Multivariate Statistical Analysis for the Assessment of Hydrogeochemistry of Groundwater in Agbabu Area, S.W. Nigeria.

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Abstract

Investigation into the hydrogeochemistry of groundwater in Agbabu Area in S.W Nigeria using physical and chemical parameters has been carried out. Samples were collected from eighty water points, comprising fifty two samples in the dry season and twenty eight water samples in the rainy season. The physical parameters measured in the field were pH, temperature, electrical conductivity and total dissolved solids. Chemical constituents analyzed for includes, bicarbonate, chloride, sulphate, nitrate, phosphate, calcium, magnesium, sodium, potassium, iron, zinc, copper, chromium, cadmium, lead, arsenic, nickel, total hardness, calcium hardness, manganese, turbidity, alkalinity, oil and grease for groundwater and were determined using established standard method. Descriptive statistics, correlation matrices, factor analysis, together with cluster analysis were used to gain an understanding of the hydrogeochemical processes in the study area. Factor analysis identify six main processes influencing groundwater chemistry which are sea water intrusion, mineral precipitation and dissolution, seasonal changes, cation exchange processes, human activity and decay organic matter. These six factors accounted for 74.6% of total variance of the groundwater.

Keywords: Groundwater, multivariate statistical analysis, hydrogeochemistry

Introduction

The chemistry of water is an important factor determining its uses for domestic, irrigation or industrial purposes. Groundwater is one of the earth's most important resources for human life. Groundwater quality depends upon the geological environment, human activity, natural movement, recovery and utilization (Reghunanth et al 2002, Senthikumar et al, 2008). Groundwater is gaining increasing importance in the supply of water to rural communities in Agbabu and its environs since surface water are easily polluted. The need for water has greatly increased due to over abstraction of groundwater from the coastal aquifer resulting into seawater intrusion and deterioration of the groundwater quality in the study area. Hydrogeochemistry of Agbabu area remain poorly understood, despite the lack of alternative water sources. Saltwater intrusion and deterioration of groundwater quality in the study area demand for comprehensive understanding of groundwater chemical evolution for optimum management of the groundwater resource. In this study, multivariate statistical analyses such as correlation coefficient, descriptive statistics, factor and cluster analyses were used for interpreting the hydrogeochemical data set obtained in the study area.

Multivariate analyses were employed because of its usefulness as a tool to reduce and organize large hydrogeochemical data sets into groups with similar characteristics and then relating them to specific changes in hydrological process. Multivariate statistical techniques have become widely accepted and used in groundwater quality assessment over the last decades (Ako et al, 2010, Reghunath et al 2002, Elueze et al. 2004).

Location and Geology of the Study Area

The study area lies within the latitudes 6^0 28^1 N and 6^0 37^1 N and longitudes $4^0 32^1$ E and $4^0 5^1$ E of the Greenwinch Meridian (Fig 1). The Elevation ranges between 50 and 250 m above the sea level. The study area has a tropical climate. There are 2 distinct seasons, the wet season and the dry season. Wet season normally commences from April to October while the dry season commences from November and ends in March.The annual rainfall ranges between 1000 mm and 1500 mm.

