total variance with an Eigen value of 1.267. The factor was positively and moderately loaded with Turbidity (0.663). The fifth factors did not make any significant contribution to the analysis and were loaded with variables that could not pose any threat because of their low concentrations in the water. However, the scree plot which is the graphical plot of the Eigen values of the different components and the plot of the rotated components in space in figures 8a and 8b were used to show the behaviors of the different factors. The scree plot displays the behavior of the curve after the fifth point where flattening of the curve commences while the rotated plot demarcated three components in space.

Table 11: Pearson Correlations Matrix

	Ca	Mg	Na	K	TH	HCO3	SO4	NO3	Cl	CO3	pH	DO	Temp	EC	Turbidity	TDS
Ca	1															
Mg	**-.610****	1														
Na	.052	.183	1													
K	.553*	-.269	.410	1												
TH	-.133	**.833****	.402	.033	1											
HCO3	-.041	.399	.331	-.073	.534*	1										
SO4	-.360	.320	.247	-.158	.078	.079	1									
NO3	.398	-.190	.121	.271	-.046	.073	.134	1								
Cl	.488*	-.350	**.685****	.557*	.074	.149	-.146	.185	1							
CO3	-.062	.290	.348	.168	.483*	**.748****	-.181	.043	.352	1						
pH	-.117	.279	.496*	-.053	.387	.352	.158	.293	.237	.448*	1					
DO	.022	-.078	.002	-.098	-.042	-.181	-.030	-.234	.165	-.211	-.360	1				
Temp	-.081	-.159	-.347	-.110	-.284	-.552*	.237	.015	-.123	-.392	-.302	.357	1			
EC	.375	-.221	**.779****	**.625****	.170	.201	-.117	.205	**.954****	.450*	.385	.037	-.226	1		
Turbidity	.201	.116	.348	.398	.244	-.022	.034	.083	.106	-.068	.048	-.124	.001	.171	1	
TDS	.365	-.218	**.783****	**.609****	.172	.199	-.116	.194	**.956****	.449*	.392	.051	-.225	**1.000****	.163	1

**. Correlation is significant at the 0.01 level (2-tailed).

Table 12: Extracted factors component with Eigen values greater than 1

Parameter	Component				
	1	2	3	4	5
Ca	.392	**-.644**	-.292	.178	.225
Mg	-.030	**.893**	.279	-.005	.233
Na	**.826**	.163	.393	.013	-.045
K	**.621**	-.444	.048	.197	.356
TH	.386	**.707**	.165	-.053	.365
HCO3	.447	**.630**	-.320	-.106	-.023
SO4	-.099	.310	**.618**	.368	-.378
NO3	.293	-.182	-.118	**.667**	-.294
Cl	**.855**	-.371	.128	-.231	-.141
CO3	**.607**	.469	-.338	-.237	-.061
Ph	**.516**	.457	-.024	.276	-.392
DO	-.121	-.265	**.463**	**-.635**	.024
Temp	-.426	-.360	**.542**	.021	-.146
EC	**.933**	-.233	.128	-.144	-.118
Turbidity	.276	-.037	.334	.431	**.663**
TDS	**.930**	-.228	.136	-.159	-.128
Eigen values	5.039	3.334	1.630	1.484	1.267
% of Variance	31.5	20.84	10.19	9.28	7.92
Total					**79.7 %**

