Hydrogeochemical Characterization and Vulnerability Assessment of Shallow Groundwater in Basement Complex Area, Southwest Nigeria

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Abstract

Thirty-five (35) groundwater samples from Owo area were analyzed for physicochemical parameters. Results show that the mean value of pH is 6.32, TDS is 208.92 mg/l, temperature is 28.77°C, EC is 545.16 µs/cm; TH is 111.09 mg/l, SO_4 is 71.73 mg/l, Cl is 0.07 mg/l, HCO_3 is 14.09 mg/l, Na is 25.06 mg/l, Ca is 37.07 mg/l, K is 24.36 mg/l and Mg is 4.41 mg/l. The results were compared to the WHO and NDSQW standards. All parameters were within the permissible limit except EC in well OW6 and K is above the stipulated standards in 69% of the total samples. The high concentration of K is linked to the use of NPK fertilizer in the area for agricultural purposes. The groundwater belongs to Ca-Na-K-SO_4 and Na-Ca-SO_4 water type respectively. The ionic concentration in the groundwater is due to the dissolution of the rock that makes up the aquifer. Plagioclase and silicate-bearing rocks are the sources of major ions in the water. SAR, PI, RSBC and KR reveals that groundwater in the area is good for irrigation purpose. DRASTIC model further revealed that groundwater in the area is less vulnerable to contamination under the current environmental conditions.

Key words: DRASTIC, Groundwater, Hydrogeochemical, Owo, Vulnerability, WQI

Introduction

Access to safe drinking water is essential to health; it is a basic human right (WHO, 2011). Groundwater is the world's largest accessible freshwater and important resource for drinking water supply, irrigation and industrial purposes as well as for global food security (Sefie *et al.*, 2015). Approximately one-third of the world’s population depends on groundwater for drinking purpose (UNEP, 1999). In response to the high demand for groundwater and increased risk of contamination, a better understanding of groundwater availability and quality is needed (Montcoudiol, 2015). Geology of an area, the degree of chemical weathering of various rock types and anthropogenic factors affect the chemistry of groundwater (Giridharan *et al.*, 2008). Hydrogeochemical studies have over the years played an essential role in interpreting mineralogical composition of the sub-surface and inherent conditions in most geological settings (Ekwere and Edet, 2012). The estimated amount of groundwater resource in Nigeria is 6×10^{18} m^3 (Rijswljk 1981). The resource plays an important role in the social and economic life of the people regarding domestic, industrial and agricultural use. However, little is done to assess and understand the quality of groundwater especially within the different aquifer systems (Edet *et al.*, 2011). According to Organization for Economic Co-operation and Development, agriculture is responsible for the use of 70% of all freshwater including groundwater (OECD, 2012). Factors which have made groundwater use quite attractive for agricultural is the relatively cheap cost of getting the water to the farm by sinking boreholes on site and not piping or channeling the water over long distances (Shah *et al.*, 2007). The 2006 Nigerian household population census revealed that 49.4% of sampled households depend on groundwater as the main source of water for domestic use (Egbinola and Amanambu, 2014). Studies revealed that 85% of all communicable diseases affecting humans are either water-borne or water-related (WHO, 2006; Amadi *et al*., 2013). Over the years the groundwater geochemistry of this area has not been carried out, although related studies had been carried out in other parts of the Basement Complex of the Southwestern Nigeria (Ikhane *et al.,* 2010; Tijani *et al.,* 2014).

Groundwater chemistry is dependent on several factors which include the nature of recharge, the residence time of the groundwater in the aquifer, rock-water interactions beneath the surface and anthropogenic activities (Andre *et al.,* 2005; Krisna *et al.*, 2011). Groundwater quality and quantity can provoke socio-economic and environmental problems (Schenider *et al.*, 2013).

Factor and cluster analysis had been used widely with conventional graphical techniques to characterize hydrochemical systems (Yidana *et al.*, 2012). This method has been used to tackle serious environmental problems and had offered better insight to groundwater flow regimes (Meng and Maynard, 2001; Guler *et al.*, 2002; Guler and Thyne, 2004; Helstrup *et al.,* 2007; Yidana *et al.*, 2008a and 2008b). The method is also used in ranking the various processes influencing hydrochemistry in order of importance (Yidana *et al.*, 2012). Factor analysis helps in data dimension reduction (Yidana *et al.*, 2012) and is useful in solving several problems in geological and allied sciences. The method makes it possible to rank hydrochemical processes in order of importance (Yidana *et al.*, 2012). Most often, factor analysis is not used in isolation but is combined with several graphical techniques to provide meaning to hydrochemical studies (Yidana *et al.*, 2012). Another method used in Hydrogeochemical analysis is the cluster analysis. Cluster analysis groups variables into cluster or associations based on perceived similarities or dissimilarities in the variation of the dataset (Yidana *et al.,* 2012). Parameters in the same hierarchical cluster have similar characteristics compared to others in different clusters.

The potential for groundwater to become contaminated because of human activity at or near the surface has been recognized in recent years leading managers of this important resource to pursue (Javadi *et al.*, 2011). The tendency or likelihood for contaminants to reach a specified position in the groundwater system after introduction at some location above the uppermost aquifer is known as groundwater vulnerability (National Research Center, 1993). It is also defined as the potential of penetration and diffusion of contaminants in the groundwater resources (Goodarzi and Javadi, 2016). Vulnerability assessments must be specific, scientific, and based on right evidence. Different methods are used to estimate groundwater vulnerability. In most cases, these methods are analytical tools that try to relate groundwater contamination to land use activities (Javadi *et al.*, 2011). These assessment methods may be divided into three general categories: Process-based simulation models, statistical methods (Harbugh *et al.*, 2000) and overlay and index methods.

Process-based models usually require large quantities of data and supplementary information necessary to run mathematical models that form the principal tool of the method. (Javadi *et al.*, 2011). Statistical methods incorporate data on known areal contaminant distributions and provide characterizations of contamination potential for the specific geographic area by extrapolation from available data in the region of interest (National Research Center, 1993). Overlay and index methods are based on combining different maps of the area by assigning a numerical index. Overlay and index methods are easy to apply, especially on a regional scale, and to use in Geographic Information Systems (GIS) (Javadi *et al.*, 2011). They, therefore, constitute the most popular class of methods used in vulnerability assessment. Among the more popular of the overlay and index, methods are GOD (Foster, 1987), DRASTIC (Aller *et al.*, 1987), AVI (van Stemproot *et al.,* 1993) and IRISH (Daly and Drew, 1999). DRASTIC has been used in several places including the USA (Shukla *et al.*, 2000), China (Yuan *et al.*, 2006), Jordan (Naqa *et al.*, 2006), Morocco (Ettazarini 2006), Iran (Mohammadi *et al.*, 2009), India (Balan *et al.*, 2012) and Nigeria (Mogaji *et al.*, 2014).

Aquifers within the Basement Complex of Nigeria are tapped within the weathered zones which are usually at shallow depths and contain smaller quantity of groundwater. This shallow depth of occurrence commonly allows for easy pollution of groundwater in the weathered overburden (Asiwaju-Bello and Ololade, 2013). For this reason, study on the hydrogeochemical and vulnerability assessment of groundwater within Owo area has been carried out. This will also significantly assist in deciphering the lithological processes affecting the groundwater in the area.

The objectives of this study are to determine groundwater flow, geochemistry and primary processes that are responsible for groundwater chemistry and quality in Owo area, southwest Nigeria. Furthermore, this study shall evaluate the vulnerability of the groundwater to contamination. To date, no survey of groundwater quality have been reported in Owo area. This study is meant to serve as a background study which shall give insight into the physical and chemical characterization of groundwater including vulnerability assessment using DRASTIC model.

To achieve these objectives groundwater was sampled in carefully selected parts of the study area and was subjected to in situ determination of physical parameters and laboratory analysis of cations and anions. To determine the groundwater flow pattern, static and dynamic levels were measured in 219 wells. The results of physicochemical analysis were subjected to multivariate statistical analysis (factor analysis combined with hierarchical cluster analysis). Groundwater samples were separated into clusters which give an insight into the primary processes responsible for groundwater chemical evolution in the region.

Study Area

The study area is in the northern part of Ondo State, Southwest Nigeria. It lies between Latitudes 7^{o}00’ and 7^{o}25’N and Longitudes 5^{o}20’ and 5^{o}45’E and occupies an area of approximately 40 km^{2} (Fig. 1). The study area covers Owo, Ayede-Ogbesse, Alayere, Uso-Owo, Amurin-Owo, Emure-Owo, Ipele-Owo, Ita-Ipele and Oba-Akoko which are accessible through asphaltic roads connecting the major towns, while minor roads connect settlements to the towns. The major highway in the area links Ibadan, Akure and Benin together.

The study area consists typically of dendritic drainage pattern (Fig. 1). The major rivers in the area are Rivers Eporo and Ubeze which run from east to west and are significant tributaries of the Ose River. Other major rivers in the study area are River Ogbesse and Aisenwen which runs from North to South. These streams are perennial, and their tributaries are mostly seasonal, reaching their maximum dryness at the peak of the dry season. During the raining season, River Ogbesse overflows its bank causing floods that extends for about 300 meters on either side of the bank. The area is located within the tropical savannah

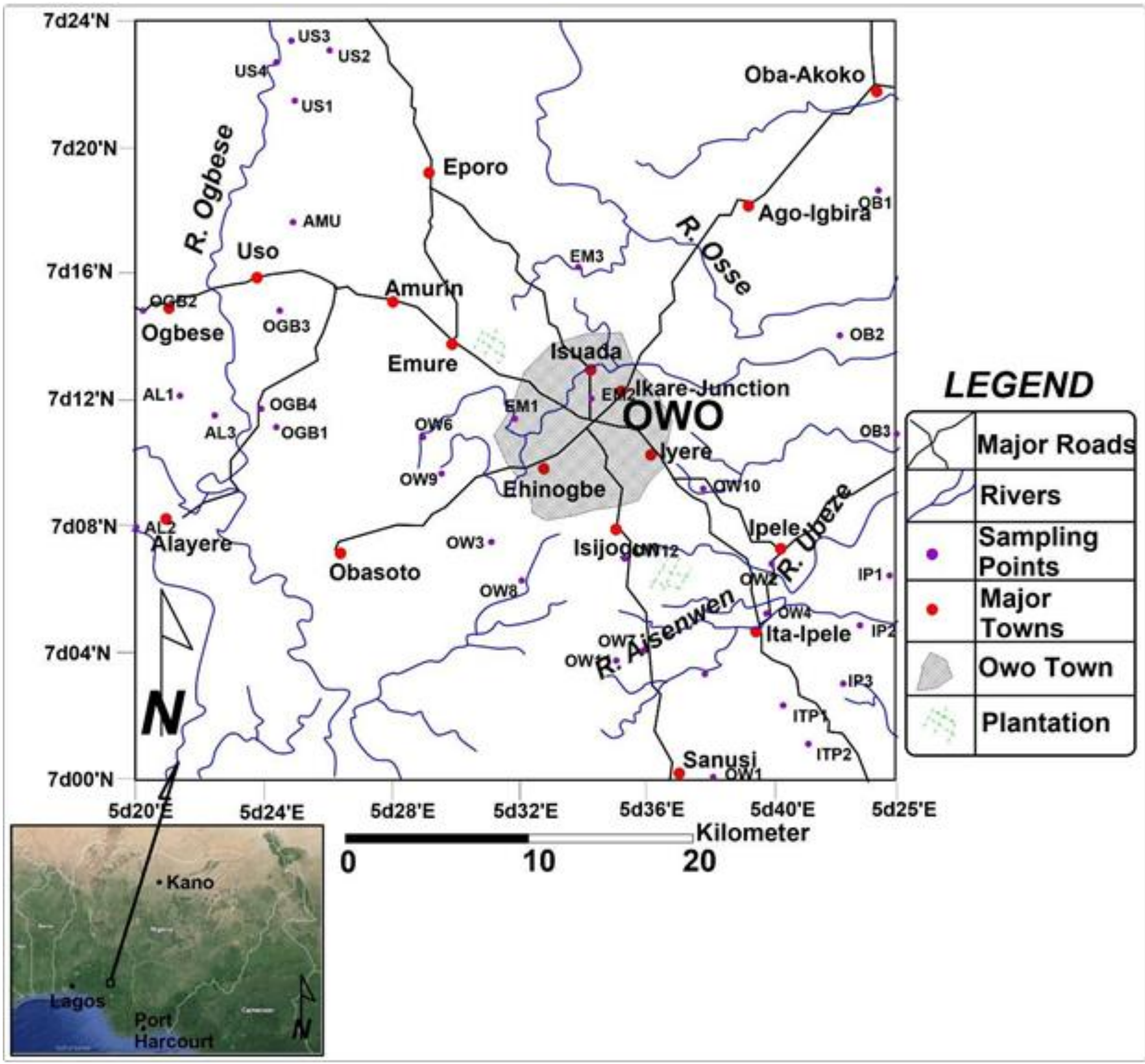

Fig.1: Location, accessibility and drainage map of the study area showing groundwater sampling points

belt of Nigeria. The soil belongs to the broad group Alfisol (USDA, 1975) of the Basement Complex, though, locally classified as Okemesi Series (Smyth and Montgomery, 1962). The rainfall of is between 1100mm to 1500mm per annum and mean monthly temperature of 24-32ºC (Agbede and Ologunagba, 2009).