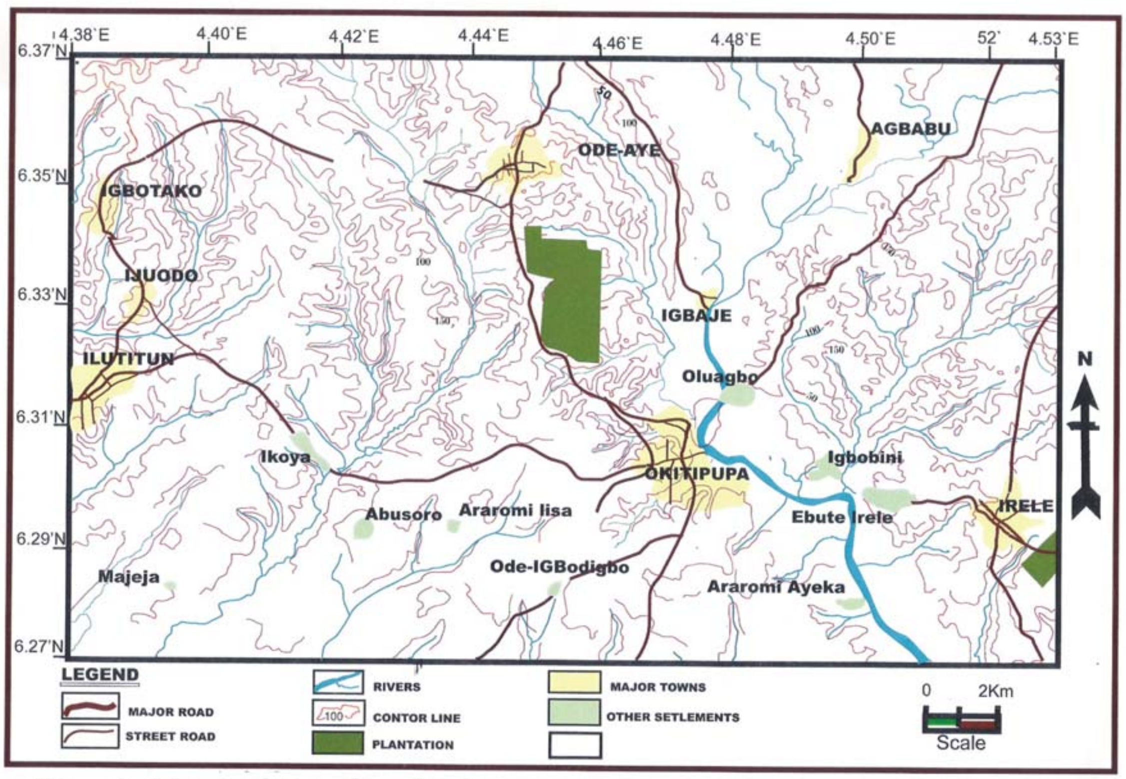

Fig. 1: Map of the Study Area

The study area lies on the central part of the Dahomey sedimentary basin and is underlain by clastic sediments which rest unconformably on the crystalline basement complex. Omosuyi (2001) identified the predominant rock types as shales and sandstones and minor rocks as limestones and unconsolidated sediments with age range of Albian to recent. Omatsola and Adegoke (1981) proposed that Dahomey basin comprises of horst and graben and are filled with Ise, Afowo and Araromi formation gently dipping cretaceous formation. Stratigraphic sequence is shown in Table 1.

Groundwater in the coastal aquifers suffers from seawater intrusion due to over abstraction and water quality degradation as a result of urbanization and agricultural practices (Liu et al, 2003; Gurugnanam et al, 2009; Aris et al, 2007; Farooq et al, 2010; Belkhiri et al, 2010; Akoteyon et al, 2010)

Table 1: Summary of the Stratigraphy in Dahomey Basin

Age	Stratigraphy	Lithology
Recent	Alluvial deposit Benin formation	Sands, Clay lenses, Lignite, Shale
Oligocene	Ijebu/Ogwashi-Asaba formation	Sands, Limestone, Bituminous sands
Eocene	Ilaro formation	Sandstone
	Ofosun formation/ Ameku formation	Sandstone, Mudstones, Glauconites, Glauconites and Phosphates
Paleocene	Akinbo formation	Shales, Fossilliferous Shales
		Limestone, Quartzs, Glauconites
Maestrictian	Araromi formation	Sand, Shales, Siltstone Limestone, Bituminous sands
Turorian	Afowo formation	Sandstones, Shales, Siltstones, Clay
Barrenian	Ise formation	Sands, Guts, Siltstone
Precambrian	Basement complex	

Sources: Omatsola and Adegoke (1981)

The aims this paper are to:

(a) Use multivariate statistical techniques to explain the hydrogeochemistry of the groundwater in the study area.

