Mining Activities and Its Hydrogeochemical Implication: A Case Study of Ijero Mining Site Southwestern Nigeria.

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ABSTRACT

This study is aimed at assessing the hydrochemical implications of mining activities on the quality of the groundwater resources in Kusa Mining Hill, Ijero Ekiti in Ekiti State, Nigeria. Water samples were taken from five mining pits within the mining site. Physicochemical parameters examined were pH, electrical conductivity, total dissolved solids (TDS), dissolved oxygen (DO), etc. The results indicate Mg>Ca>Na>K. Chloride is the dominant anions among bicarbonate, sulphate and nitrate. Heavy metals which include Copper, Zinc and Iron were present at a trace level. Results show that the water were within the standards approved by WHO and NAFDAC which makes the water accepted for domestic, agricultural and industrial use, although bacteriological analysis and treatment may be required to remove odor and color. The research highlights the danger associated with unregulated mining act and related diseases that accompany this practice.

(Keywords: physicochemical, hydrochemical, electrical conductivity, mining activities, bacteriological analysis, Ijero-Ekiti)

INTRODUCTION

Mineral resources are the major sources of raw materials in several manufacturing industries all over the world such as tin smelting, glass, chalk, fertilizer, iron and steel, cosmetics and construction to mention a few. The Nigerian government through the geological survey of Nigeria has played an active role in the exploration for these mineral deposits, which dates back to 80 years. An important parameter in determining the importance of mineral resources in Nigeria economic and nation development is the usefulness of these minerals in the manufacturing industry and their place in international trade. The degree of industrialization of a nation is directly related to the level of utilization of its mineral resources. Fortunately, the Nigeria government has recently focused its attention on the development of solid mineral, whose production has been declining over the years.

Mining is an integrated, multiphase activity involving geological reconnaissance, prospecting, exploration, extraction, processing and mine closure (Oladele, 2003). Mining activities provide employment opportunities, infrastructures and raw materials for local industries and for exports. However the industry is characterized by high visible environmental problems, including noise and vibrations, water and air pollution, destruction of terrestrial and wildlife habitat, encroachment on archaeological and historical resources as well as cultural and recreational sites. Hence, this study is focused in assessing the implications (if any) that mining activities will have on the groundwater within the study area.

GEOLOGY OF THE STUDY AREA

Ijero-Ekiti area which is located around the eastern margin of Ife-Ilesha Schist belt, underlain by Precambrian Basement Complex rocks. It is characterized by the abundance of pegmatite (Figure 2) which harbors minerals such as gem-stones and rare earth metals as well as metallic-ores such as lepidolite among other minerals (Olusiji, 2011). Ijero is situated in southwestern Nigeria between longitudes 5^0 03^1 to 5^0 07^1 E of the Greenwich Meridian and Latitude 7^0 45^1 to 7^0 49^1 N of the equator (UNAD, 2009). Other towns around the study area include Aramoko, Ikoro, Aiyegunle, Ipoti, and Oke-Asa, with Aiyegunle in the Northeast, Ikoro in the Northwest and Oke-Asa in the Southwest. The study area can be rated moderately accessible due to the road network systems which include the major and minor roads and also footpaths which link the study area.