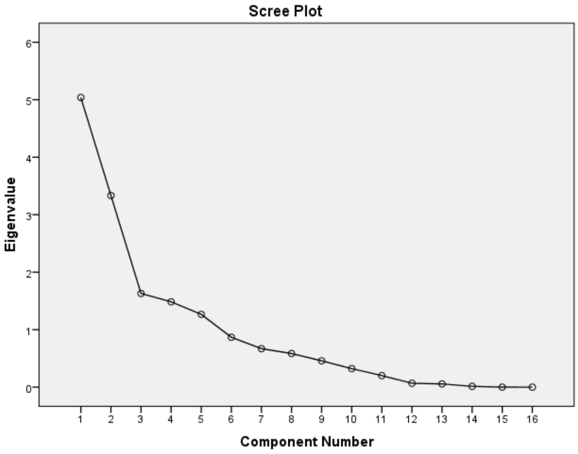


Figure 8a: Scree plot of the different factors

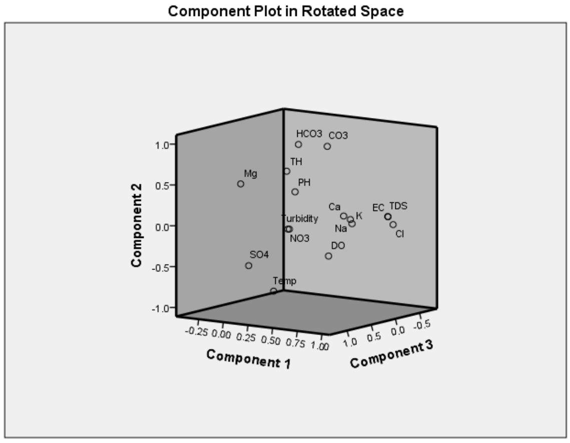


Figure 8b: Rotated component in space

Cluster analysis

The cluster analysis was employed to bring out the relationship between the physico-chemical parameters as well as their sources. The Dendrogram in figure 9, four clusters were demarcated, the largest cluster containing 12 physico-chemical parameters that consist of K, NO_3, Turbidity, DO, P^H, Na, Cl, CO_3, Temp, Mg, Ca and SO_4, the cluster can be favorably compared to the first component of the factor analysis with these being from the rock weathering and rock-water interaction process. The cluster also contains ions that determined the salinity of groundwater. The second cluster had 6 variables that include Temp, Mg, Ca, SO_4, TH and HCO_3, the cluster can be compared with the second factor of the factor analysis the cluster was loaded with elements controlling the hardness of groundwater and were derived from the weathering products of silicate and calcite rich minerals in the subsurface during the passage and percolation of water into the aquiferous layers. The third cluster is loaded with Ca, SO_4, TH, HCO_3, and TDS which were probably derived as the product of the breakdown of calcite, dolomite or anhydrite. The fourth and last cluster contains only EC which could be identified as index parameter whose presence depends on the concentrations of other chemical species in the groundwater. Magnitude of EC also controls the salinity of groundwater.

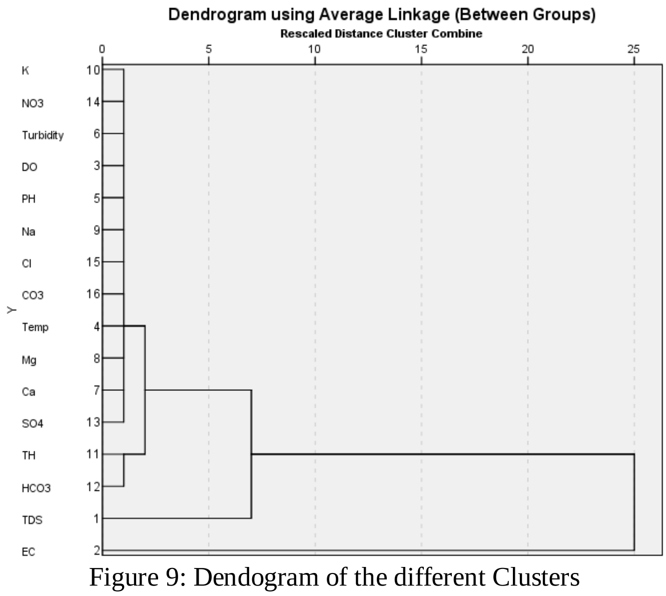


Figure 9: Dendogram of the different Clusters

IV. Conclusion

The suitability of groundwater for drinking (potable) and irrigation uses were assessed using quality indices and multivariate statistical approaches in the industrial areas of Sharada and Challawa in Kano metropolis. Analyzed groundwater samples revealed low concentrations for both cations and anions with orders of abundance given as Ca > Mg >Na >K, and $HCO_3 > CO_3 > SO_4 >$ Cl respectively. Mg exceeded the NSDWQ (2015) in nine samples (45 %) while bicarbonate was above the recommended limit in 5 samples (5 %). The groundwater total hardness average of 207 mg/L classified the groundwater in the area as hard water, while the

P^H mean value of 6 has categorized the water to be weakly acidic. Drinking water quality index for the area has revealed an excellent to good quality groundwater. The suitability of groundwater for irrigation was assessed using the irrigation water quality indices and all computed indices had excellent to good quality irrigation water in 70 to 100 % of the groundwater samples analyzed. Multivariate hydrogeochemical statistical analysis performed on the hydrochemical data brought out a good correlation between the different elements and revealed a natural rock-water interaction, base ion exchange and anthropogenic sources for the chemical elements in groundwater. While groundwater type was the Ca+Mg-HCO_3 which is shallow, fresh and hard.

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