(b) Identify the geochemical evolution of groundwater in Agbabu area and delineate the saline water intrusion in the coastal aquifers.

Materials and Methods

A total of eighty water samples were collected from hand dug wells and boreholes from the study area (fifty two water samples in the dry season and twenty eight in the rainy season). Two litres of water samples were collected using polythene bottles in the month of March, the end of dry season, and October, the end of rainy season. Water sampling points were located using Global Positioning System (GPS). Twenty seven physico-chemical analyses were determined using the established method of analyses (APHA1992). pH, EC, TDS, and temperature were measured in the field using PH 2603. Bicarbonate, SO_4, Cl, PO_4 NO_3, total hardness, alkalinity, turbidity, calcium, oil and grease and Mg were determined by wet analyses. Cd, Pb, Cr, Cu, Fe, Zn, Mn, were determined by Atomic Absorption Spectrophotometer while Na and K were determined by flame Photometric methods.

Results and Discussion

Descriptive Statistical Analysis

Statistics of the hydrogeochemical data of the groundwater samples are presented in Tables 2. Groundwater in the study area have pH values ranging from 4.1 to 7.1 in the dry season and 6.73 and 8.70 in the raining season, indicating that the groundwater is changing from acidic to alkaline due to influx of HCO_3 ions as a result of percolation of rainwater through soils in the rainy season . Electrical conductivity ranges between 10 micros/cm and 300 micros/cm at 25^{o}C in the dry season and between 10 micros/cm and 870 micros/cm at 25^{o}C in the rainy season. The concentration of cations is in the order of Na >K > Ca> Mg. Sodium concentration varies from 2.98 mg/l to 21.07 mg/l, potassium from 1.26 mg/l to 19.86 mg/l, calcium from 0.80 mg/l to 18.82 mg/l and Mg from 0.01 mg/l to 11.18 mg/l in dry season. For the rainy season, the order is Mg > Ca > Na > k. The concentration of Nitrate is between 0.01 mg/l and 0.26 mg/l for dry season and between 0.01 and 0.70 mg/l for rainy season. The increase in the concentration of nitrate in the rainy season over the dry season period may be attributed to application of agricultural chemicals and atmosphere precipitation.

Table 2: Descriptive statistics of groundwater in dry season

S/N	Parameter	Minimum	Maximum	Mean	Std dev	Std error
1	HCO_3	1.83	112.85	39.45	24.91	3.49
2	Cl	1.00	63.81	37.54	15.42	2.16
3	NO_3	0.01	0.26	0.06	0.06	0.01
4	PO_4	0.12	0.82	0.33	0.15	0.02
5	SO_4	0.01	0.55	0.19	0.12	0.02
6	Ca	0.80	18.82	4.67	3.67	0.51
7	Ca hard	2.00	47.00	11.65	9.17	1.28
8	Total hard	4.02	69.95	17.79	12.14	1.70
9	Mg	0.01	11.18	2.26	2.21	0.31
10	Oil and grease	0.10	176.65	6.65	26.03	3.65
11	Na	2.98	21.07	11.05	4.04	0.57
12	K	1.26	19.86	7.04	4.00	0.56
13	PH	4.10	7.10	5.41	0.70	0.10
14	EC	10.00	300	95.29	73.74	10.33
15	TDS	2.00	220.00	65.22	54.70	7.66
16	Temp	24.00	36.90	29.99	3.24	0.45

Cluster Analysis

Cluster analysis was used here to determine if the samples could be grouped into statistically hydrogeochemical groups that may be significant in the geology context. In the study area, the clustering resulted into four major water groups (Fig. 2). Group 1 is composed of the wells 36, 38, 27, 25, 33, 42, 44, 46, 48, 40, 41, 43, 3, and 49 and this account for 29.4% of the total groundwater samples. This type of water is relatively fresh with a mean EC of 65.3 microsiemens/cm at 25^{o}C. This group is basically chloride dominated.

