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CHARACTERIZATION OF GROUNDWATER HYDROCHEMISTRY AND QUALITY ASSESSMENT IN ETI –OSA, LAGOS-NIGERIA

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Abstract

Water samples collected from forty-four hand dug wells using random sampling technique were measured for pH, electrical conductivity, total dissolved solids. Total hardness, calcium, chloride, bicarbonate and carbonates were analyzed using titrimetry method. Magnesium, potassium and sodium by Atomic Absorption Spectrophotometer while sulfate was analyzed using spectrophotometer. The study is aimed at characterization of groundwater hydrochemistry and quality assessment in Eti –Osa, Lagos-Nigeria using multivariate statistical techniques, piper diagram, surfer software and water quality indices. Factor 1 explains 71.19% of the total variance, with loading on TDS, Cl, Na, TH, SO_4, Mg, EC, K and Ca while Factor II accounts for 13.731% of the total variance with moderate loading on HCO_3,CO_3 and pH. The residual sodium carbonate shows that 18.2%, 13.6% and 15.9% of the samples are suitable, marginal and unsuitable water respectively for irrigation purpose. Magnesium ratio shows that 75% of the samples are suitable while the remaining 25% are unsuitable for irrigation purpose. Computed water quality index shows that, 31.8% has excellent water quality, 50%, 15.9% and 2.3% indicate good, poor and water unfit for drinking respectively. The hydrochemical facies of the study area is characterized by Ca-HCO_3 and Ca-Cl types. It was concluded that water quality of the study area is unsuitable for irrigation whereas, it is suitable for domestic and drinking purposes. Appropriate treatment methods to make it more potable for human consumption, routine monitoring and periodic water quality testing coupled with appropriate treatment for agricultural activity should also be employed in the study area.

Key words: *Assessment, characterization, Groundwater quality, Hydrochemical facies, Lagos-Nigeria*

INTRODUCTION

Natural groundwater is usually free from contamination compared to surface water that is mostly prone to contamination due to anthropogenic activities. Despite this importance, groundwater quality can become deteriorated due to several factors influencing groundwater hydrochemistry and consequently, its suitability for various purposes. Among these factors includes lithology, the residence time of groundwater in the host rock, the ambient temperature and pH, chemical composition of the aquifer, climatic conditions prevailing during formation, quantity of water available in the aquifer and its rate of circulation among others (Todd and Mays, 2005). The chemical and biological interactions between groundwater and geological materials through which water flows acquire a wide variety of dissolved inorganic chemical constituents in various concentrations (Todd and Mays, 2005).

Mineral weathering processes contribute immensely to the hydrochemistry of surface and groundwater resources world over (Yidana *et al.*, 2012). Literature abounds on hydrochemical analysis of groundwater (Wen *et al.*, 2005; Coetsiers and Walravens, 2006; Cloutier *et al.* 2008; Banoeng-Yakubo *et al.* 2009; Yidana *et al.*2012).

Saline intrusion and anthropogenic activities also play a vital role in groundwater contamination especially in shallow aquifer. Over-exploitation of groundwater resource due to increased population growth also poses a major problem in coastal regions. Over-exploitation of the groundwater resource causes drawdown, land subsidence and consequently disequilibrium in the hydrostatic balance between freshwater and seawater interface causing seawater intrusion into the aquifer and thus causing deterioration of the quality of the groundwater. Hydrochemical study usually involves the consideration of the sum total of all possible sources of groundwater contamination or

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ionic constituents of groundwater (Yidana *et al.,* 2012).

Various methods have been developed for the visual understanding of hydrochemical data of groundwater in order to look for discernible patterns and trends. The simplest methods include plotting distribution diagrams, bar charts, and pie charts, radial and stiff diagrams. Although these methods are easy to construct, they are not convenient for graphical presentation of large number of analyses and hence, other techniques such as ternary, piper, and Durov diagrams have been widely used (Todd and Mays, 2005).

One of the limitations of the graphical methods is that, limited number of parameters can be used. Unlike the statistical methods such as cluster and factor analyses, these methods provide a powerful tool for analyzing groundwater data for grouping into distinct hydrochemical zones (Meng and Maynard, 2001; G¨uler *et al.* 2002; G¨uler and Thyne, 2004; Thyne *et al.* 2004; Helstrup *et al.* 2007; and Yidana *et al.* 2008a, 2008b).

Factor analysis (FA) is one of the widely used multivariate statistical methods in water quality assessment studies. FA is a data dimension reduction technique used to reduce a large number of data of so many variables into a smaller number of uncorrelated factors which are easier to handle and interpret (Yidana *et al.*2012*)*.It is also used to uncover the latent structure in the datasets of hydrochemical variables (Yidana *et al.* 2008a).FA makes it possible to rank hydrochemical processes in order of importance and also to identify areas most impacted by a particular process in a given basin.

Usually, FA is combined with several graphical techniques to provide a meaningful hydrochemical analyses. Unlike CA technique, it is used to classify clusters / associations into categories based on their similarities or dissimilarities in the variation of the datasets using Hierarchical cluster analysis (HCA) (Richard and Dean, 2002). The study aimed at characterizing groundwater hydrochemistry using multivariate statistical techniques, and piper diagram; and water quality indices for quality assessment in the study area.

The Study area

The area lies approximately between latitudes 6°24'N and 6° 33'N and longitudes 3°24'E and 3°39'E with an aerial extent of 192.3km^2 land (Figure 1).

It is a zone of coastal creeks and lagoons (Longe *et al.*1987). The topography is relatively flat with low relief which attains approximately 3-15m above sea level (Odumosu *et al.*1999). The climate is tropical type and is characterized by wet and dry seasons. Annual average rainfall is about 1,532mm with an annual average temperature of about 27^{0}C (Adepelumi *et al.* 2008). The vegetation is dominated by brackish and freshwater swamp (FEPA, 1997). The drainage system is characterized by Lagos and Lekki Lagoon fed by River Oni in the North Eastern part and by Rivers Oshun and River Saga in the north western parts (Emmanuel and Chukwu, 2010). The geology is the Benin Formation. It is characterized by sediments laid down under fluviate, lascustrine and marine environments and varies widely in lateral extent and thickness (Adepelumi *et al.* 2008). The area is underlain by recent/alluvial aquifer. The depth ranged between 0.4–21m below ground level. It is tapped by hand dug well. One of the major challenges of this aquifer is pollution due to its nearness to the ground surface (Longe, 2011).

The influx of people into the area due to its tourism potential, and both diplomatic and commercial establishments in the area has resulted in the rise in demand for water supply to meet the growing needs of the population. Thus, both individual and private organizations have resorted to drilling/digging well for various purposes in the area. Major sources of water supply in the area include public piped borne water, borehole, hand dug well and vendor provided water.