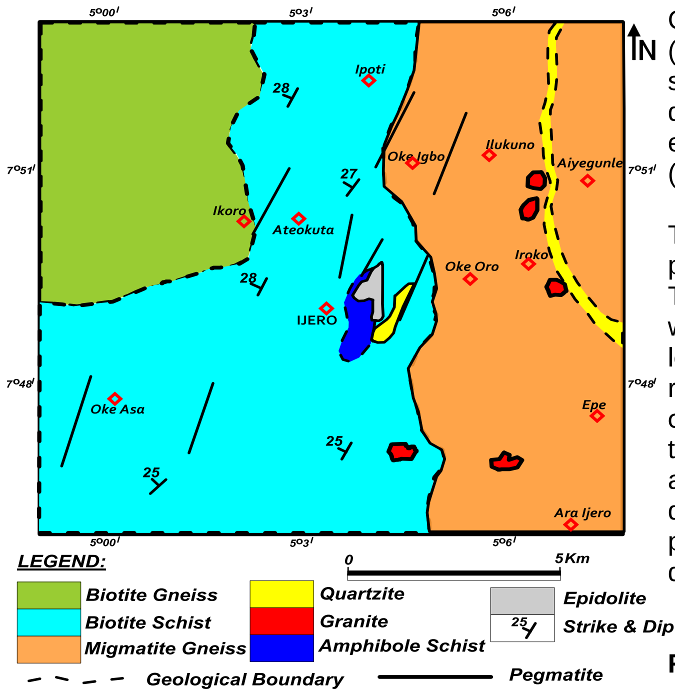

Figure 1: Geological Map of Ijero Local Govt. area of Ekiti State.

The study area is characterized by rock types such as pegmatites, biotite gneisses, quartzites, migmatite gneisses. The pegmatite's intruded the biotite gneiss and migmatite gneiss that occupies the central part of the study area, covering about three-quarter of the total landmass. The pegmatites are very coarse-grained with Phenocrysts. The biotite- gneisses are highly foliated with alternating bands of black tints imposed by biotite impregnations, alongside felsic minerals such as quartz and feldspar. The quartzites in the study area are the massive and schistose types with some impregnations of smoky quartz and mica. The migmatite-gneiss is the oldest of the rock types in these areas. It is not widely distributed in the study area compared to the pegmatites, and it is characterized mostly by alternating light and dark color bands.

MATERIALS AND METHODS

For this study physical and chemical parameters responsible for determining the effects (if any) of the mining activities on the subsurface water were measured and interpreted to establish the quality of water within the study area. Groundwater samples were collected from five (5) mining pits at different locations within the study area at the peak of dry season to prevent dilution effect of precipitation and contamination effects associated with storm water runoff (Thomson, 1996).

The samples were collected with five (5) new plastic bottles and labelled L1, L2, L3, L4 and L5. The location and elevation of sampling points were measured with a GPS and depth to water level was measured at each location and recorded. Nitric acid (HNO_3) was added to the cation's bottle to prevent metals from adhering to the walls of the bottles before further laboratory analysis. The groundwater sampling followed the description of (APHA, 1995). The other untreated pair of samples was used for anion determination.

RESULTS AND DISCUSSIONS

<u>Physiochemical Parameters and Measurement</u>

The physiochemical analyses carried out on the samples are shown in Table 1 below. The last three Parameters i.e. Electrical Conductivity (EC), Hardness and Sodium Absorption Ratio (SAR), were carried out for consistency of result and to ascertain the true characteristics of the water from different points.

The results shows that pH values for groundwater within the study area ranges from 6.06 - 6.97 which falls within 2006 WHO maximum standards in Table 4. Temperature values for the five locations are the same at 28.5^{o}C, the standard value for groundwater temperature is about 28 degree. Electrical conductivity of all sampled locations is between ranges of 40 - 560 µs/cm which is below the maximum WHO value.

Table 1: Physical Parameters Measured.

PARAMETER	L1	L2	L3	L4	L5
PH	6.82	6.87	6.97	6.06	6.07
Turbidity (NTU)	2.7	12.9	14.5	2.31	0.93
Temperature (^{0}C)	28.5	28.5	28.5	28.5	28.5
Electrical Conductivity (EC) (µs/cm)	130	110	40	240	560
Hardness (Mg and Ca) (mg/L)	0.13	0.13	0.12	0.15	0.14
Total Hardness	0.13	0.13	0.12	0.15	0.14
Total Dissolved Solids (TDS)	0.32	0.41	0.45	0.43	0.4
Total Suspended Solids (TSS)	5.97	4.78	4.57	4.76	4.7
Total Solid	6.29	5.14	5.34	5.19	5.1
Dissolved Oxygen (DO) (mg/L)	32	30	28	29	31
Biological Oxygen Demand (BOD) (mg/L)	68	48	43	48	46

The color, electrical conductivity and total dissolved solids in the groundwater are within maximum acceptable and maximum allowable concentrations of WHO standards for drinking water. This implies that based on physical parameters alone, the groundwater is potable, although filtration and chlorination might be required to remove the color and taste from the water. The results obtained from water analysis using the various physical and chemical parameters are presented in Table 1 and 3. These results were compared with the World health Organization (2006) standard in Table 4.