Geology

Geologically, the area is underlain by the Basement Complex of Nigeria, which are classified as migmatite-gneiss-quartzite group and schist belt (Rahaman, 1971) are Precambrian in age and is within the zone of Pan African reactivation (Oyawoye, 1964). Rocks outcropping in the area are quartzite, schist, granite gneiss and migmatite gneiss. The quartzite/quartz schists are found in Owo and Emure areas, mostly trending from NW to SE (Fig. 2). Granite gneiss is observed in Ogbesse and Eporo which are low-lying. Migmatite gneiss covers the whole of Oba-Akoko peaking at 1000 meters and forming inselbergs. Joints and fractures are the most visible structures in the area, and they trend mostly in the NE-SW, ENE-WSW and NW-SE directions (Adewumi *et al.*, 2017).

Hydrogeology

The Basement Complex rocks underlie the study area. Hydrogeologically, these rocks are poor aquifers, causing problems of potable groundwater supply due to the fact the underlying rocks lack pore spaces that can hold water. However, when these rocks are fractured, they can accommodate groundwater that can be used for domestic and industrial purposes (Adewumi, 2015). Compared to other parts of the study area, the Owo metropolis which is underlain by Quartzite and schist that is mostly fractured. (Fig. 2). This serves as conduit through which the aquifers in the area are recharged (Adewumi and Anifowose, 2017).

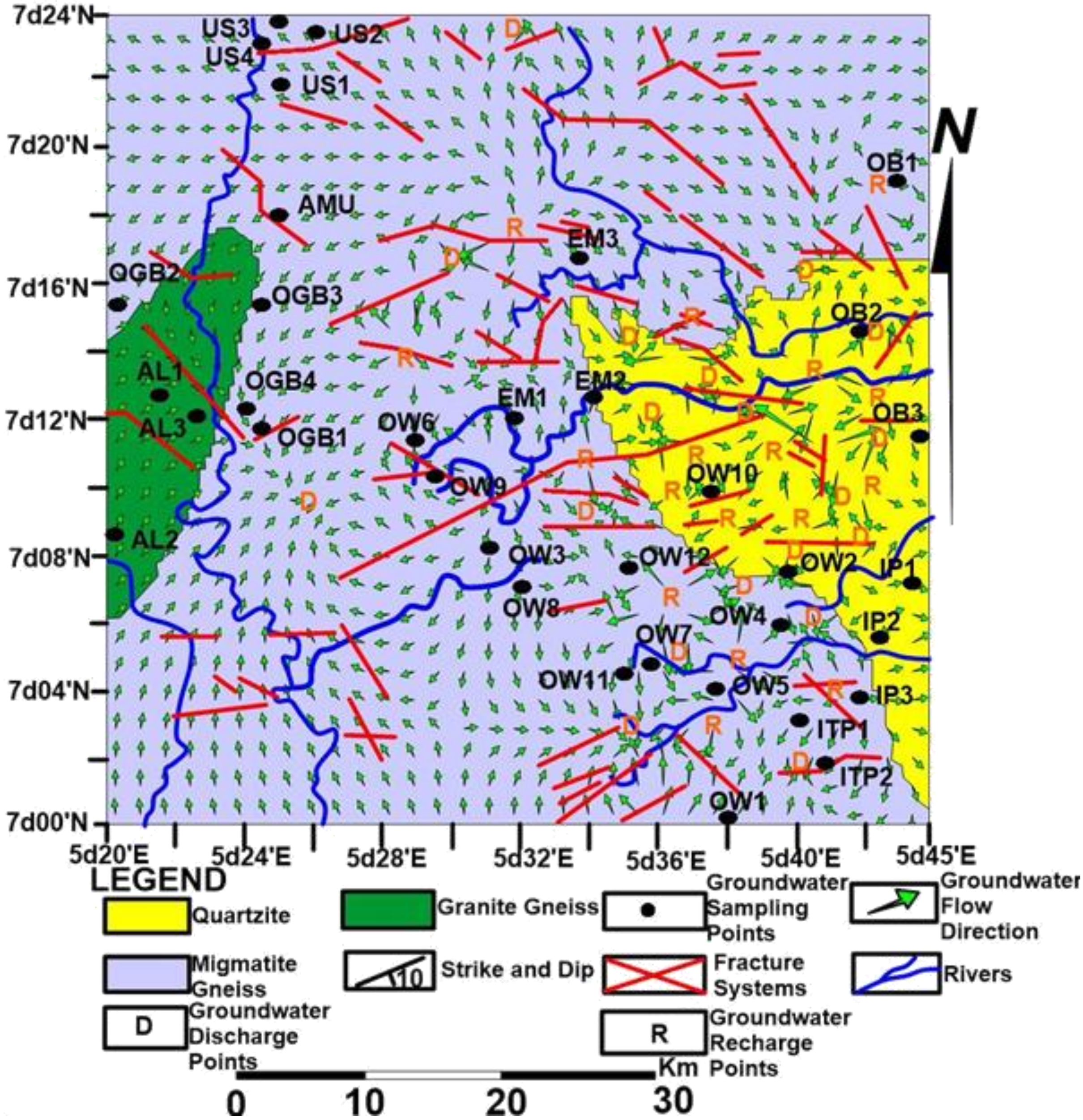

Fig.2: Geological map of the study area showing groundwater flow pattern.

Materials and methods

A total of 35 shallow groundwater samples were collected from shallow (<22.0 m depth) wells across the study area in January 2014 from nine locations. The sampling locations were chosen to represent the groundwater quality in the study region (Fig. 1). The groundwater samples were collected after the well was pumped out for about 10 minutes to remove the stagnant water. The physical parameters measured were measured in-situ using the multiparameter instrument package. The physical parameters measured are pH, temperature, electrical conductivity (EC), and total dissolved solids (TDS). The groundwater samples were filtered through 0.45 μm membrane filter which was acidified with nitric acid (HNO_3) to a pH of less than 2 to minimize adsorption of metals to container walls and reduces biological activity. All groundwater samples are stored at approximately 4°C. All the groundwater collection method and the water sample analysis following standard procedure (APHA, 1998). Chemical parameters measured in the groundwater samples are SO_4, Cl, HCO_3, Na, Ca, K and Mg using flame spectrometer.

Salinity indices

The salinity of groundwater in the area was calculated using Sodium Adsorption Ratio (SAR), Kelly Ratio (KR), Magnesium Adsorption Ratio (MAR), Residual Sodium Carbonate (RSC), Permeability Index (PI), Soluble Sodium Percentage (SSP) and Chloro-Alkaline Indices (CAI) equations.

Hydrogeochemical assessment and statistical analysis

Factors influencing the chemistry of groundwater were determined by using plots such as the log TDS versus:

$$\frac{Na}{Na + Ca}\ (mg/l);$$

the log TDS versus:

$$\frac{Cl}{Cl/HCO_3}\ (mg/l);$$

$$\frac{(Na + K - Cl)}{(Na + K - Cl + Ca)}\ (mg/l) \text{ and}$$

$$\frac{Na}{(Na + Cl)}\ (mg/l).$$

Groundwater in the area was classified using Piper's diagram for groundwater classification. Statistical analysis used in this study are the descriptive, bivariate correlation, factor and hierarchical cluster analysis.

Vulnerability assessment of groundwater

Vulnerability assessment of groundwater in the area was carried out using the DRASTIC model. The model makes use of the follow hydrogeologic parameters: Depth to water table from soil surface (D), Net recharge (R), Aquifer media (A), Soil media (S), Topography (T), Impact of the vadose zone media (I) and Conductivity (hydraulic) of the aquifer (C) (Aller *et al.*, 1987). The DRASTIC parameters are weighted from 1 to 5 according to their relative importance in contributing to the contamination potential (Aller *et al.* 1987). The resulting index is a relative measure of vulnerability to contamination; areas with a higher index value are more vulnerable than those with a lower index. The weights and rates of the original DRASTIC model parameters are presented by Aller *et al.* (1987).

Results and Discussions

Flow regime

Groundwater flow, discharge and recharge points in the study area are shown in Fig. 2. Groundwater flow towards Owo area, which is underlain by metasediments and is highly jointed. Groundwater discharge areas are more than the recharge areas when compared to other parts of the study area. The lineaments in the area serve as the conduit through which groundwater flow in the area. Also, joints in the area are passages through which the aquifer in the area is recharged. The area is underlain by granite gneiss loss their groundwater to River Ogbesse which is Perennial River.

Physicochemical analysis

The summary and spatial maps of the physicochemical parameters in groundwater of the study area are shown in Table 1 and Fig. 3 and 4 respectively. The pH of groundwater in the study area ranges from 6.00 to 6.85 with an average of value of 6.32. This shows that the groundwater in the area is slightly acidic and is found within the maximum permissible limits of the WHO and NSDWQ standards. The EC values range from 33.00 to 1619 µs/cm with an average value of 545.16 µs/cm. Only OW6 show high value of EC and may not be suitable for drinking purposes, while the other 34 samples are within the WHO standard for drinking water. The TDS values vary between 38.00 and 601.00 mg/l with an average value of 208.92 mg/l. TDS value for all samples in the is below the permissible TDS value. TDS in groundwater of the area may be mainly due to the weathering of underlying rocks. Total hardness in the samples is between 7.18 and 263.11 mg/l with a mean value of 111.09 mg/l. These values are within the maximum limit of the WHO standard. The temperature of groundwater in the area ranged between 28.00 and 29.60°C with an average of 28.77°C. The temperature is within the ambient temperature as described by the NSDWQ standards. The concentrations of SO_4 range from 43.15 to 130.45 mg/l with an average of 71.73 mg/l. The sulphate concentration in groundwater of the study area is below the WHO standard. The concentration of Mg is between 0.82 and 5.23mg/l with an average of 4.41 mg/l, which is within the maximum permissible limit of WHO.

Chloride concentration ranges from 0.01 to 0.16 mg/l with an average of 0.07. These values are far below the WHO standards. The bicarbonate values range from 8.00 to 20.00 mg/l with an average value of 14.09 mg/l. Sodium concentration in groundwater of the area is between 1.51 and 97.10 mg/l with a mean value of 25.06 mg/l. The concentration of sodium and chloride which are below the maximum permissible standards is a precursor to low salinity in groundwater of the area.