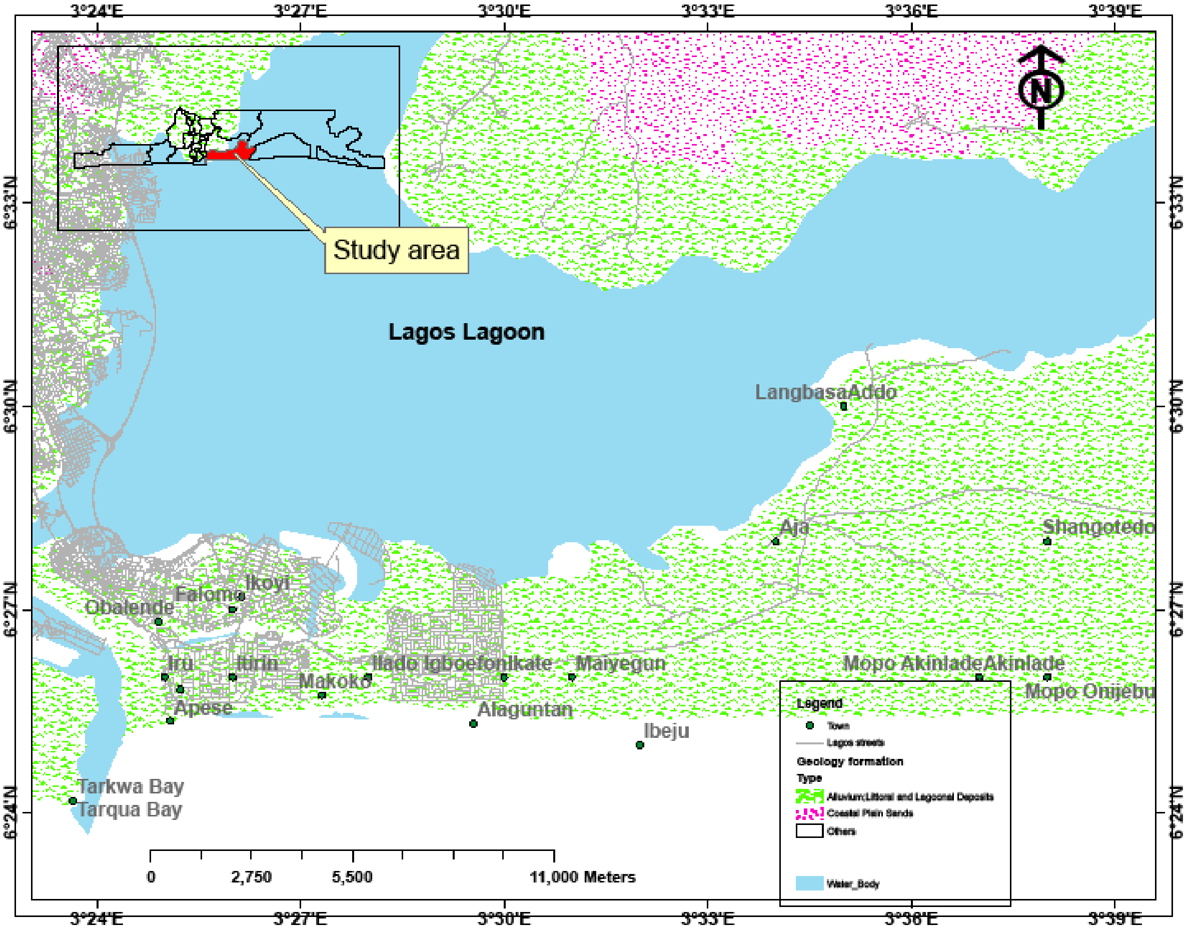

Figure 1 Study area

MATERIALS AND METHODS

Sampling

A total of forty-four groundwater samples from hand dug wells were analyzed for the concentrations of the major hydrochemical parameters. Standard sampling and analytical procedure were adopted so as to obtain a representative data from each of the sampling locations. The samples were collected in August 2011 and stored in clean 150mL polyethylene bottles and preserved in ice chests for onward delivery to chemistry department, University of Lagos, Akoka for analyses using standard methods (APHA, 1998). *In-situ* parameters were measured for electrical conductivity (EC), pH, temperature, and total dissolved solids (TDS) using portable hand held (HI98303, Hanna model), (PH-102, RoHS model) and TDS/TEMP HM Digital model respectively. The *in-situ* measurement was necessary because these parameters are likely to change on transit to the laboratory. Thus chloride,calcium,total hardness, carbonate and bicarbonate were determined using titrimetry method. Atomic Absorption Spectrophotometer (AAS), HI 98180 model was used to analyze magnesium, potassium and sodium while sulfate was determined using spectrophotometer, HACH DR/2000 model. Co-ordinates of the sampled well were recorded using Global Positioning System (GPS) and thereafter were plotted using ArcMap 9.3 software to generate map of the sampling locations (Figure 2).

Spatial variations of the examined parameters were mapped using surfer 6.0 while the hydrogeochemical facie/ groundwater composition was mapped using Rockware Aq.QA version 1.1.1[1.1.5.1] 2006 edition.