Hydrochemical Analysis

Groundwater interacts with its surrounding and this influences its hydrochemistry. The mobility of water makes it an excellent exploration tool. As water moves through weathered bedrock, major changes occur in its chemical composition. However, direct effects of rock weathering and metal mobility are usually reflected on the composition of soils and surface water (Taylor and Eggleton, 2001). Depending on the climatic condition such effects can easily extend to the groundwater systems through leaching by percolating/recharging water (Tijani et. al., 2006). The results in Table 3 below gives a list of elements, metals and ions present in the analyzed water samples in mg/L.

Some Elements and Trace Metals detected in water analyzed are Calcium (Ca), Magnesium (Mg), Sodium (Na), potassium (K), Copper (Cu), Iron (Fe) and Zinc (Zn). No Lead and Mercury were detected in all water samples, which show that the water is virtually free from industrial waste.

Calcium hardness, magnesium hardness, (Ca and Mg) in all the water analyzed was within the limits allowable by 2006 WHO standard for potable water. Na and K concentrations were within the ranges recommended by WHO for potable water (Table 4). Fe was detected at relatively moderate values for all locations, ranging from 0.12 - 0.31 mg/L. The recommended WHO value is between 1 – 3 mg/L, which implies that the groundwater of that area is relatively free from dissolved iron concentration.

From Table 4, Magnesium (Mg) has the highest concentration in the groundwater of this area, followed by Chlorides, Sulphates, Nitrates and Carbonates. Major Elements and Metals occur in minor concentrations. (Cu) content is very low in comparison to WHO standards, which is very good. The average Zinc (Zn) concentration of the water is higher than that of the WHO minimum requirements; this is probably due to disposal of industrial waste into groundwater and the activities at the site.

Table 2: Water Classification based on TDS and Hardness (After Todd, 1980).

TDS (mg/L)	Class	Hardness (mg/L)	Class
<1,000	Fresh	0 – 60	Soft
1,000 - 3,000	Slightly Saline	61 – 120	Moderately Hard
10,000 - 35,000	Very Saline	121 – 180	Hard
>35,000	Brine	>180	Very Hard

Table 3: Showing list of Elements, Metals and Ions Present in the Analyzed Water Samples in mg/L.

PARAMETER	L1	L2	L3	L4	L5
Chloride (mg/L)	58	53	72	62	60
Sulphate (SO_4) (mg/L)	54.4	54.8	57.54	55.51	54.6
Phosphate (mg/L)	11.5	12.62	20.4	16.85	14.5
Nitrate (NO_3) (mg/L)	40.12	41.28	41.26	41.26	40.3
Zinc (Zn) (mg/L)	0.895	0.142	0.165	0.268	0.426
Iron (Fe) (mg/L)	0.31	0.27	0.2	0.24	0.12
Copper (Cu) (mg/L)	0.612	0.065	0.079	0.063	0.053
Potassium (k) (mg/)L	22.5	24.5	22.5	20.4	23.9
Magnesium (Mg) (mg/L)	92	86	91.01	97	85
Carbonate (CO_3) (mg/L)	32	31	30	34	36
Bicarbonate (HCO^{-3}) (mg/L)	24.3	26.2	20.1	24.8	24.5
Sodium (Na) (mg/L)	5	4	6	2	2
Calcium (Ca) (mg/L)	25	29	25	25.25	20.55
Lead (Pb) (mg/L)	NIL	NIL	NIL	NIL	NIL
Mercury (Hg) (mg/L)	NIL	NIL	NIL	NIL	NIL

Table 4: Descriptive Statistics of Groundwater Quality according to WHO 2006.