Ca has concentration that ranges between 1.56 and 97.60 mg/l with an average value of 37.07 mg/l. These values are below the maximum permissible limit. The concentration of potassium in the groundwater samples is between 9.50 and 88.60 mg/l with an average value of 24.36 mg/l. The maximum permissible is 12 mg/l. 31% of the total samples are within the acceptable limit while 69% of these samples are above the permissible limit. High concentration of potassium is due to the impacts of NPK fertilizers application and other anthropogenic activities near the study area.、

Groundwater Quality Classification

Hydrochemical facies

The geochemical origin of groundwater can be unravelled by plotting the concentration of major cations and anions in the Piper (1944) trilinear diagram. The diagram was constructed using Aquachem software version 2014.2. To understand the geochemical history/ hydrochemistry of groundwater in the area, analyzed concentrations of cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and anions (HCO_3^-, SO_4^{2-}, and Cl^-) in meq/l. This diagram shows the similarities and differences among groundwater samples because those with similar qualities will tend to plot together as groups (Todd, 2001; Selvakumar *et al.*, 2014). The plot shows that 31% of the groundwater samples plot in the

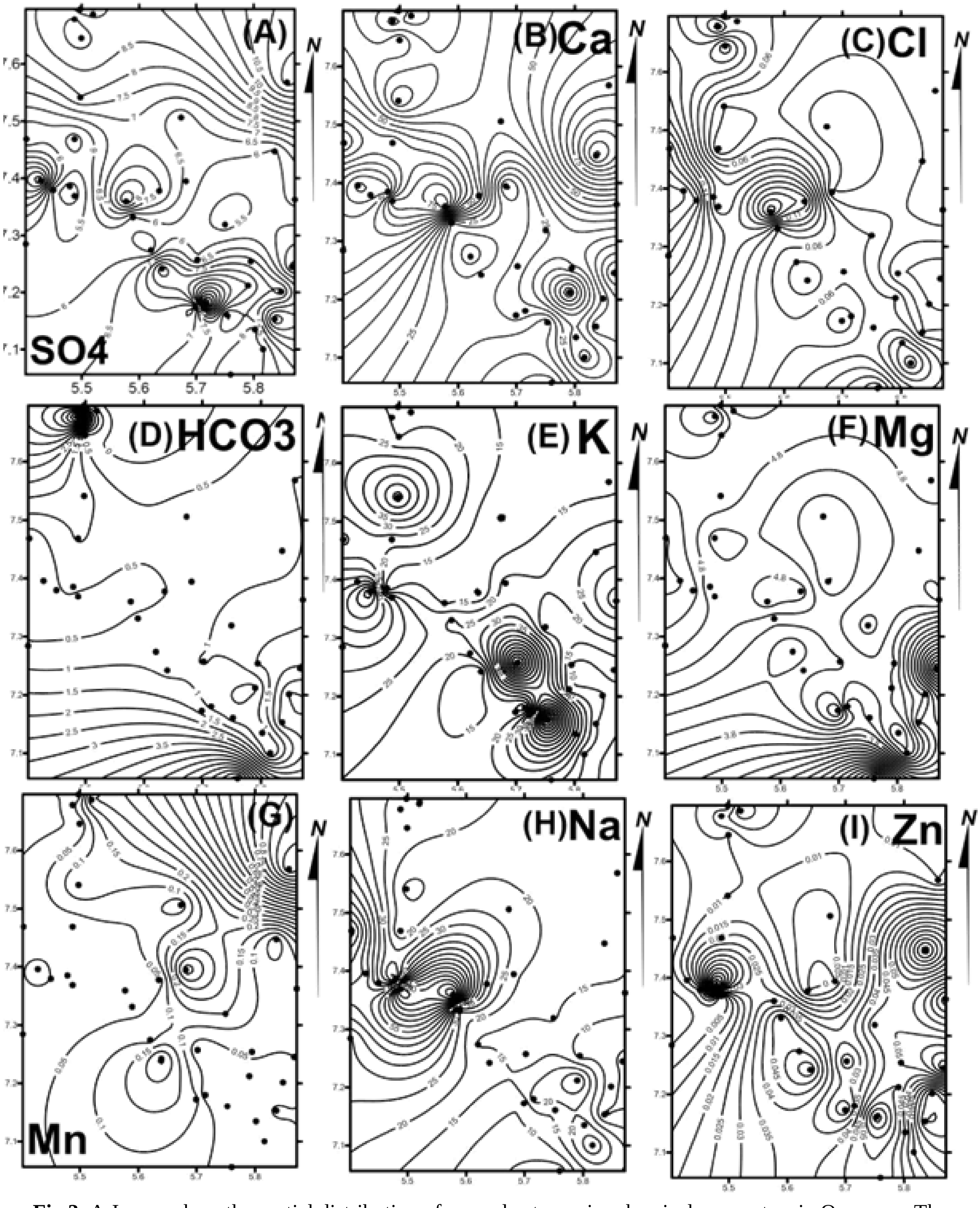

Fig.3. A-I maps show the spatial distribution of groundwater major chemical parameters in Owo area. The concentrations are in mg/L.

field of Ca-Na-K-SO_4 and Na-Ca-SO_4 water type respectively, 9% falls within Ca-SO_4 facies, 6% falls into the Na-Ca-SO_4, K-SO_4, Na-Ca-Mg-SO_4 respectively and 3% of the samples fall into the Ca-Na-Mg-SO_4, Ca-Mg-SO_4, K-Ca-SO_4, and Na-Ca water type respectively (Fig. 5). The dominance of SO_4 ion in almost all the groupings show that silicate weathering of

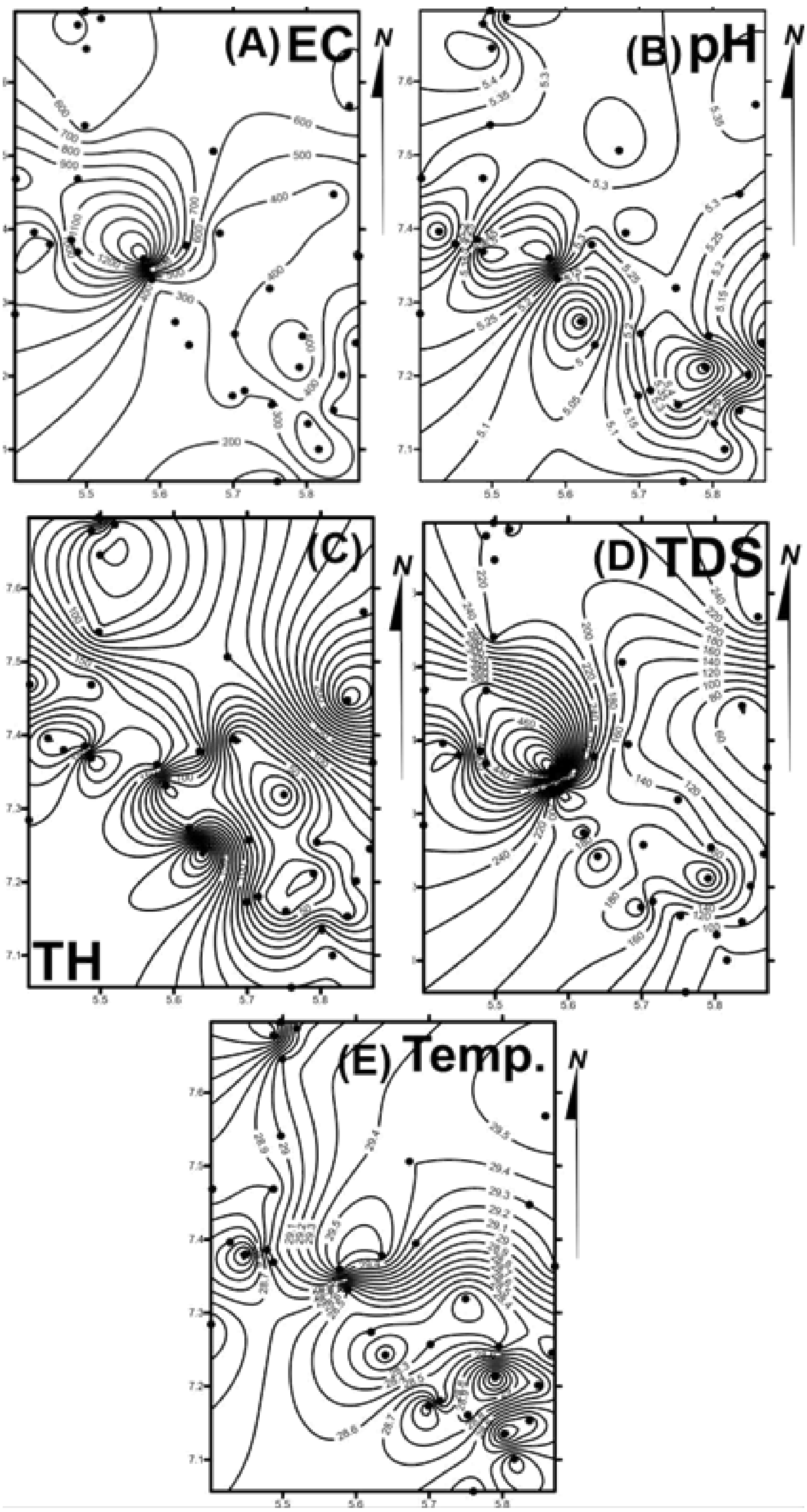

Fig.4. A-E maps show the spatial distribution of groundwater major physical parameters in Owo area. The concentrations are in mg/L.

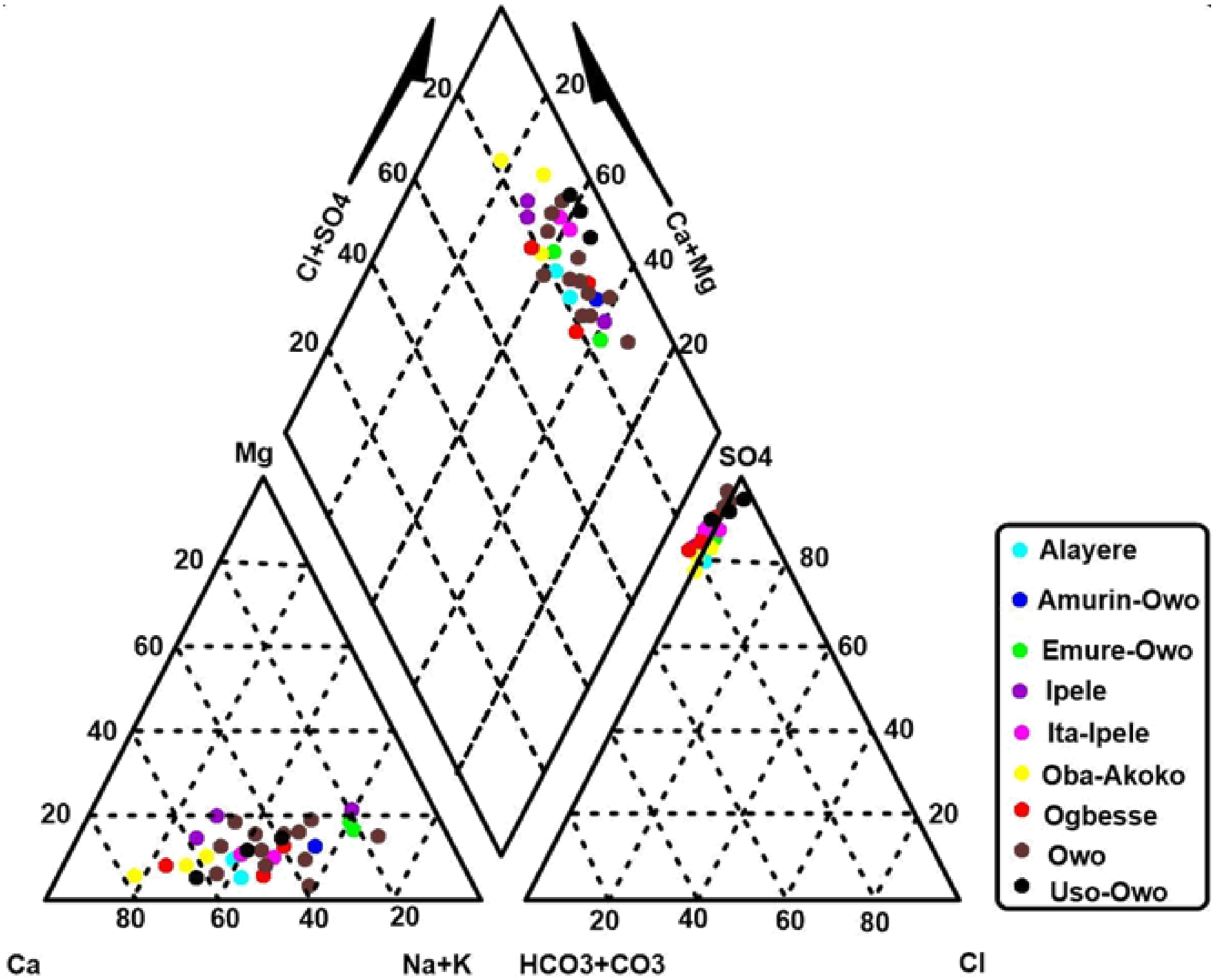

Fig.5. Piper trilinear diagram showing groundwater classification in the study area.

the bedrock is the most dominant process affecting groundwater in the area.