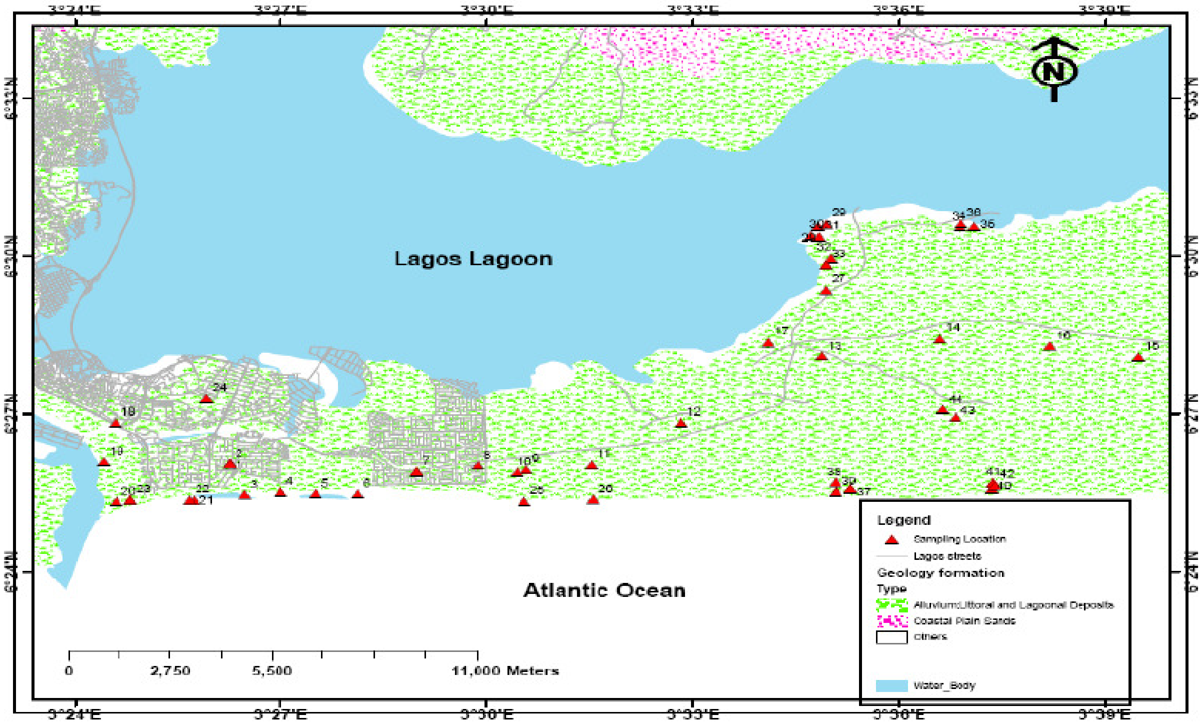

Figure 2 Sampling locations

Evaluation of water quality assessment for irrigation, industrial and drinking purposes was determined based on the application of:

- Magnesium Hazard (MR).It is given as :
- $$MR = \left[\frac{Mg}{Ca + Mg}\right] X\ 100$$ (1)
- Residual Sodium Carbonate (RSC). It is given as:

$$(CO3 + HCO3) - (Ca + Mg) \ldots.$$ (2)

where all ionic concentrations are expressed in milliequivalents per liter (meq/L).

- Determination of industrial water quality-application of HCO_3 of more than 400 mg/L, and pH less than 7 (Johnson, 1983).
- Determination of drinking water quality - application of Water Quality Index (WQI) using World Health Organization (2004) standard. The stages of calculating the WQI includes;

$$qn = 100\,[Vn - Vio\,] / [Sn - Vn]$$ (3)

Where *n* is water quality parameters and quality rating or sub index (*qn*) corresponding to *nth* parameter (i.e a number reflecting the relative value of this parameter with respect to its standard, (maximum permissible value).

where;

qn = Quality rating for the nth water quality parameter,

Vn = Estimated value of the nth parameter at a given sampling point,

Sn =Standard permissible value of the nth parameter.

Vio =Ideal value of nth parameter in pure water (i.e. 0 for all other parameters except pH and Dissolved Oxygen (7.0 and 14.6 mg/l respectively). The Unit weight (*Wn*) is calculated by a value inversely proportional to the recommended standard value *Sn* of the corresponding parameter.

- $W_n = K/S_n$ (4)

Where Wn = unit weight for the nth parameters,

Sn = standard value for the *nth* parameters

- *K* = constant for proportionality.

The overall WQI is calculated by aggregating the quality rating with the overall WQI which is calculated by aggregating the quality rating with the unit weight linearly as:

- $WQI = \Sigma q_n W_n / \Sigma W_n$ (5)

The resulting data for the major ions were subjected to internal consistency tests. The concentrations of the major anions and cations were compared to ensure that these concentrations were within ±5% of each other, using the charge balance error formula (Appelo and Postma, 2005).

$$\Sigma \text{ cations} - \Sigma \text{ anions}) / \Sigma \text{ cations} + \Sigma \text{ anions} \times 100\% \qquad (6)$$

where the concentrations of the anions and cations were expressed in meq/L. All the 44 samples passed the internal consistency test and were used for analysis of the research.

Results and Discussion

The statistical summary of the hydrochemical data from the study area is also presented in Table 1. The result shows that pH varied between 3.4 and 8.55 with a mean of 6.04, indicating a slightly acidic condition (Todd and Mays, 2005). The determination of pH of water is useful for water treatment to address probable issues of corrosiveness of iron pipe (Hem, 1991). Electrical conductivity ranges between 40 and 4,040 μScm^{-1} with a mean of 522.7 μScm^{-1} . Rao *et al.,* (2012) classified EC as low enrichment of salts (EC<1,500 μScm^{-1}), medium (EC: 1,500 and 3,000 μScm^{-1}) and high (EC>3,000 μScm^{-1}). According to this classification, of the study samples, 95.4% of the sampled water revealed low EC indicating low salt enrichment while 2.3% shows medium and high enrichment of salts respectively (Figure 3).

The measured TDS showed a wide variation between 30 and 6,112mg/L^{-1} with a mean of 430.45 mg/L^{-1} . The degree of TDS can be classified as fresh, if it is less than 1,000 mg/L^{-1}; brackish, (1,000 to 10,000 mg/L^{-1}), saline (10,000 to 1,000,000 mg/L^{-1}) ; and brine more than 1,000,000 mg/L^{-1} (Carroll, 1962). Based on this classification, 95.5% of the sampled wells were classified as fresh water while the remaining 4.5% represents brackish type (Figure 4).

Calcium and Magnesium ions in water are responsible for total hardness in water. TH is an important criterion for determining the suitability of water for domestic, drinking, and industrial supplies (Karanth, 1987). TH varied from 20.6 to 1,786.6 with mean value 205.58. According to Heath (1998), TH can be classified as soft, if the TH is between 0 and 60 mg/L^{-1} , moderately hard if it lies between 61 and 120 mg/L^{-1} , hard if it is from 120 to 180 mg/L^{-1} , very hard if it is higher than 180 mg/L^{-1} . Thus, approximately 36.4%, 34.1%, 15.9% and 13.6% of the sampled wells are very hard, hard, moderately hard and soft, respectively (Figure 5).