Group 2 is represented by the well 24, 26, 34, 35, 28, 29, 21, 15, 7, 9, 8, and 4 and this represents 23.5 % of the groundwater samples. The mean electrical conductivity of this group is

27.4 microsiemens/cm at 25^{o}C. This water type is bicarbonate dominated and has low concentration of sulphate. This water type can be interpreted as the first step of water-rock interactions occuring in dilute solutions because of the abundance of bicarbonate in the aquifers.

Group 3 include samples from well 30, 31, 6, 20, 16, 45, 12, 50, 2, 22, 23, 19, and 1. Chloride content is also high with respect to bicarbonate concentration. The mean electrical conductivity is 107.5 microsiemens/cm at 25^{o}C.

Group 4 comprises wells in stations 37, 39, 11, 5, 17, 18, 32, 13, 14, 51, and 10. The mean electrical conductivity is 227.8 microsiemens/cm at 25^{o}C and the dominant ion is chloride. Based on the geological and geographical position, the source of high concentration can be traced to sea water intrusion. Group four water samples have the greatest contamination.

Correlation Coefficient

The correlation coefficient is presented in Table 3. There is a positive correlation between Mg and Cl in the groundwater samples. Mg also shows positive and significant correlation with all the analyzed parameters except SO_4. The Mg-Cl positive correlation shows the influence of seawater and groundwater in mixing. The correlation coefficient between Mg and Cl is around 0.96 in this study. In general, anthropogenic factor due to over-abtraction of fresh water is responsible for the saltwater intrusion. There is also a high correlation coefficient between TDS and EC. Mg and Cl ions present in the water sample gave rise to the high TDS values.

Factor Analysis for Groundwater

The analysis generated six factors which together account for 74.6 % of variance. The rotated loading, eigen values, percentage of variance and cumulative percentage of variance of all the six factors are given in Table 4 and their screen plot in Figure 3. The first eigen value is 4.45 which account for 27.82 % of the total variance and this constitutes the first and main factor. The second eigen value is 1.91 and this account for 11.98 %. The third, fourth, fifth and sixth eigen values are 1.50, 1.43, 1.33 and 1.31 and accounts for 9.40 %, 8.93 %, 8.31 % and 8.18 % of the total variance respectively.

Factor 1 exhibit 27.82 % of the total variance of 74.6 % with positive loading on Ca, Ca hardness, total hardness, Mg, EC and TDS. This factor indicates strong association ($r = 0.6 – 0.9$) between Ca, calcium hardness, total hardness, Mg, EC and TDS in groundwater. This factor is attributed to geogenic influence of these chemical constituents on groundwater as a result of water – rock interaction and this account for the temporary hardness of the water. The dissolution of carbonates and substitution of sodium with magnesium in the transient of water flow may be identified with this factor. The highest EC in the groundwater was 300 µS/cm at 25^{o}C and minimum was 10 µS/cm 25^{o}C. This is showing a high total mineralization, calcium and magnesium are major ions in the water and relatively related to the natural condition. Therefore, this factor is related mainly to the dissolution process of carbonate minerals such as calcite and aragonite due to the fact that Mg and Ca are abundant and mobile.

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Dendrogram using Average Linkage (Between Groups)