PARAMETER	MIN	MEAN	MAX	WHO Standard
pH	6.06	6.52	6.97	6.5 - 8.5
Turbidity (NTU)	0.93	7.715	14.5	5.0
Temperature (^{0}C)	28.5	28.5	28.5	28
Electrical Conductivity (EC) (µs/cm)	40	300	560	1000
Hardness (Mg and Ca) (mg/L)	0.12	0.135	0.15	0-75 (Soft)
Total Dissolved Solids (TDS)	0.4	0.425	0.45	500 – 1500
Chloride (Cl) (mg/L)	53	62.5	72	250
Sulphate (SO_4) (mg/L)	54.4	55.97	57.54	500
Nitrate (NO_3) (mg/L)	40.12	40.7	41.28	50
Calcium (Ca) (mg/L)	20.55	24.775	29	200
Copper (Cu) (mg/L)	0.053	0.066	0.079	2
Magnesium (Mg) (mg/L)	85	91	97	50 – 150
Potassium (k) (mg/L)	20.4	22.45	24.5	200
Iron (Fe) (mg/L)	0.12	0.215	0.31	1 - 3
Sodium (Na) (mg/L)	2	4	6	100 – 200
Zinc (Zn) (mg/L)	0.142	0.519	0.895	3

The low concentration of the major elements Fe, Zn Cu, Mg, K, Na, observed in the samples is attributed to the fact that the area is underlain by rocks that are low in olivine, pyroxene, amphibole and other minerals that bear the elements.

The five locations sampled contain alkalinity which is within the WHO standard for drinking water. Nitrate concentration values were within the standards of WHO 2003 for drinking water. Carbonate (CO_3) and Bicarbonate (HCO^{-3}) concentration values of the groundwater vary from 30 to 36 mg/L and 20.1 to 26.2 mg/L, respectively. SO_4 concentration value of the groundwater varies from 54.4 to 57.54 mg/L. These concentration levels are still lower than the maximum concentration acceptable for drinking water **(**Table 4). This implies that sulphate concentration in study area groundwater cannot be a threat to human health if consumed. All water samples in the area of study contained no detectable level of PO_4^{3-} or PO_4^{2-}.

Piper and Schoeller Diagrams

The chemical affinity of water is expressed as its chemical facies. Piper's trilinear diagram (Piper, 1944) and Schoeller graph (Hemm, 1985) of the chemical analysis of the water showing their ionic characteristics was made in milliequivalent per litre (meq/l) and from the plot we could decipher our dominant cations and anions to know the water type in the study area.

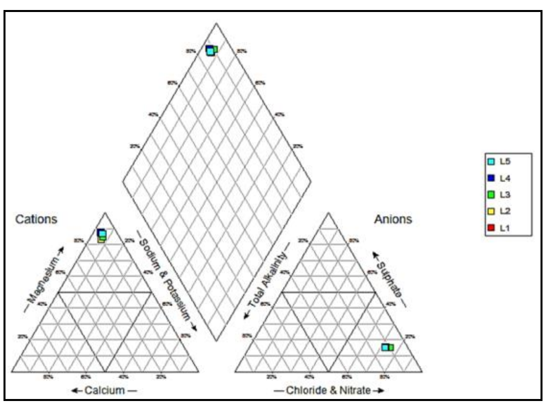

Figure 2: Trilinear (Piper) Diagram plot of the Chemical Data showing different Hydrochemical species in the Study Area.