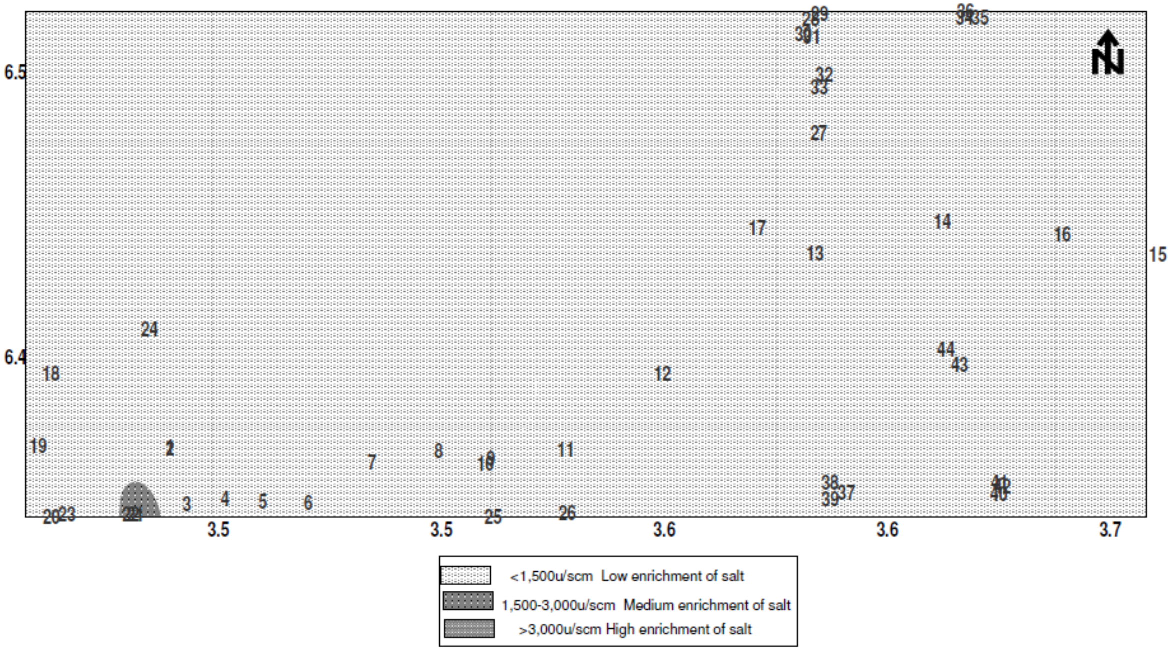

Figure 3 Spatial variation of Electrical conductivity

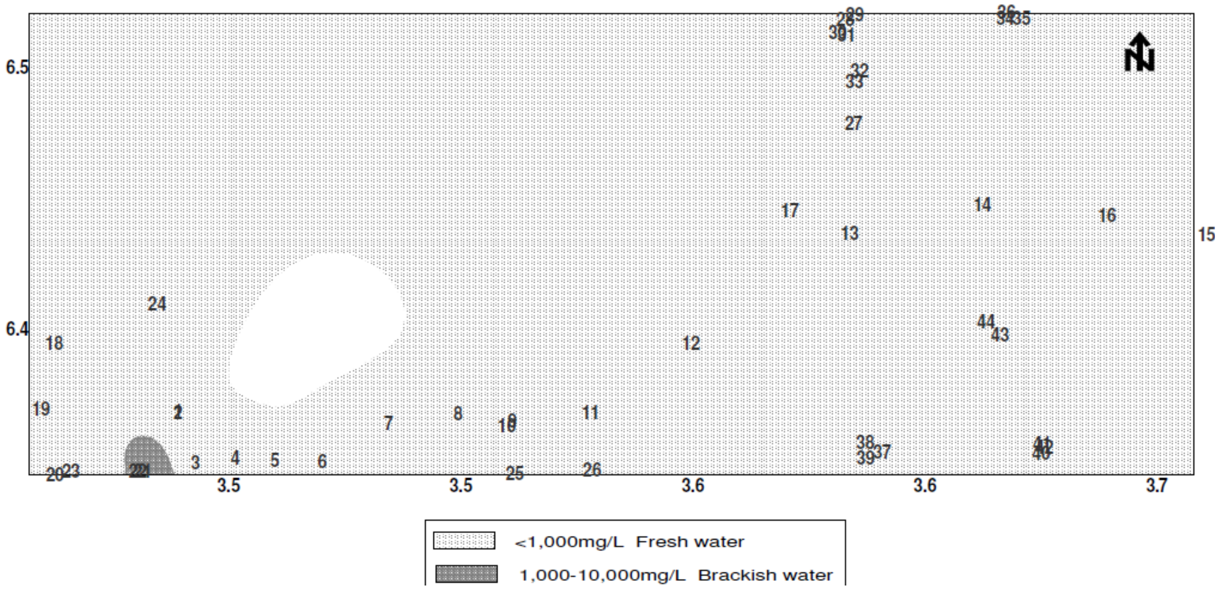

Figure 4 Spatial variation of Total Dissolved Solids

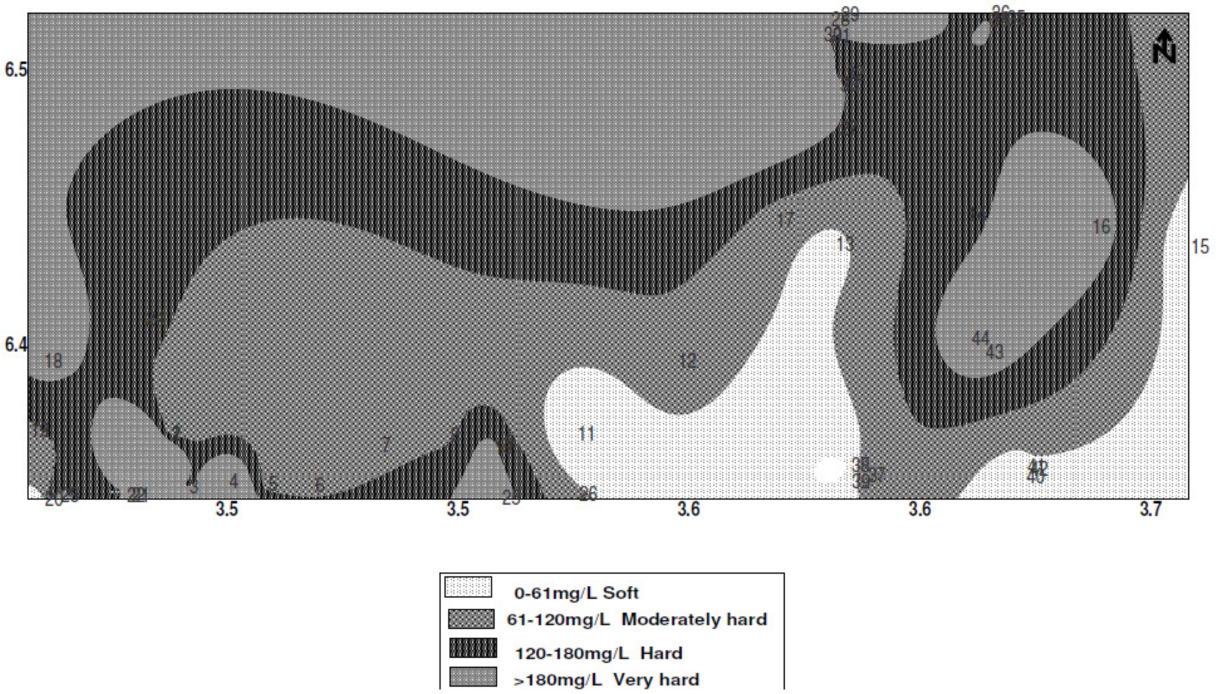

Figure 5 Spatial variation of Total Hardness

The cations (Ca, Mg, Na and K) varied between 12 and 1,200, 2 and 580, 0.63 and 1,080.10 and 0.17 and 52. 32 mg/L^{-1} , respectively while the anions (CO_3, Cl, HCO_3 and SO_4) varied from 0 to 848, 6 to 3,400, 0 to 621.60 and 2 to 1, 250 mg/L^{-1} , respectively. The dominant cations and anions are in the order of: $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$; $Cl^{-} > CO_3^{2-} > HCO_3^{-} > SO_4$ respectively.