Rescaled Distance Cluster Combine

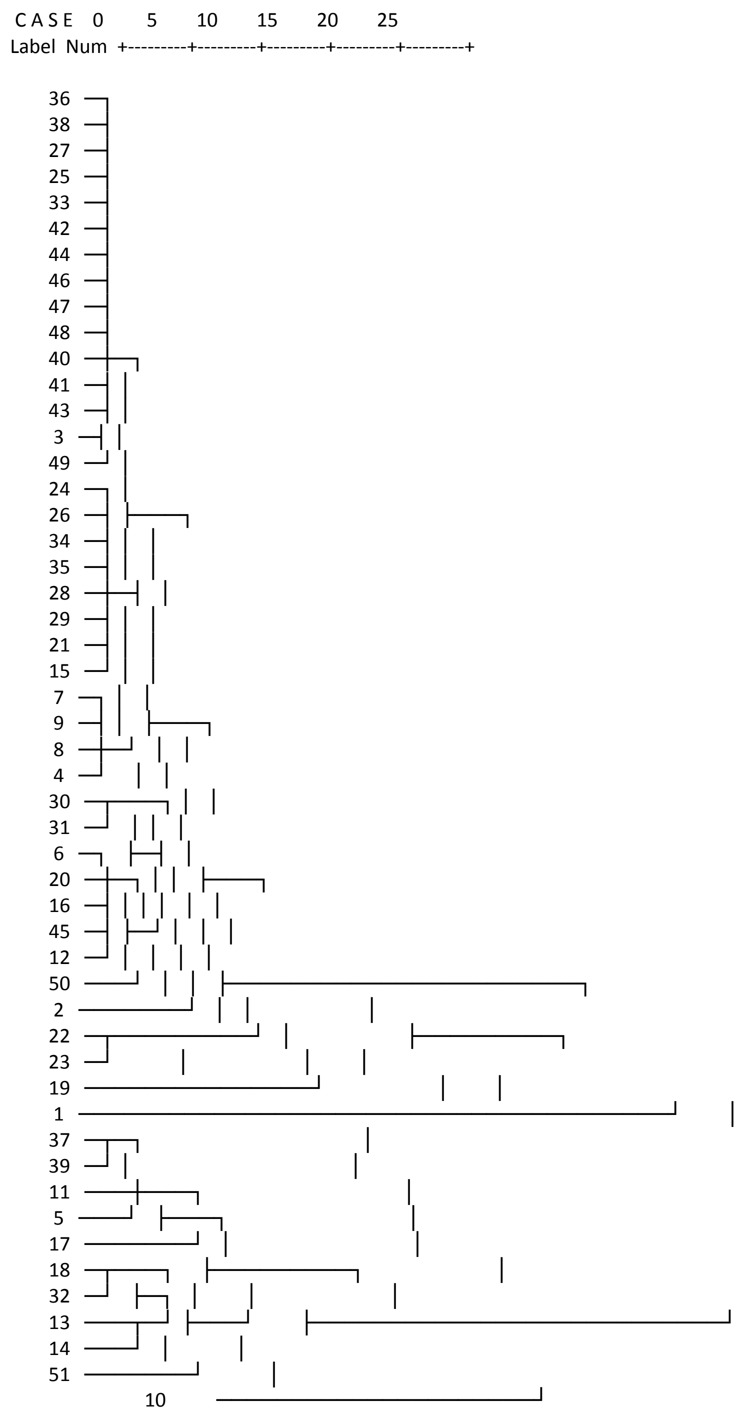

Fig. 2: Dendrogram for groundwater in dry season

Table 3: Correlation Matrix of Groundwater in Dry Season

		TABLE:														
Paras	Hco3	Cl	No3	PO4	So4	Ca	Ca Ha	TH	Mg	Oil/G	Na	K	PH	EC	TDS	TEM
Hco3	1															
Cl	0.28	1														
No3	0.05	0.33	1													
Po4	0.13	0.1	-0.04	1												
So4	0.18	0.05	0.09	0.33	1											
Ca	-0.05	0.15	0.08	0.05	-0.01	1										
Ca Hard	-0.05	0.15	0.08	0.05	-0.01	1	1									
TH	0	0.12	-0.04	0.08	-0.01	0.91	0.91	1								
Mg	0.05	0.3	0.14	0.1	-0.01	0.33	0.33	0.41	1							
Oil/G	-0.21	-0.24	-0.1	-0.11	0.11	0.27	0.27	0.27	-0.15	1						
Na	-0.2	0.05	-0.09	0.14	0.05	0.24	0.24	0.22	-0.03	0.28	1					
K	0.9	0.15	0.12	0.12	-0.05	0.11	0.11	0.12	0.23	0.02	-0.07	1				
PH	-0.13	0.24	-0.04	0.01	-0.22	0.14	0.14	0.12	0.17	0.09	0.2	0	1			
EC	0.08	0.4	0.08	-0.06	-0.04	0.65	0.65	0.67	0.61	-0.13	-0.03	0.13	0.16	1		
TDS	0.07	0.34	0.05	-0.04	-0.03	0.68	0.68	0.69	0.58	-0.11	0.02	0.07	0.16	0.95	1	
Temp	0.23	-0.07	-0.01	0.16	0.09	0.19	0.19	0.25	0.18	0.12	0.07	0.27	-0.05	-0.05	-0.02	1