Mechanism controlling groundwater chemistry

The mechanism that controls the chemical composition of groundwater to establish a close relationship between chemical composition of water and aquifer lithological characteristics (Selvakumar *et al.*, 2014). This mechanism established by Gibbs (1970) recognize three distinct mechanism that controls groundwater chemistry. These are evaporation dominance (rate of evaporation), rainfall dominance (chemistry of precipitated water), and rock-water interaction on water chemistry. Two plots are used to decipher these mechanisms. In the first plot, $Cl/(Cl+HCO_3)$ (for anions) values are plotted against TDS, and in the second plot, the values of Na/(Na+Ca) (for cations) of the groundwater samples are plotted against the values of TDS. Fig. 6 indicates that all the groundwater samples fall under rock dominance zone. This implies that the chemistry of groundwater in the area is as a result of the dissolution of the rock that makes up the aquifer in which the groundwater is stored. Dissolution of rocks is a dominant process in areas within the tropical zone. In Nigeria, groundwater occurs within the weathered zones in Basement Complex terrain (Akanmu and Adewumi, 2016) where intense weathering has occurred. Therefore, there is a high tendency for ionic dissolution from these rocks in the groundwater of the area.

Rock source deduction

To understand the source of the ions in groundwater of the area, it is important to know the rock from which they are dissolved. Aquachem software was used to deduce the source rocks contributing ions to groundwater in the area. To deduce the source rocks that contributes to the ionic components of the groundwater three factors are put into consideration. Firstly, if the value of TDS is greater than 500 mg/l carbonate rocks is deduce as a possible source rock but if it is lesser than 500 mg/l a silicate bearing rock is deduced as a possible source rock. Also, ionic ratios of equations 1 and 2 are used to decipher a plagioclase weathering and sodium/halite solution source rock respectively.

$$\frac{(Na + K - Cl)}{(Na + K - Cl + Ca)} (mg/l) \quad (1)$$

$$\frac{Na}{(Na + Cl)} (mg/l) \quad (2)$$

If the values of

$$\frac{(Na + K - Cl)}{(Na + K - Cl + Ca)} (mg/l)$$

are between > 0.2 and < 0.8, the possibility of plagioclase weathering is inferred, but if it is less <0.2 or >0.8 then plagioclase:

$$\frac{Na}{(Na + Cl)} (mg/l)$$

weathering is unlikely. If ratio is >0.5 a sodium source other than halite, albite and ionic exchange can be deduced, if it equals to 0.5 halite solution is inferred. If it is <0.5 with a TDS value >500 mg/l, then a reverse softening can be inferred. When is <0.5 with a TDS value <500 mg/l an analysis error can be inferred. If it is <0.5 with TDS value less than 50, then rainwater can be inferred. For this study:

$$\frac{(Na + K - Cl)}{(Na + K - Cl)} (mg/l)$$

values range between 0.182 and 0.712. Only ions in 81% of the samples are released through plagioclase weathering, while in 9% (OB_1, OB_2 and OW_2) the plagioclase weathering is unlikely (Fig. 7). Based on the TDS values, ions in 98% of the samples are released by silicate weathering while 2% (OW_6) are released through carbonate weathering (Fig. 8). The values of:

$$\frac{(Na +)}{(Na + Cl)} (mg/l)$$

values range from 0.995 to 0.999, which implies sodium source other than halite, albite and ionic exchange.

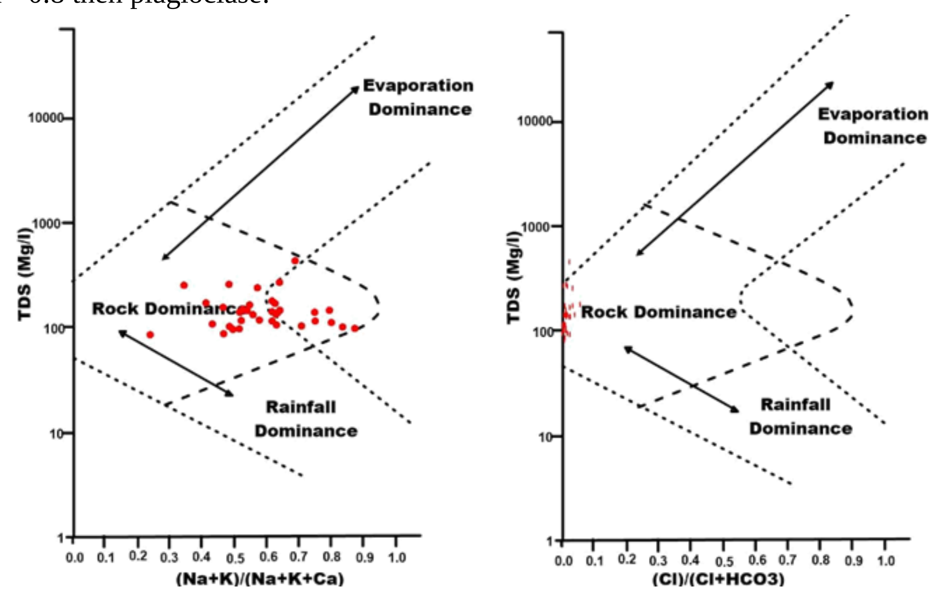

Fig.6. Gibbs plot showing the processes that releases ions into groundwater of the study area

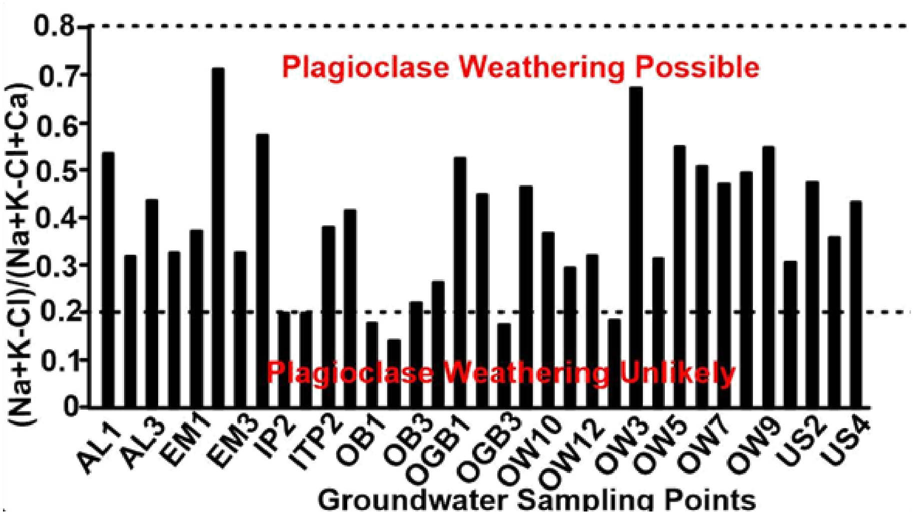

Fig.7. Plagioclase weathering chart. The chart shows that plagioclase weathering might have introduced ions into 87% of samples from the area.

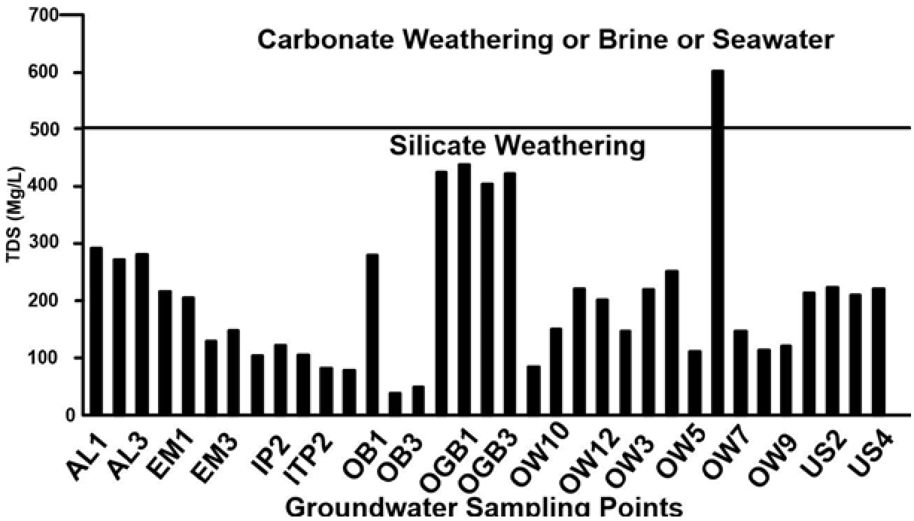

Fig.8. Silicate weathering chart. The chart shows that silicate weathering might have introduced ions into 97% of samples from the area.

Statistical Analysis

Correlation analysis

Bivariate correlation is used to evaluate and establish the relationships between two variables. Correlation between major ions was carried out by using Spearman's correlation matrix. Table 2 shows the coefficient between the major ions in the study area. A significant and positive correlation (≥ 0.5) have been obtained for pH, TDS, temperature, EC, TH, $SO4^{2-}$, Cl and Ca. The strong correlation of Mg^{2+} ion with Cl^- (≥ 0.58) and $SO4^{2-}$ (≥0.638) reflects that the groundwater in the area might have been contaminated due to excessive application of fertilizers and anthropogenic activities (Selvakumar *et al.*, 2014).

Principal Component Analysis (PCA)

Principal component analysis is a statistical method that is used to analyze the interrelationship within a set of variables by reducing the complex information to an easily interpretable form (Selvakumar *et al.*, 2014). In this work, the PCA was carried out using dataset consisting of 35 groundwater samples to identify the factors that affect the hydrochemistry of the study area. The PCA result which includes the loadings, eigenvalues and percentages of the total variance are summarized in Table 3. Four factors explain 72.71% of the total variance in the dataset. Parameters with loadings whose absolute value is more than 0.50 are considered significant in this study. Factor I explained 41.15% of the total variance and have strong positive loadings on TDS, Temperature, EC, TH, Cl, Na, Ca, K and Mg. The high loadings for the major ions such as Ca^{2+}, Mg^{2+}, Na^{+} and Cl^{-} possibly reveal that mineral-water reaction is influenced by anthropogenic activities (Selvakumar *et al.*, 2014). Factor II explained 12.20% of the total variance and had strong positive loadings on the pH. The high loading of pH reveals a strong impact that the lithology which makes up the aquifer has on the groundwater. Within the Basement Complex pH tends to be slightly acidic to neutral. Factor III explained 10.28% of the total variance. The high loading of HCO3 may be due to some chemical fertilizers used in agriculture and effluent from industries in the area (Selvakumar *et al.*, 2014). Factor IV explained 9.08% of the total variance. The high loading of SO_4 may be linked to the effect of the underlying lithology on the groundwater. Figs. 9 and 10 show the plot of factor I against factor II and factor II against factor III. The clustering of Na, Cl, K, Ca and TDS in fig. 9 may be indicative of a possible anthropogenic activity which is probably the use of fertilizers for farming in the area. In fig. 10 the clustering of HCO_3 and Ca on the same section also indicate a possible impact of agricultural practices on groundwater in the area.

Hierarchical Cluster Analysis (HCA)

HCA attempts to identify relatively homogeneous groups of cases (or variables) based on selected characteristics, using an algorithm that starts with each case (or variable) in a separate cluster and combines clusters until only one is left. You can analyze raw variables, or you can choose from a variety of standardizing transformations. Distance or similarity measures are generated by the Proximities procedure (IBM Knowledge Center, 2017). Fig. 11 shows the hierarchical cluster groups of groundwater sampling points in the study area. Eight groups were generated based on the physicochemical properties of the groundwater samples.

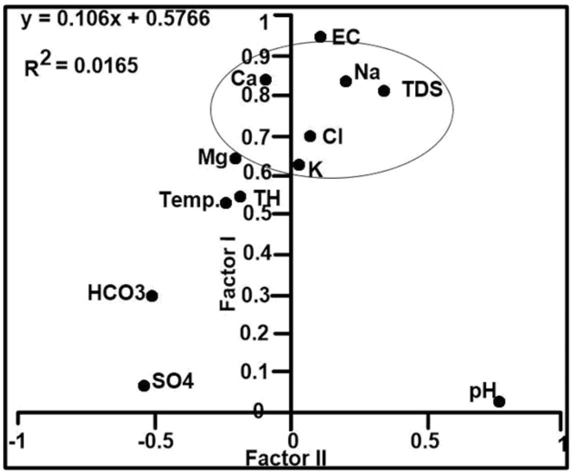

Fig.9. Plot of Factor I against Factor II.