Table 1 Statistical summary of hydrochemical parameters

Parameters	Min	Max	Mean	S.D
pH	3.4	8.6	6.04	0.87
EC(µScm^{-1})	40.0	4040.0	522.701	619.18
Total Dissolve Solids(mg/L^{-1})	30.0	6112.0	430.46	898.44
Sodium(mg/L^{-1})	0.6	1080.1	47.08	161.99
Potassium (mg/L^{-1})	0.2	52.3	5.19	8.22
Calcium(mg/L^{-1})	12.0	1200.0	147.84	188.42
Magnesium(mg/L^{-1})	2.0	580.0	51.134	87.72
Total Hardness (mg/L^{-1})	20.6	1786.6	205.58	268.89
Chloride(mg/L^{-1})	6.0	3400.0	169.61	508.26
Bicarbonate (mg/L^{-1})	0.0	621.6	123.62	153.047
Carbonate (mg/L^{-1})	0.0	848.0	154.39	196.37
Sulfate (mg/L^{-1})	2.0	1250.0	36.34	187.27

Result of the FA indicates two factors (Table 2) that can be related to the various processes controlling groundwater hydrochemistry of the study area. The rotated factor loading matrix show that the two factors extracted explain 83.93% of total variance.

Table 2 Factor loadings marix from R-mode analysis

Parameters	F_1	F_2
pH	0.057	0.619
EC	0.963	0.143
TDS	0.992	0.049
Na	0.986	0.067
K	0.956	0.210
Ca	0.949	0.124
Mg	0.965	0.069
TH	0.980	0.109
Cl	0.990	0.058
HCO_3	0.193	0.786
CO_3	0.037	-0.735
SO_4	0.965	-0.021
% of variance	71.19	13.73
cumulative %	71.19	84.93

Factor I, which explains 71.19% of the total variance, has strong positive loading on TDS, Cl, Na, TH, SO_4, Mg, EC, K, and Ca. The chemical constituents of Mg^{2+}, Cl^-, Na^+, K^+, and SO_4 represents the dominant components of seawater (Lu *et al.,* 2011). It also reflects the contribution of evaporation, recharge and anthropogenic sources of the groundwater system (Aiman and Mohamed, 2010).Factor II accounts for 13.73% of the total variance and is characterized by loading of HCO_3, CO_3 and pH.

The cluster analysis technique was used to classify the examined parameters of groundwater into categories or clusters based on their similarities (Richard and Dean, 2002).Ward's method was used to carry out the CA (Lu *et al.,* 2011) while the hierarchical agglomerative clustering with standardized Square Euclidean distance was used as a dissimilarity measure (Maria *et al.,* 2011; Stephen and Brian, 2005). Dendrogram of the sampling locations model resulting from the CA of the measured parameters is shown in (Figure 6). The CA grouped 44 sampling locations into 4 clusters under the similarity of groundwater quality parameters.

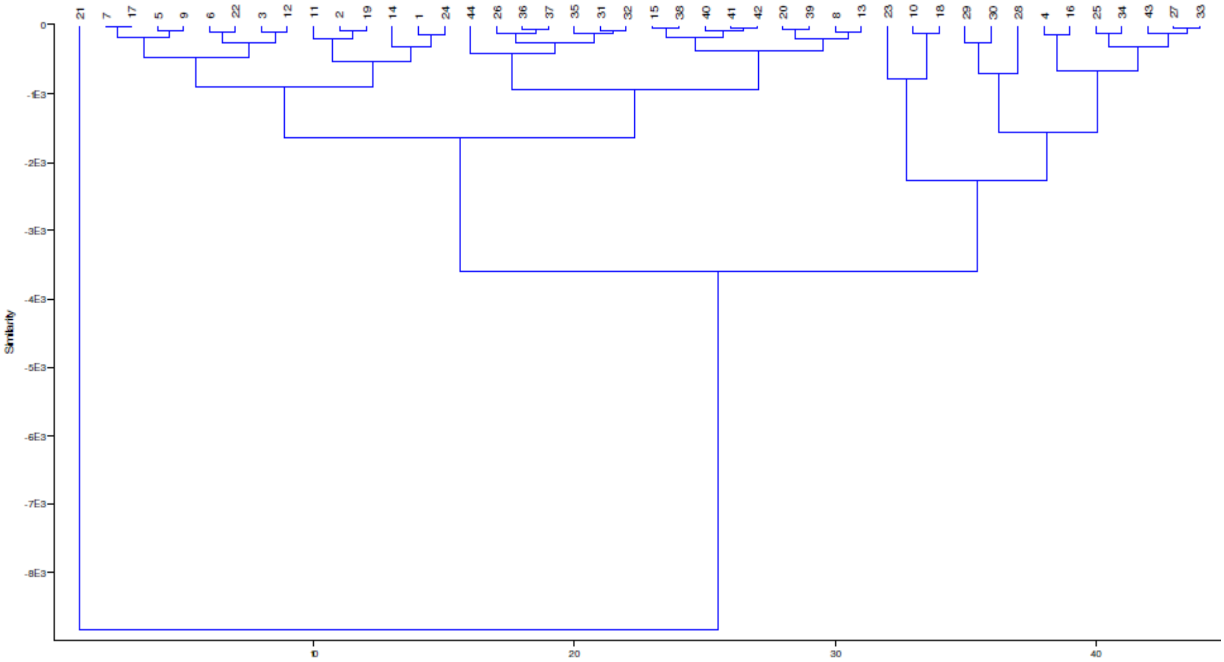

Figure 6 Dendrogram of the sampling locations

Cluster I corresponds to 14 sampling locations (1, 2, 3, 5-7, 9-11, 12, 14, 17, 19, 22 and 24. Cluster II corresponds to 13 sampling locations (4, 10, 16, 18, 23, 25, 27-30, 33-34 and 43. Cluster III corresponds to 16 sampling locations (8, 13, 15, 20, 26, 31, 32, 35-42 and 44) while Cluster IV has location 21.

The result of the adopted CA indicates that for any rapid assessment of groundwater quality within the study area, only one sampling location in each cluster will be required to represent a fairly accurate spatial assessment of groundwater quality for the entire study area. Thus, CA technique reduces the need for a large number of sampling locations.

Water quality assessment

Irrigation purpose

Excessive concentrations of dissolved ions in the water used for irrigation affect plants and the physical and chemical parameters of soil by lowering the osmotic pressure in the plant structural cells (Rao *et al.,* 2012). This process prevents water from reaching the branches and leaves, thus reducing the agricultural productivity. Residual sodium carbonate (RSC) and Magnesium hazard (MR) indices were adopted for the assessment of the suitability of water quality for irrigation purpose in the study area.