Factor 2, which explains 11.96 % of the total variance, includes the high loading of oil and grease, Na, Ca hard and Mg. The high loading of oil and grease suggest pollution through spillage or through wastes from oil industries or may be as a result of decomposition of some forms of aquatic life, since the concentration of oil and grease increases toward the seashore in the study area. The presence of Na may be due to cation exchange process by which calcium and magnesium are replaced by the sodium ions. This can be link with the high loading of oil and grease which indicate the alkaline nature and this represent the role of dissolved CO_2 in the groundwater system as a result of the interaction between the groundwater and oil and grease.

Table 4: Rotated varimax matrix for groundwater in dry season

S/N	Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
1	HCO_3	0.03	-0.50	0.37	0.27	-0.22	0.00
2	Cl	0.25	-0.42	0.20	0.00	0.36	0.54
3	NO_3	0.02	0.02	-0.01	0.06	-0.08	0.91
4	PO_4	-0.02	-0.07	0.77	0.15	0.21	-0.10
5	SO_4	0.00	0.08	0.75	-0.10	-0.32	0.20
6	Ca	0.90	0.31	0.06	0.10	0.02	0.04
7	Ca Hard	0.90	0.31	0.06	0.10	0.02	0.04
8	Total hard	0.90	0.24	0.08	0.16	0.02	-0.10
9	MG	0.55	-0.35	-0.07	0.25	0.20	0.14
10	Oil & Grease	0.09	0.79	-0.02	0.11	-0.06	-0.02
11	Na	0.11	0.55	0.29	-0.06	0.44	-0.09
12	K	0.07	-0.08	-0.09	0.76	0.08	0.22
13	PH	0.11	0.05	-0.09	-0.01	0.85	0.01
14	EC	0.89	-0.30	-0.08	-0.07	0.10	0.11
15	TDS	0.90	-0.26	-0.05	-0.09	0.09	0.05
16	Temp	0.10	0.10	0.21	0.78	-0.11	-0.16
	Total	4.45	1.91	1.50	1.43	1.33	1.31
	% Of variance	27.82	11.96	9.40	8.93	8.31	8.18
	Cumulative	27.82	39.78	49.18	58.11	66.42	74.60