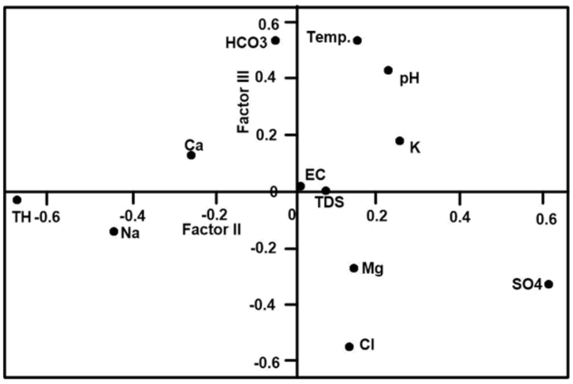

Fig.10. Plot of Factor II against Factor III

Evaluation of water quality for irrigation use

Sodium Adsorption Ratio (SAR)

SAR for the groundwater from the study area was estimated by the formula in equation. Water having SAR values <10 is considered excellent,

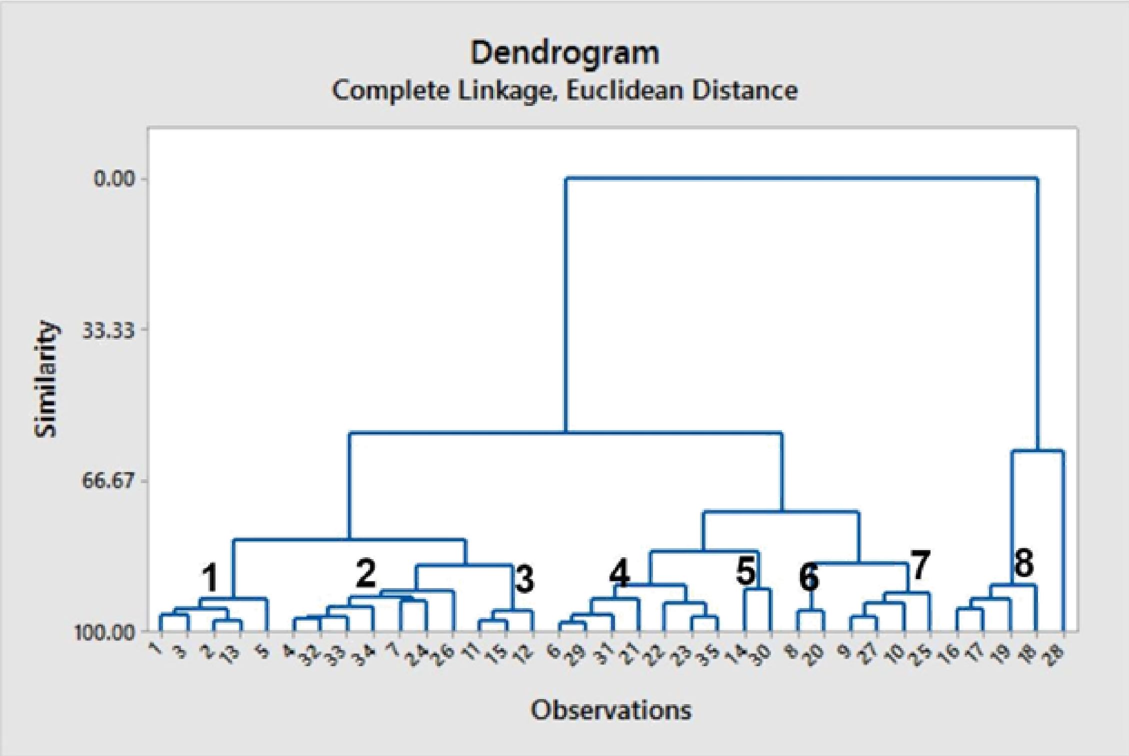

Fig.11. Hierarchical cluster dendrogram of Groundwater Sampling Points

10-18 is good, 18-26 is fair and above 26 is unsuitable for irrigation use (Wilcox, 1955). In the present study area, all the sample are excellent for irrigation purpose. The SAR values calculated are presented in Table 4. The Wilcox plot (Fig. 12) shows that 13% of the groundwater samples belong to the C1S1 class indicating low sodium and salinity hazards. 14% of the samples belong C3S1 class indicating low sodium and high salinity hazards. 74% of the groundwater samples fall into the C2S1 group indicating low sodium and medium salinity hazards.

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}} \tag{3}$$

Permeability Index

Long-term use of irrigation water affects soil permeability. It depends on various factors like total soluble salt, sodium, calcium, magnesium and bicarbonate content of the water. Doneen classified irrigation waters into three classes based on the Permeability Index (PI) (Doneen, 1964). If permeability index is < 60 it suitable for irrigation but if it is > 60 then it is unsuitable for irrigation purpose. In this study 27 (Table 4) samples representing 77% of the total samples have PI values < 60, which means that they are suitable for irrigation, but 8 samples representing 23% of the total samples have PI values < 60, which implies they are unsuitable for irrigation.

$$PI = \frac{(Na + K) + \sqrt{HCO_3}}{Ca + Mg + Na + K} \tag{4}$$

Soluble Sodium Percentage (SSP)

The suitability of groundwater for irrigation depends on the mineralization of water and its effect on plant and soil (Selvakumar *et al.*, 2014). If the concentration of sodium is high in irrigation water, Na^+ tends to be absorbed by clay particles displacing Mg^{2+} and Ca^{2+} ions, thereby reducing soil permeability (Selvakumar *et al.*, 2014). SSP is represented by equation 5.

If the sodium percentage is < 20, the groundwater is excellent for irrigation, if it is between 20 and 40 then it is good for irrigation, if it is between 40 and 60, then it is permissible to be used for irrigation, if it is between 60 and 80 it doubtful and may be dangerous for use as irrigation water, if it is > 80 the water is unsuitable for irrigation. The calculated values of soluble sodium percentage of the groundwater samples indicate that 100% of the water samples are excellent for irrigation purposes (Table 4).

$$SSP = \frac{(Na^{+} + K^{+}) \times 100}{(Ca^{2+} + Mg^{+} + Na^{+} + K^{+})} \quad (5)$$

Magnesium Adsorption Ratio

The Ca^{2+} and Mg^{2+} ions maintain a state of equilibrium in most groundwater (Hem, 1985). In equilibrium, Mg^{2+} in water affects the soil by making it alkaline and results in decrease of crop yield (Kumar *et al.,* 2007). The measure of the effect of magnesium in irrigated water is expressed as the magnesium adsorption ratio (Table 4). Paliwal (1972) developed an index for calculating the magnesium hazard. MR is calculated using the formula:

$$MAR = \frac{(Mg^{2+}) \times 100}{(Ca^{2+} + Mg^{2+})} \quad (6)$$

If MR value is < 50, then the groundwater may be used for irrigation purpose. If it is > 50, it is unsuitable for irrigation purpose. The results of the MR calculation show that 100% of the total sample is suitable for irrigation.

Residual sodium Bicarbonate (RSBC)

Residual sodium bicarbonate (RSBC) exists in irrigation water when the bicarbonate (HCO3) content exceeds the calcium (Ca) content of the water. Where the water RSBC is high (>2.5meq/l), extended use of that water for irrigation will lead to an accumulation of sodium (Na) in the soil. This may result in (1) Direct toxicity to crops, (2) Excess soil salinity (EC) and associated poor plant performance, and (3) Where appreciable clay or silt is present in the soil, loss of soil structure occurs through clogging of pore spaces thereby hindering air and water movement (SAI, 2010; Naseem *et al.*, 2010). The RSBC value of the study area is between -4.61 to 0.12 (Table 4), indicating good quality for irrigation purpose.

$$RSBC = HCO_3 - Ca^{2+} \quad (7)$$

Kelly Ratio

This is an important parameter formulated by Kelley (1946) based on the level of Na against Ca and Mg. It is expressed by equation. Groundwater with a Kelly ratio < 1.0 is deemed suitable for irrigation purpose, while KR value between 1 and 2 is classified as marginal and may portend danger for the groundwater and if the KR is > 2, then it is unsuitable for irrigation purposes. The KR value of the investigated groundwater has about 83% of it samples suitable for the irrigation while 17% are found to be unsuitable for irrigation purpose.

$$KR = \frac{Na}{Ca + Mg} \quad (8)$$

Groundwater Vulnerability

The groundwater vulnerability was determined based on the model of Aller (1987) shown in Table which assigns weights to different parameters that contribute to groundwater pollution. Each DRASTIC factor was assigned a rating, typically from 1 to 10, based on a range of information within the parameter (Table 5). Each DRASTIC factor was further assigned weight values ranging from 1 to 5 (Table 5). The values of the ratings and weights for each parameter were input into equation (Equation 9) to determine the pollution potential known as the DRASTIC INDEX which is a numerical value representation.

Where subscripts R and W refer to rating and weighting of the hydrogeological parameters. The spatial map for the DRASTIC parameters in the area is shown in figs 13A to 13D. The result shows that weight value (WV) for depth to water level (DW) ranges from 35 to 45, for net recharge (RW) it ranges from 12 to 32. The WV for aquifer media (AW) and impact of vadose zone (IW) in the area is 12 and 15 respectively for all the locations. Furthermore, the WV for soil media (SW) ranges between 6 and 10, for topography (TW) between 1 and 5 and hydraulic conductivity (CW) it is between 3 and 24. The drastic index (DI) (Fig. 14) for the area is between 88 and 123.

The vulnerability assessment of the groundwater in the study area show 83% falling into the low vulnerable class and 17% falling into moderate class (Table 7). Emure-Owo, Uso-Owo and Eporo areas exhibited areas of moderate vulnerable classes due to the high hydraulic conductivity, nearness to drainage systems, and higher degree of weathering of the basement complex rocks thereby promoting the increased rate of flow and direction of contaminants which will endanger the groundwater quality in the future.

The two classes were classified based on the calculated hydrogeological factors for the area under study (Table 6). The calculated drastic index values were used to generate the groundwater vulnerability map which showed that about 80% of the study area falls within the low groundwater vulnerability class. The present state of vulnerability is due to the significant thickness of the aquifer media, percentage of clay in the soil media and steepness of slope aiding the longer travel time of contaminants to the water table. The land use pattern also favoured the DRASTIC model with the vegetated areas occupying larger portion than cultivated and built up areas, but this can only be guaranteed if sustained in years to come. These areas could also pose a problem due to the long-term effect of agricultural practices (pesticides and fertilizers), and irrigation return flows. Concentrations and flux of contaminants will pose no danger in groundwater this study.

4.7 *Water Quality Index*

Weighted arithmetic water quality index method classified the water quality according to the degree of purity by using the most commonly measured water quality variables. The method has been widely used by the various scientists (Chauhan and Singh, 2010; Chowdhury *et al.*, 2012; Balan *et al.*, 2012) and the calculation of WQI was made Brown *et al.*, 1972 by using the following equation:

$$D_RD_W + R_RR_W ++ A_RA_W + S_RS_W + T_RT_W + + I_RI_W + C_RC_W = \text{DRASTIC index (DI)} \quad (9).$$

$$WQI = \frac{\sum Q_iW_i}{\sum W_i} \quad (10).$$

$$Qi = 100[{}^{V_i - V_o}/_{S_i - V_o}] \quad (11)$$

The quality rating scale (Qi) for each parameter is calculated by using this expression:

Where, V_i is estimated concentration of ith parameter in the analyzed water, *Vo* is the ideal value of this parameter in pure water, *Vo* = 0 (except pH =7.0 and DO = 14.6 mg/l), *Si* is recommended standard value of ith parameter.

The unit weight (Wi) for each water quality parameter is calculated by using the following formula:

$$Wi = {}^{K}/_{S_i} \quad (12)$$

Where K is the proportionality constant and can also be calculated by using the following equation:

$$K = \frac{1}{\sum ({}^{1}/_{S_i})} \quad (13)$$

Tab.1. Drinking Water Standard Specifications and Statistical Information of Ionic Concentration.