Residual sodium carbonate

The relation between carbonates concentration and alkaline earths (Ca^{2+}+Mg^{2+}) concentration can be used to explain the suitability of water for irrigation purpose (Rao *et al.,* 2012). Groundwater can be classified as suitable, if the RSC value is less than 1.25 meq/L; marginally suitable, if the RSC value is between 1.25 and 2.50 meq/L; and unsuitable, if the RSC value is more than 2.50 meq/L. High RSC value leads to increase of adsorption of Na^+ in soil, which reduces the soil permeability and hence do not support plant growth (Rao *et al.,* 2012).

The computed RSC value ranged between -101.05 and 16.15meq/L in this study. It is observed that approximately 15.9% of the groundwater samples (3, 5, 10 to 12, 15 and 18) have RSC values greater than 2.50meq/L and hence unsuitable for irrigation. About 13.6% of the groundwater samples (6, 7, 15, 17, 22 and 38) fall under the category of marginally suitable (1.25 to 2.50 meq/L) for irrigation. Approximately 18.2% (1, 2,9,13,14,20,23 and 40) were classified as suitable (>1.25meq/L) while the remaining 52.3% (4, 8, 16, 19, 21, 24 to 37, 41 to 44) show negative values of RSC, as the carbonates are less than the alkaline earths (Figure 7).

Magnesium hazard

Szaboles and Darab (1964) proposed a magnesium hazard classification system for assessing the suitability of water quality for irrigation purpose. Magnesium hazard (MR) is expressed as a ratio of Mg ion concentration to combination of Ca and Mg ions concentration, multiplied by 100. If MR exceeds 50meq/L, such water is considered to be harmful and hence is unsuitable for irrigation. In this study, MR varied from 8.41 to 70.16meq/L. MR exceeds 50meq/L in about 25% of the groundwater sample locations (1, 6, 9, 10, 12, 13 and 22 to 26) and hence are not suitable for irrigation purpose. The remaining 75% (2, 3 to 5, 7, 8, 11, 14 to 21 and 27 to 44), have MR less than 50meq/L and hence suitable for irrigation purpose (Figure 8).

Industrial purpose

The water quality requirements for industrial supplies are very broad and virtually almost every industrial sector has its own criteria. The major water quality problems often encountered in industrial operations arise from incrustation and corrosion, which results from the chemical reactions caused by low/ poor water quality (Rao *et al.,* 2012).

Johnson (1983) proposed criteria for determining the incrustation and corrosion properties of water in an area. According to Johnson (1983), water with HCO_3 of more than 400mg/L may cause incrustation whereas, water with pH less than 7 may cause corrosion. The HCO_3 exceeds the limit of 400mg/L in approximately 6.8% of the sampled groundwater (23, 28, 29) (Figure 9). Furthermore, approximately 93.2% had less than 7.The only exceptions are samples from locations 2, 23 and 42 (Figure 10). Thus, it is inferred that corrosion of metals surfaces can arise from the use of these waters for industrial purposes.

Drinking water purpose

Water Quality Index (WQI) reflects the composite influence of different water quality parameters. WQI is a very useful and efficient method of assessing the suitability of drinking water quality. The suitability of groundwater for drinking water purpose in the present study was determined based on the method proposed by Sahu and Sikdar (2008) while the World Health Organization (WHO, 2006) guidelines were adopted as the permissible limit.

The computed WQI show that, the WQI ranged between 21.59 and 550.97 within the study area. According to the classification system proposed by Sahu and Sikdar (2008) about 31.8% of the sampled wells had excellent water quality. Furthermore, while 50 % of the well samples indicate good quality water the remaining 15.9 % and 2.3 % reveal poor quality water and water unfit for drinking purposes respectively. However, none of the sampled wells fall under the very poor category (Figure 11).

Hydrochemical characterization of groundwater composition of the study area

The Hydrochemical facies of groundwater based on the Piper diagram show that, the groundwater composition of recent/alluvial aquifer of the study area is characterized by Ca-HCO_3 representing 65.9% from locations (1-5, 6-20,22-24,31,32,34,38-40) and Ca-Cl representing 34.1% from locations (21,25-30,33,35-37,41-44) (Figure 12).