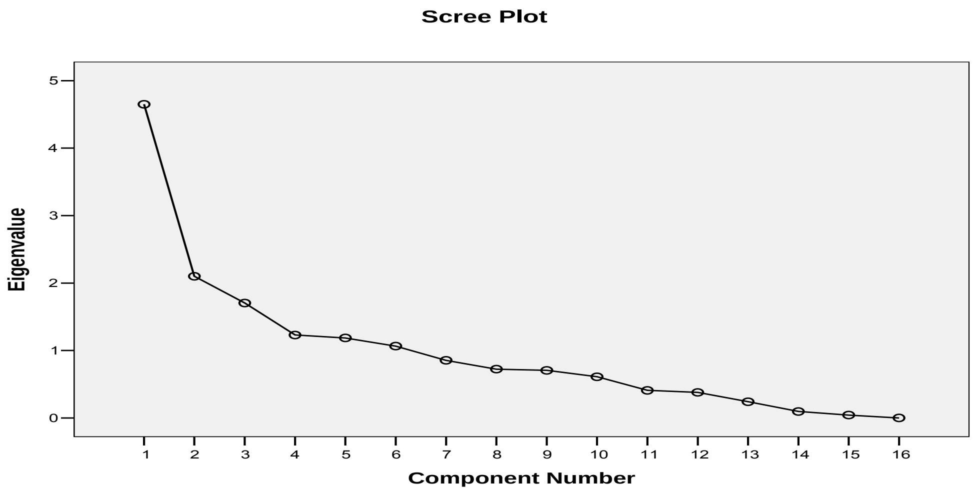

Fig. 3: Scree plot for Groundwater for dry season

Calcium and magnesium may be released into the water as a result of weathering of feldspars, amphiboles and pyroxenes. The lower concentration of Mg and Ca compared to Na is a result from the cation exchange process that occurs naturally when seawater intrudes into the aquifer system.

Factor 3 represent 9.4 % of the total rotated variance matrix of 74.6 % with positive loading of PO_4, SO_4, and weak loading of HCO_3. The presence of phosphate may be traced to agricultural activities in this area, which is the application of phosphate fertilizer. Although SO_4 concentration is more enhanced in seawater than freshwater, but SO_4 shows poor correlation with sodium ($r = 0.05$), Ca ($r = 0.01$) and Cl ($r = 0.05$) in this study. This indicates that the derivation of SO_4 is more related to other processes than extraction from seawater (Olobaniyi and Owoyemi, 2006). The source of SO_4 may be associated with precipitation and evapo - transpiration. Bicarbonate concentration may be due to seasonal changes associated with chemical reactions during rainstorm.

Factor 4 is associated with high loading of K and temperature. The high loading of K suggests pollution from application of potash fertilizer to the agricultural lands. The fourth eigen value is 1.43 and this account for 8.93 % of the total variance. The mean temperature of 30.0 ^oC was recorded in the study area during the dry season. It is known that the water temperature is controlled by the intensity of solar radiation, which reflects the temperature during the dry season, when the sampling was done. Temperature here plays an important role in the weathering process of the groundwater. The association of temperature and potassium indicates also the influence of temperature resulting into the hydrolysis of K – feldspar and plagioclase feldspar due to the fact that the contact time is long enough for significant dissolution of silicate minerals. Good examples of this process was observed in well 8 (19.86 mg/l), well 21 (17.48 mg/l) and well 16 (15.53 mg/l) where relatively high concentration of K is associated with higher temperature.

Factor 5 has a positive loading of pH, Na and Cl. Factor 5 account for 8.31 % of the total variance. The association of Na and Cl suggest salinity and it is an indication that the seawater mixes with the freshwater system.

Factor 6 accounted for 8.18 % of the variance with positive loading of NO_3 and Cl. The presence of chloride may be associated with environmental and atmospheric precipitation. The high loading of NO_3 in the groundwater samples may be attributed to atmospheric influence, plant remains, agricultural practices as well as sewage disposal at the recharge area of the groundwater. Nitrogen is a large component of both synthetic and organic fertilizer. Nitrate is a highly soluble compound and thus is extremely mobile in the environment. After fertilizer application, all nitrogen that are not absorb by the crops migrates into the groundwater.

Conclusion

Hydrogeochemical and contaminants studies of the groundwater in Agbabu and its environs were carried out through comprehensive interpretation of multivariate analysis of the chemical and physical data obtained. It can be concluded from the study that

The quality of the groundwater in the study area has been degraded by anthropogenic factors.

There are saltwater intrusion into the coastal aquifer leading to increase in the concentration of some ions, particularly chloride and magnesium, at the deeper depth.

Majority of the dissolved constituents found in the groundwater are as a result of weathering of minerals from the host rock. The sources of some of the constituents may be linked to the effluent water discharge, decay of organic matter, agricultural practices, as well as oil spillage.

Cluster analysis confirmed the existence of four types of water quality: low, medium high and very high polluted surface and groundwater. From factor analysis, the overall hydrochemical characters of the samples from surface and groundwater does not show evidence of mixing but are affected by cation exchange processes. Some of the groundwater is of good quality based on their physical chemical properties. Therefore, they are good for domestic purposes but those that are contaminated should be discarded or treated before use.

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