Parameters	Minimum	Maximum	Mean	WHO 2004
pH	6.00	6.85	6.32	6.50-8.00
TDS (mg/l)	38.00	601.00	208.92	1,000.00
Temp. (ºC)	28.00	29.60	28.77	-
EC	33.00	1619.00	545.16	1,500.00
TH (mg/l)	7.18	263.11	111.09	500.00
SO_4 (mg/l)	43.15	130.45	71.73	250.00
Cl (mg/l)	0.01	0.16	0.07	600.00
HCO_3 (mg/l)	8.00	20.00	14.09	500.00
Na (mg/l)	1.51	97.10	25.06	200.00
Ca (mg/l)	1.56	97.60	37.07	200.00
K (mg/l)	9.50	88.60	24.36	12.00
Mg (mg/l)	0.82	5.23	4.41	150.00

Tab.2. Bivariate correlation of physicochemical data obtained from groundwater of the study area

	pH	TDS	Temp.	EC	TH	SO_4	Cl	HCO_3	Na	Ca	K	Mg
pH	1											
TDS	0.19	1										
Temp.	**0.58**	0.09	1									
EC	**0.78****	**0.89**	0.45	1								
TH	-0.20	0.33	0.23	0.45	1							
SO_4	-0.22	**0.82**	0.36	**0.94**	**0.75**	1						
Cl	**0.51**	**0.55****	0.33	**0.61**	0.12	**0.57****	1					
HCO_3	0.33	0.43	0.34	0.13	0.35	**0.69**	**0.79**	1				
Na	0.45	**0.71**	0.29	**0.78**	0.41	**0.79**	**0.68**	0.39	1			
Ca	**0.82**	**0.55**	**0.56**	**0.75****	**0.66**	**0.87**	0.45	0.23	**0.62**	1		
K	**0.72**	0.49	0.32	**0.61**	0.30	**0.58**	0.07	0.21	0.44	0.42	1	
Mg	0.39	0.37	0.28	**0.54**	0.28	**0.64**	**0.58**	0.25	0.41	**0.52**	0.07	1

**Significant at 0.05 level

Tab.3. Principal Component Analysis (unrotated) of physicochemical data using VARIMAX

	Factor I	Factor II	Factor III	Factor IV
pH	0.03	**0.77**	**0.43**	0.22
TDS	**0.81**	0.34	0.00	0.07
Temp.	**0.53**	-0.24	**0.54**	0.15
EC	**0.95**	0.11	0.02	0.01
TH	**0.55**	-0.19	-0.03	**-0.67**
SO_4	0.07	**-0.54**	-0.33	**0.61**
Cl	**0.70**	0.06	**-0.55**	0.13
HCO_3	0.30	-0.51	**0.54**	-0.05
Na	**0.84**	0.20	-0.14	**-0.44**
Ca	**0.84**	-0.09	0.13	-0.25
K	**0.63**	0.03	0.18	0.25
Mg	**0.64**	-0.21	-0.27	0.14
Eigenvalues	4.94	1.46	1.23	1.09
% of Variance	41.15	12.20	10.28	9.08
Cumulative %	41.15	53.36	63.63	72.71

Tab.4. Summary of irrigation indices calculated for groundwater of the area.

Parameters	Range	Groundwater Class (Irrigation Uses)	Samples (n=35)	
			In (no.)	In (%)
SAR (Herman Bouwer, 1978)	<6 6-9 >9	No Problem Increasing Problem Severe Problem	35 - -	100 - -
Permeability Index (PI) (Doneen, 1964)	<60 >60	Suitable Unsuitable	27 08	77 23
Na % (Wilcox 1955)	<20 20-40 40-60 60-80 >80	Excellent Good Permissible Doubtful Unsuitable	35 - - - -	100 - - - -
Magnesium Hazard (Paliwal, 1972)	<50 >50	Suitable Unsuitable	35 -	100 -
SSP (Tood, 1980)	<20 20-40 40-80 >80	Excellent Good Fair	04 30 01	11 86 03
EC	<700 700-3000 >3000	Excellent Good Fair		
RSBC (Nasem et al., 2010)	<2.5 meq/l >2.5 meq/l	Suitable Not Suitable	35 -	100 -
KR (Kelly, 1946)	<1 1-2 >2	Suitable Marginal Unsuitable	29 06 -	83 17 -

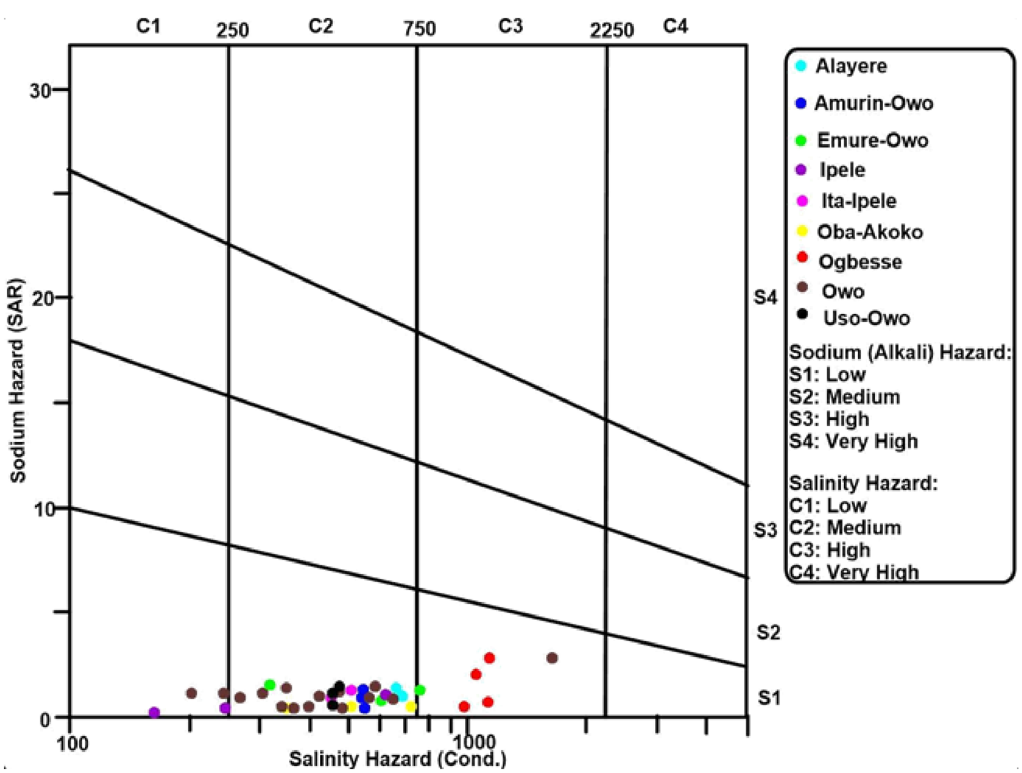

Fig.12. Wilcox Diagram for groundwater in the study area.

Tab.5. The aquifer media rating and weighting of DRASTIC model (Aller *et al.*, 1987)

Depth to water table		**Net Recharge**		**Aquifer Media**		**Soil Media**		**Topography (slope)**		**Impact of vadose zone**		**Hydraulic Conductivity**	
Range (ft)	**Rating**	**Range (inches)**	**Rating**	**Type**	**Rating**	**Type**	**Rating**	**Range (% slope)**	**Rating**	**Type**	**Rating**	**Range (gpd/ft^2)**	**Rating**
0-5	10	0-2	1	Massive Shale	2	Clay	1	0-2	10	Fresh rock	**1**	1-100	1
5-15	9	2-4	3	Metamorphic/igneous	3	Clay	2	2-6	9	Sand, silt and clay	3	100-300	2
15-30	7	4-7	6	Weathered meta/igneous	4	Clay loam	3	6-12	5	Metamorphic rock	4	300-700	4
30-50	5	7-10	8	Bedded sst/lst/shale	5	Silty loam	4	12-18	3	Sand and gravel	6	700-1000	6
50-75	3	>10	9	Massive sandstone	6	Sandy loam	5	>18	1	Limestone	6	1000-2000	8
75-100	2			Massive limestone	6	Peat	8			Boulders/Rubbles	9	>2000	10
>100	1			Sand & gravel	8	Sand	9						
				Basalt	9	Gravel	10						
				Karst limestone	10	Thin/ Absent	10						
**5			**4		**3				**2		**5		**3

Tab.6. Factors used for DRASTIC weightage in the study area (After Adewumi, 2015)

Location	Towns	av. DWL (m)	Slope (º)	Elevation (m)	Mean rainfall (mm)	Lineament Intersection (km/km^2)
1.	Ago-Igbira	5.50	15.2876-22.9014	1025	1488	0.1014-0.2028
2.	Alayere	5.20	50.2727-58.2105	700	1509.64	0.1014-0.2028
3.	Amurin-Owo	5.71	29.9973-36.9873	1080	1509.64	0-0.1014
4.	Ayede-Ogbese	5.00	58.2106-74.9680	1060	1509.64	0.1014-0.2028
5.	Ehingbe	5.53	43.5109-50.2725	1100	1341.4	0.4057-0.5071
6.	Emure-Owo	4.45	43.5109-50.2725	1070	1509.64	0.1014-0.2028
7.	Eporo	4.00	6.7618-15.2976	1080	1509.64	0-0.1014
8.	Ijegunma	5.00	6.7618-15.2976	1050	1341.4	0.2028-0.3042
9.	Ikare-Junction	5.77	29.9973-36.9873	1050	1488	0-0.1014
10.	Ipele-Owo	4.32	43.5109-50.2725	900	1341.4	0-0.1014
11.	Isijogun	4.00	6.7618-15.2976	1100	1341.4	0.6065-0.7100
12.	Isuada	4.00	29.9973-36.9873	1060	1341.4	0.1014-0.2028
13.	Iyere	4.00	22.9314-29.9672	1100	1341.4	0.4057-0.5071
14.	Oba-Akoko	3.90	43.5109-50.2725	1050	1488	0.2028-0.3042
15.	Obasoto	4.00	15.2876-22.9014	1060	1341.4	0-0.1014
16.	Owo	4.00	15.2876-22.9314	1050	1341.4	0.1014-0.2028
17.	Sanusi	4.85	22.9314-29.9672	1000	1341.4	0-0.1014
18.	Uso-Owo	5.61	36.7490-50.2728	1060	1509.64	0.4057-0.5071

**5: The Assigned weights for the hydrogeological factors in DRASTIC generic model (Aller *et al.*, 1987) used in this study