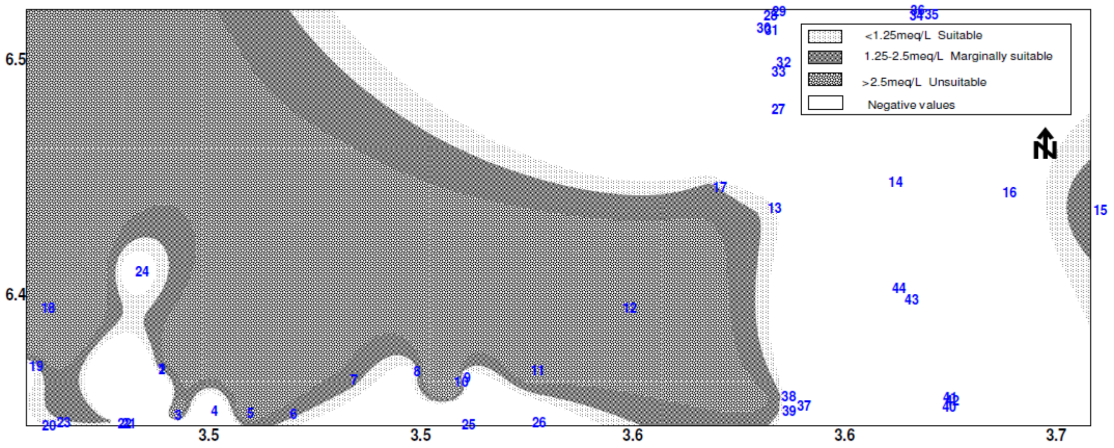

Figure 7 Spatial variation of Residual Sodium Carbonate

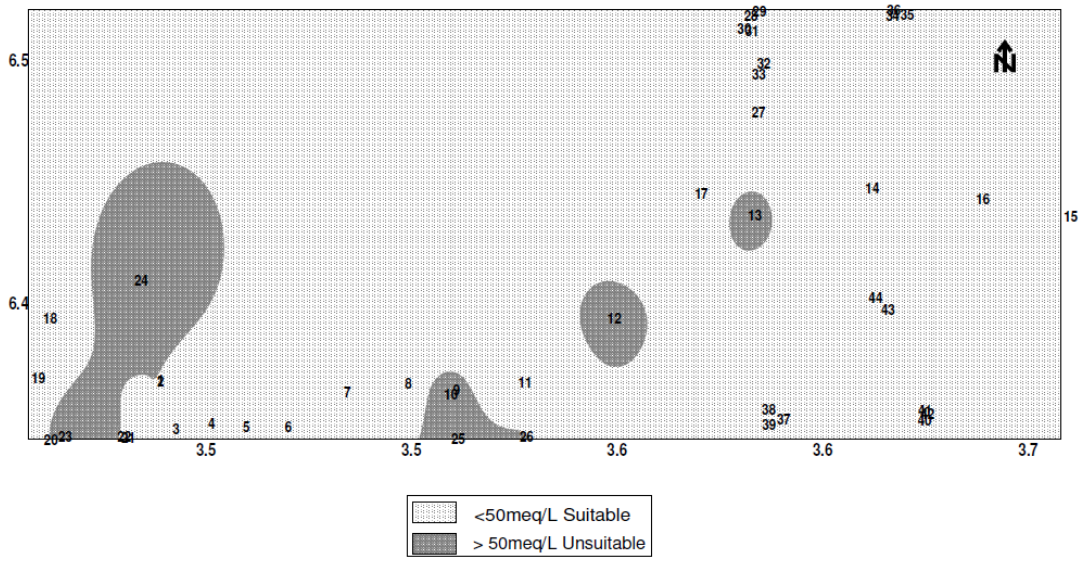

Figure 8 Spatial variation of Magnesium hazard

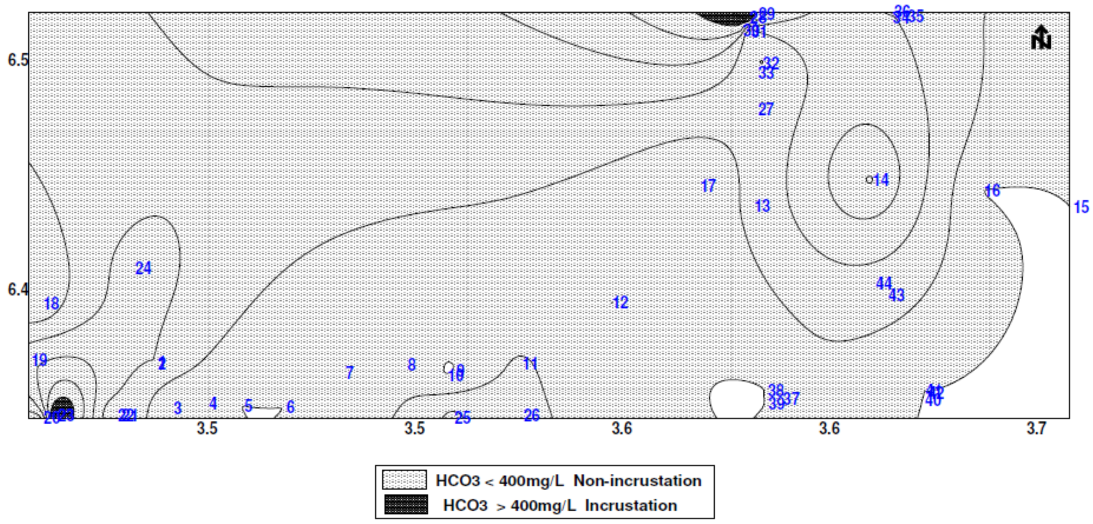

Figure 9 Spatial variation of bicarbonate

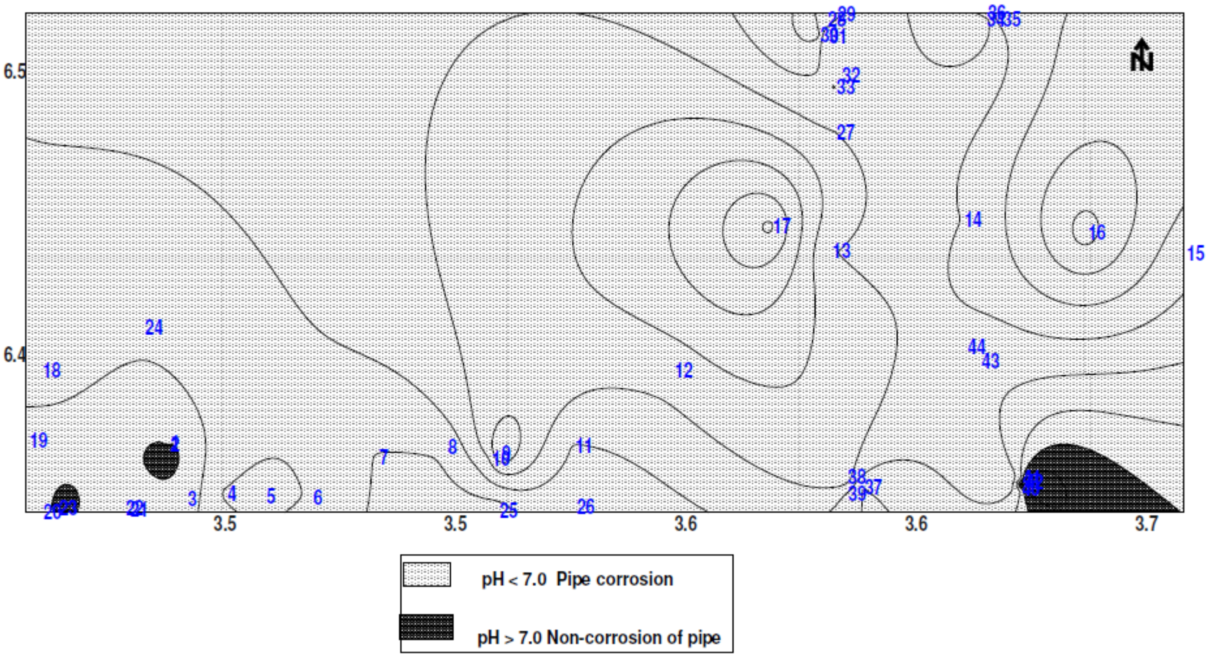

Figure 10 Spatial variation of pH

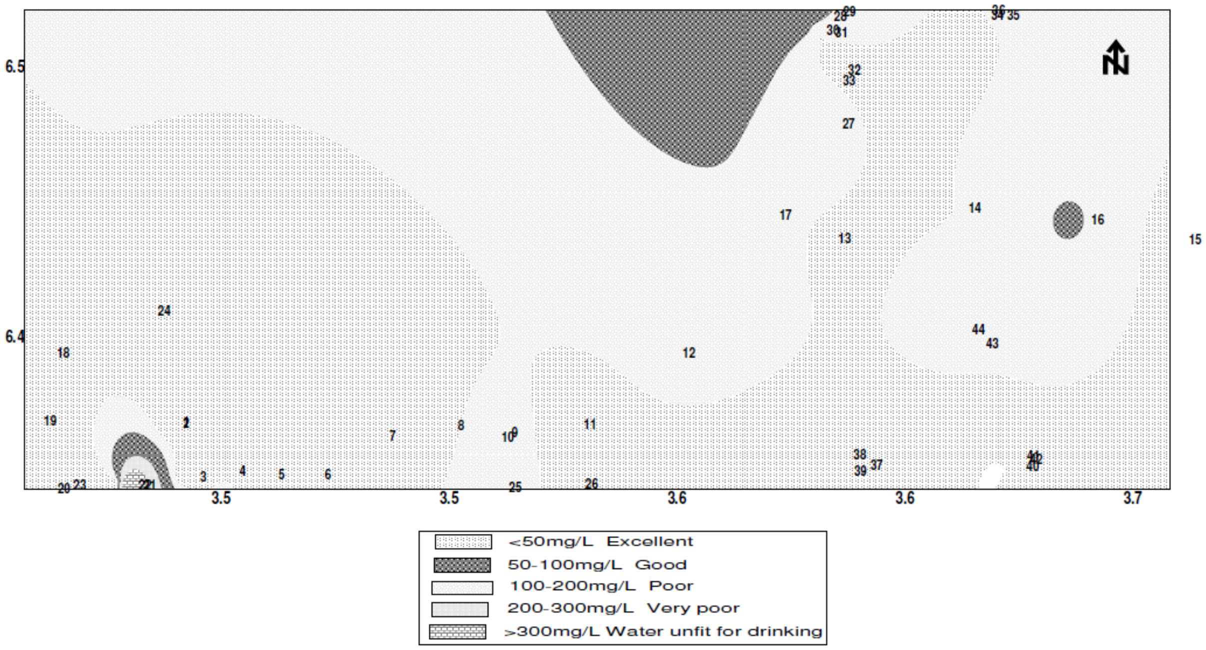

Figure 11 Spatial variation of Water Quality Index

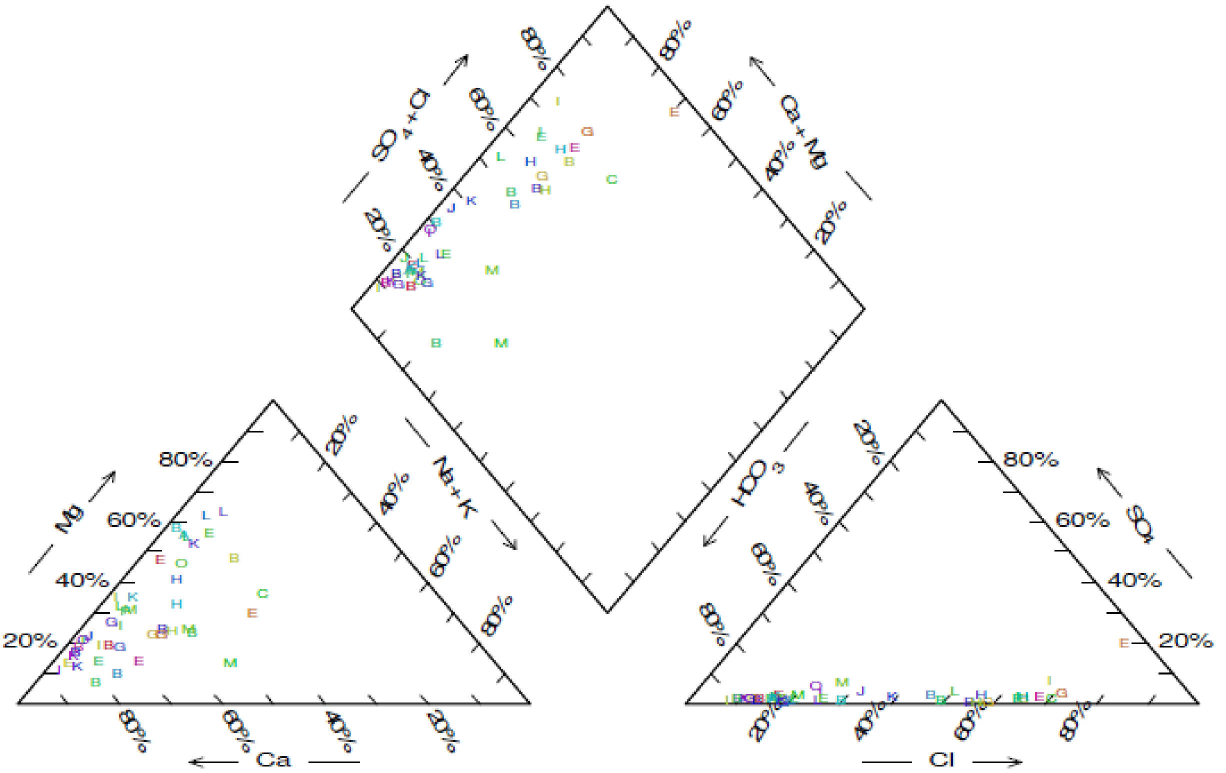

Figure 12 Piper diagram of groundwater composition of the study area

Conclusion

The study revealed that pH varies for 3.4 to 8.55 indicating slightly acidic condition. About 95.4 % of the measured EC indicate low enrichment of salts while 2.3 % revealed medium and high enrichment of salts. Ninety-six percent of the sampled wells are fresh while 4.5 % displayed brackish water. The TH level in the sampled water suggests that 36.4%, 34.1%, 15.97% and 13.6% are very hard, hard, moderately hard and soft waters, respectively.

Both cations (Ca, Mg, Na and K) and anions (CO_3, Cl, HCO_3 and SO_4) had wide variation. The FA extracted four factors which explained 91.71 % of total variance. Factor I explained 71.19% of the total variance, with strong positive loading on TDS, Cl, Na, TH, SO_4, Mg, EC, K and Ca respectively. Factor II accounts for 13.731% of the total variance, and is characterized by HCO_3,CO_3 and pH. The dendrogram of the sampling locations using CA of the measured parameters grouped the 44 sampling locations into 4 clusters under the similarity of groundwater quality parameters. This implies that one sample each from a cluster is representative of the group for sample collection within the study area.

RSC ranged between -101.05 and 16.15meq/L whereas, 15.9% of the groundwater samples are unsuitable for irrigation. However, the remaining 13.6% and 18.2% are marginally suitable and suitable, respectively. The MR varied from 8.41 to 70.16meq/L and while 75% is suitable for irrigation, the remaining 25% are not. 6.8% of the groundwater samples exceeded the WHO (2006) limit of HCO_3 while 2.3% and 11.4% of the samples exceeded the WHO (2006) limits of SO_4 and TH and hence are not suitable for industrial purpose.The pH, TDS and Cl in the waters also largely precludes their industrial use. The WQI ranged between 21.59 and 550.97mg/L. Thus, while 31.8% had excellent water quality the remaining 50%, 15.9% and 2.3% respectively indicate good, poor and water unfit for drinking purposes.

Based on the computed WQI, it is concluded that though waters of the HDW within the recent /alluvial aquifer are suitable for drinking purposes. However, appropriate treatment methods to make it more potable and fit for human consumption should be employed. It is also concluded that the water is not suitable for irrigation purpose due to the high computed RSC indices. The Hydrochemical facies of the recent/alluvium aquifer is characterized by Ca-HCO_3 and Ca-Cl .Routine monitoring and periodic water quality testing are also recommended.

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