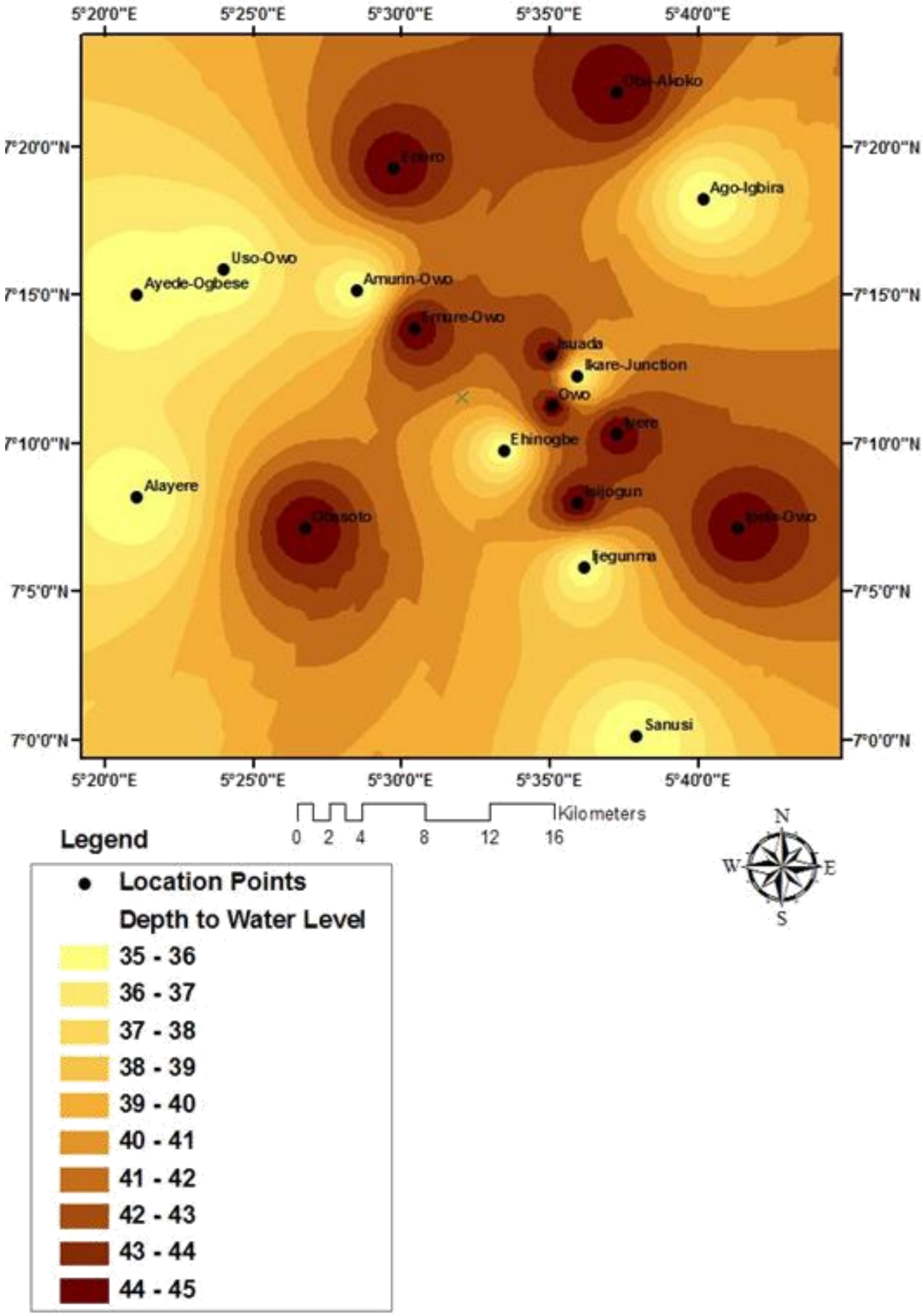

Fig.13A. Spatial map of Depth Water Level in the Study Area

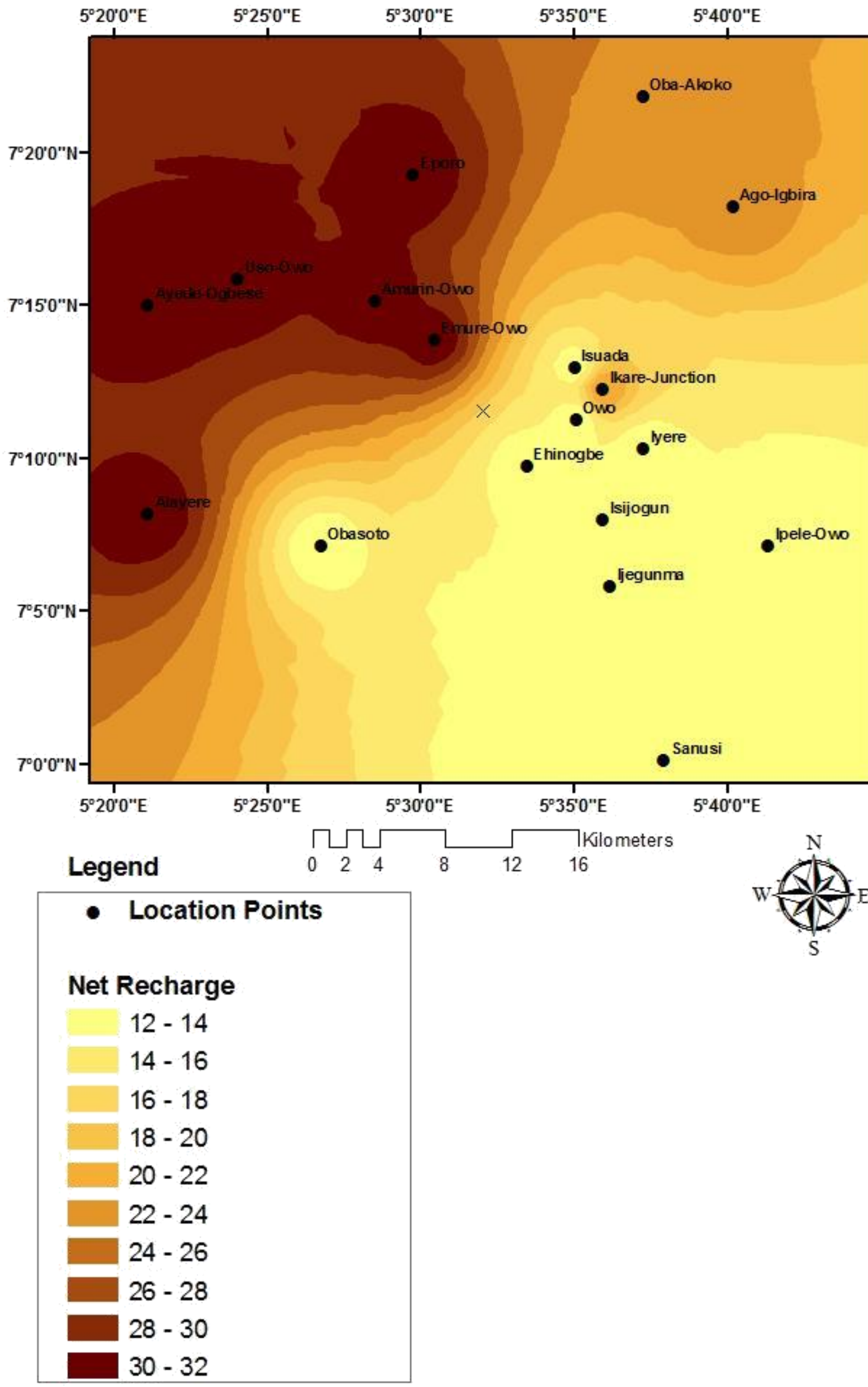

Fig.13B. Spatial map of Net Recharge in the Study Area

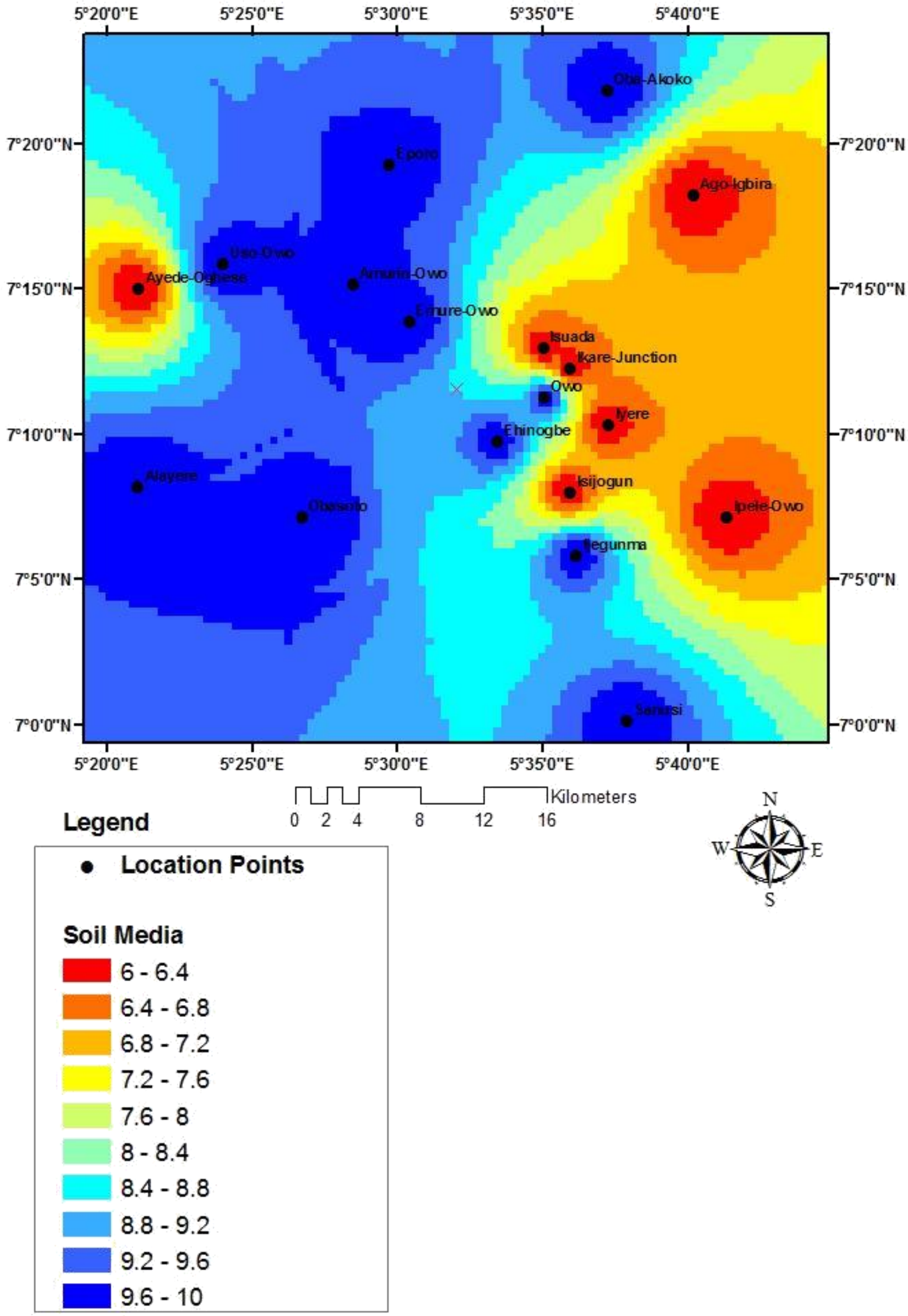

Fig.13C. Spatial map of Soil Media in the Study Area

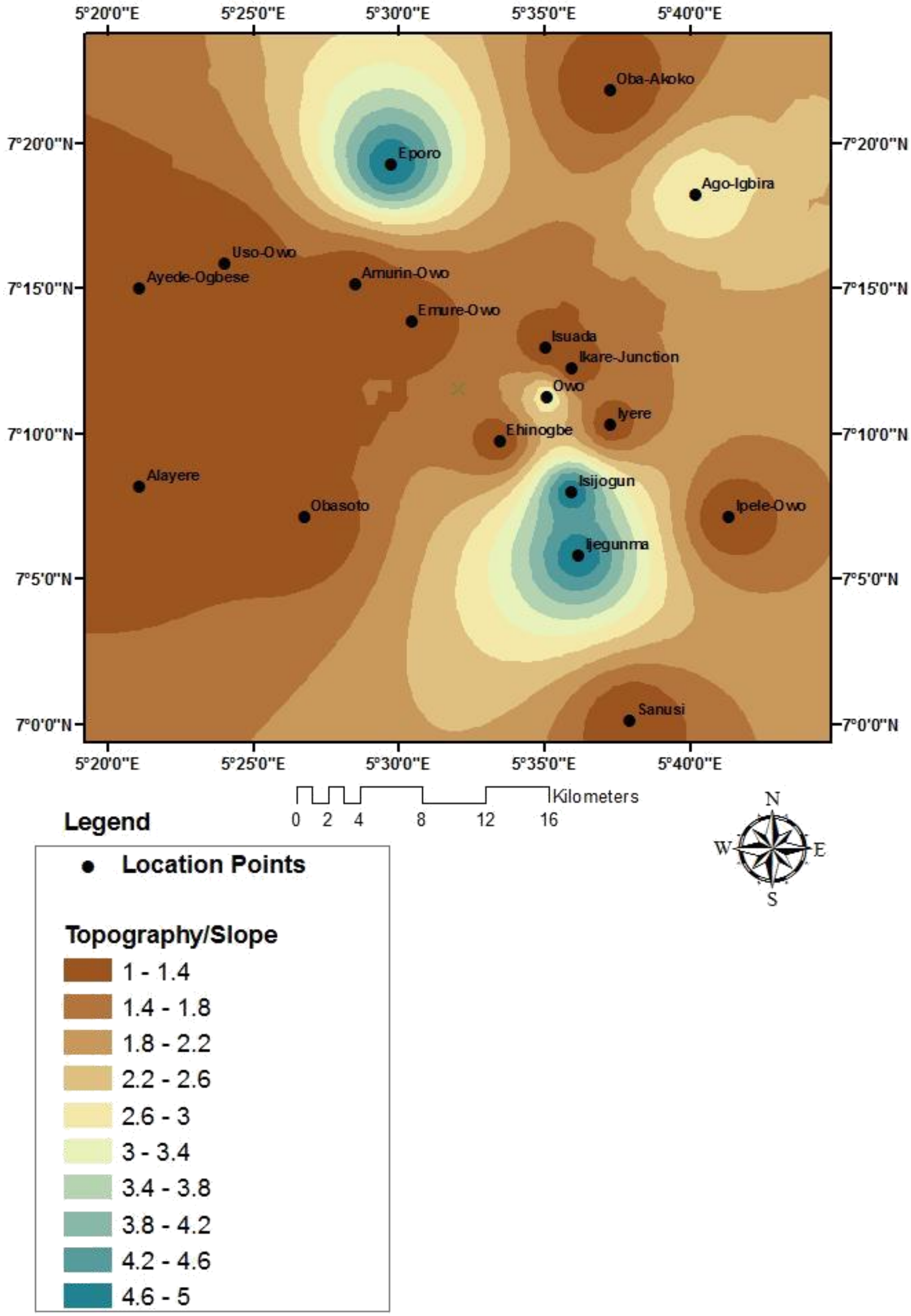

Fig.13D. Spatial map of Slope in the Study Area

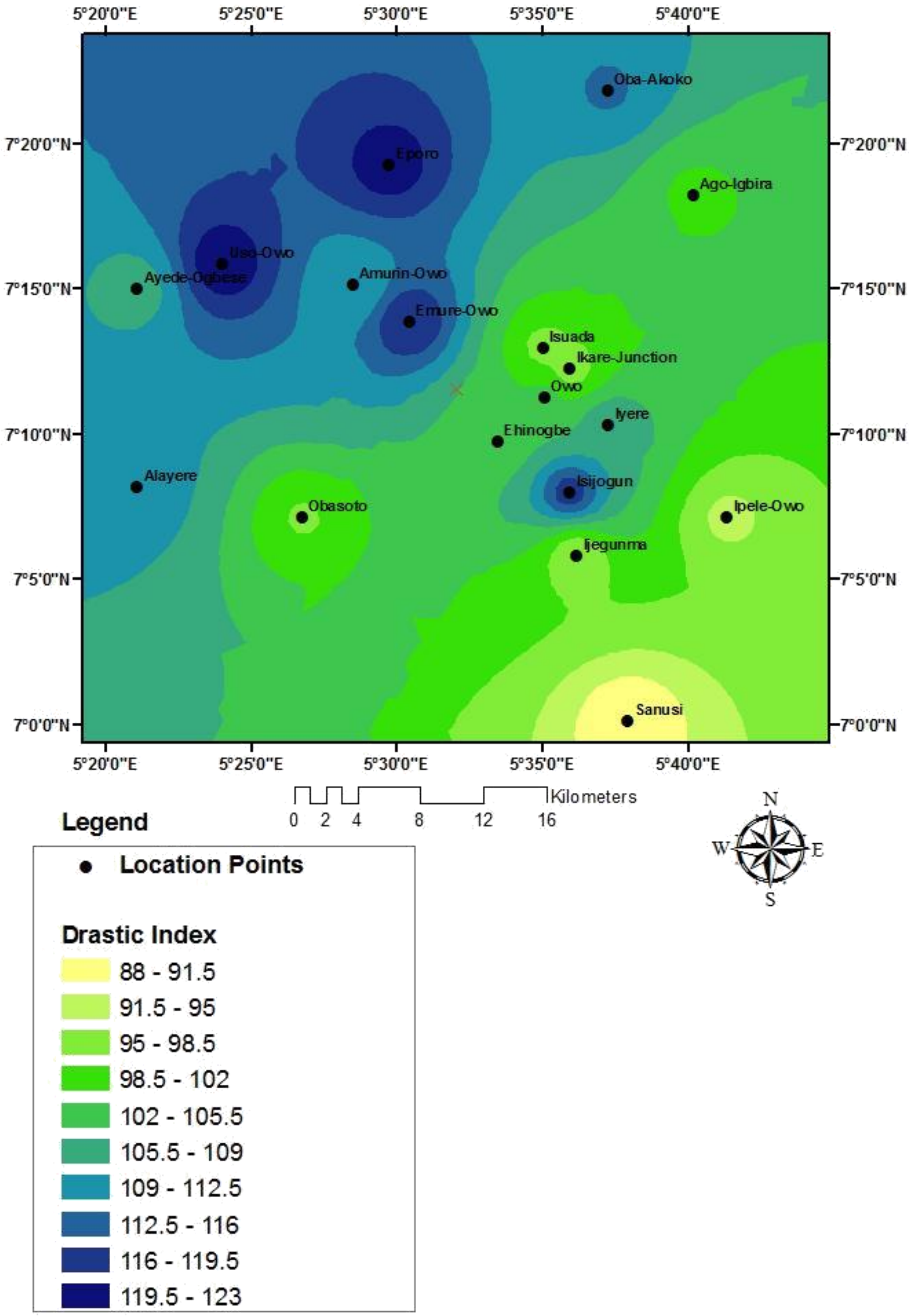

Fig.14. Spatial map of DRASTIC INDEX in the Study Area

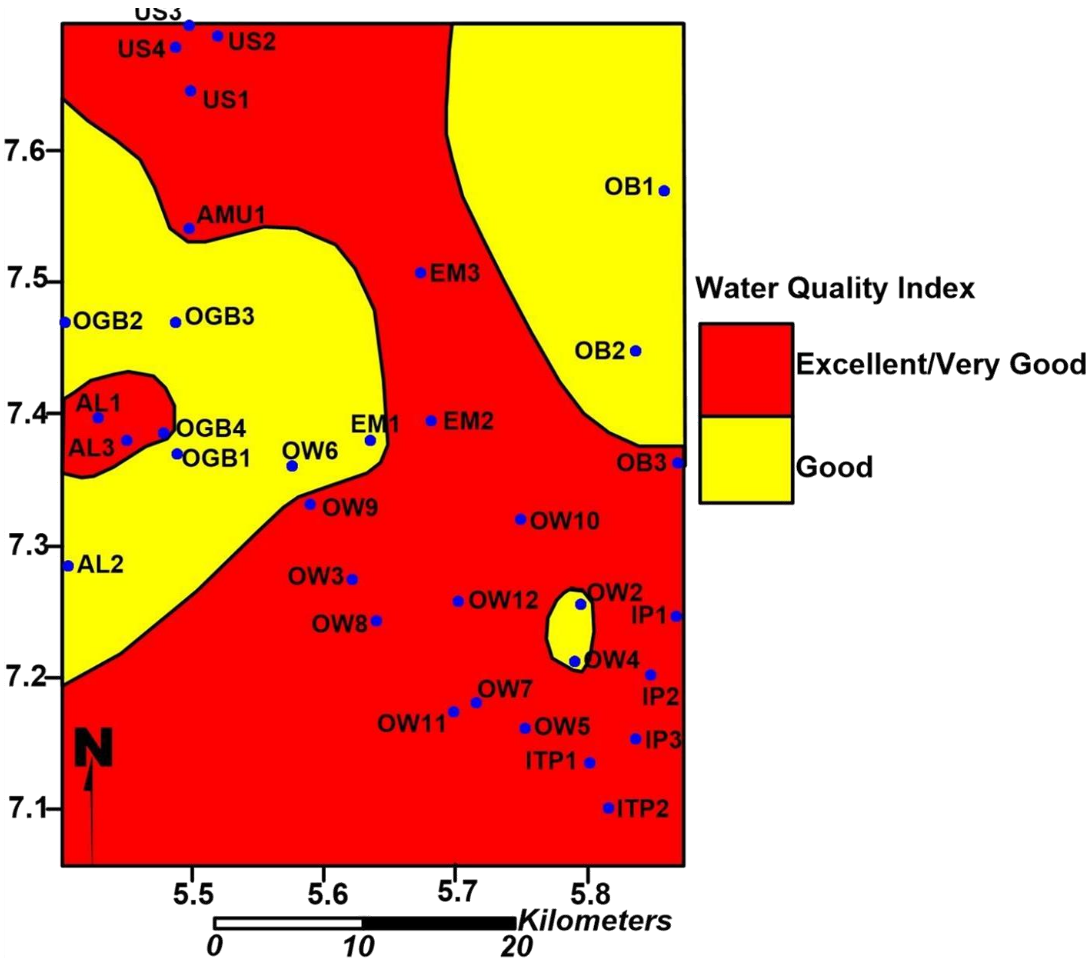

Fig.15: Water Quality Index Map of the Study Area

Tab.7. Calculated DRASTIC Index and Its Qualitative Risk Category for the Study

S/N	Towns	Northing	Easting	DW	RW	AW	SW	TW	IW	CW	DRASTIC Index	Interpretation
1.	Ago-Igbira	7.3037	5.6702	35	24	12	6	3	15	6	101	Low
2.	Alayere	7.1364	5.3512	35	32	12	10	1	15	6	111	Low
3.	Amurin-Owo	7.2522	5.4747	35	32	12	10	1	15	3	108	Low
4.	Ayede-Ogbese	7.2504	5.3510	35	32	12	6	1	15	6	107	Low
5.	Ehinogbe	7.1627	5.5575	35	12	12	10	1	15	18	103	Low
6.	Emure-Owo	7.2308	5.5070	45	32	12	10	1	15	6	121	Moderate
7.	Eporo	7.3208	5.4954	45	32	12	10	5	15	3	122	Moderate
8.	Ijegunma	7.0973	5.6027	35	12	12	10	5	15	6	95	Low
9.	Ikare-Junction	7.2040	5.5992	35	24	12	6	1	15	3	96	Low
10.	Ipele-Owo	7.1189	5.6893	45	12	12	6	1	15	3	94	Low
11.	Isijogun	7.1335	5.5986	45	12	12	6	5	15	24	119	Low
12.	Isuada	7.2164	5.5839	45	12	12	6	1	15	6	97	Low
13.	Iyere	7.1723	5.6207	45	12	12	6	1	15	18	109	Low
14.	Oba-Akoko	7.3638	5.6207	45	24	12	10	1	15	6	113	Low
15.	Obasoto	7.1188	5.4460	45	12	12	10	1	15	3	98	Low
16.	Owo	7.1879	5.5850	45	12	12	10	3	15	6	103	Low
17.	Sanusi	7.0019	5.6324	35	12	12	10	1	15	3	88	Low
18.	Uso-Owo	7.2646	5.4001	35	32	12	10	1	15	18	123	Moderate

Tab.8. Weight Value of physicochemical parameters in the study area

Parameters	Relative weight (Wi)	Standard concentration (mg/l or ppm)(Si)
Calcium	0.183	75
Magnesium	0.275	50
Sodium	0.069	200
Potassium	0.138	100
Bicarbonate	0.138	100
Sulphate	0.069	200
Chloride	0.055	250
Total Dissolved Solids	0.028	500
Total Hardness	0.046	300

Tab.9. Range of Water Quality Index (WQI) for drinking purpose

S/N	Range	Type of water	This Study
1	0-25	Excellent/Very Good	68.57% fall within the category
2	26-50	Good	31.42% fall within the category
3	51-75	Poor	nil
4	76-100	Very poor	nil
5	>100	Unsuitable for drinking purpose	nil

The rating of water quality according to this WQI is presented in Table 8. Calculated water quality index of the area ranges between 7.35 and 50.83 (Table 9 and Figure 15). This implies that groundwater in the area is good for drinking purposes.

Conclusions

The assessment of the hydrogeochemistry and vulnerability of groundwater around Owo area show that the subsurface water in the area is good for drinking, industrial and irrigation purposes. All parameters studied are within the permissible limits of the national and international standards for groundwater except EC in OW6 and K that is above the stipulated standard in 69% of all the samples. This shows that the use of NPK fertilizers for agricultural activities in the area is a threat to groundwater protection. Anthropogenic activities are probably the primary source of groundwater contamination in the area. The high loading of SO_4 from factor analysis indicates a possible effect of underlying geology. Vulnerability assessment of the groundwater show that they are less vulnerable to contamination. However, as industrialization takes over, the groundwater vulnerability may increase.

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