The low presence of heavy metallic ions is attributed to little or no effect of distributed industries of variable categories in the area. Hydrochemically, high values of Mg^{2+} and NO_3^- are present in virtually all the available water samples observed. The results of piper diagram (Figure 2) indicate that the water samples (and hence the water sources) are dominated by Mg^{2+}, NO_3^- , SO_4^{2-}, Carbonates and Bi-carbonates. Chemical data of representative samples from the study area presented by plotting them on a Piper trilinear diagram (Figure 2) reveal the following water types in the study area; Mg-Na-K-Ca, Cl-NO_3-SO_4 and K-CO_3-HCO_3.

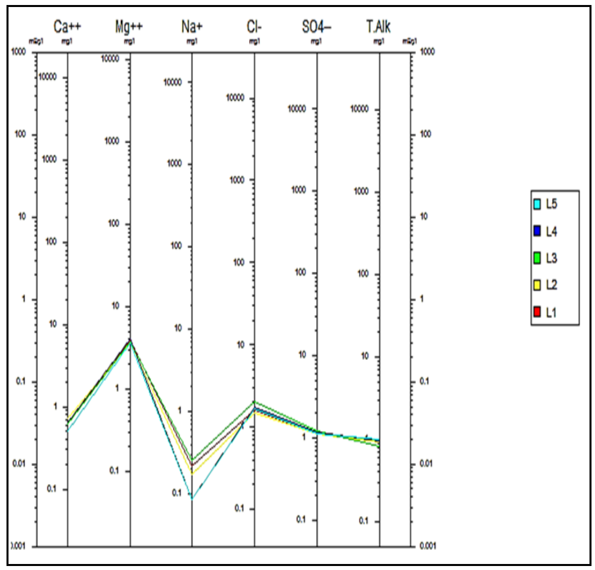

Figure 3: Schoeller Diagrams showing the Hydrochemical Composition Flow Paths for the Ions Present in Water.

The Scheoller diagrams (Figure 3) shows, a decreasing flow path in the Na^+ and SO_4^{2-} ion present in all the water samples, with Na^+ relatively having least concentrations of ions composition of the water. There is an increasing flow in the Mg^{2+} and Cl^- present in the water. This implies that the major ions present in the water are the Mg^{2+} and Cl^- hence the dominant water type. Thus, the various hydrochemical species that can be observed include the following: Mg-Na-K-Ca, Cl-NO_3-SO_4, K-CO_3-HCO_3, and Mg - Cl - SO_4 - NO_3 - CO_3-HCO_3 – Ca.

Durov and Expanded Durov Diagrams

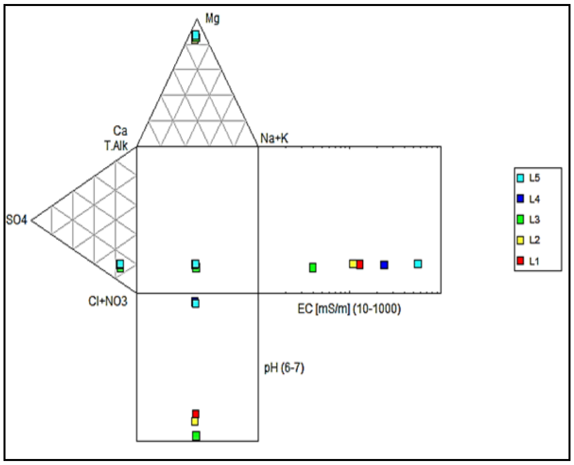

Figure 4: Durov Diagram of Ionic Species in Water Samples.

The Durov diagram (Figure 4) gives a pictorial description and plot of the anions, cations, pH and electrical conductivity of the water samples. It clarifies their relationship and presents a more simplified study of the water physical and chemical representation of the analyzed water samples. According to the Durov diagram, all water samples have high magnesium (Mg) values, they have relatively moderate Cl and NO_3 values with minimal values of Na and T. Alkaline and they also have pH values ranging between 6 - 7.

The electrical conductivity (EC) values range between 40 - 560 µs/m, which is below the desirable value according to WHO 2006 guidelines (1000 µs/cm). L1 has an EC value of 130 µs/cm, L2; 110 µs/cm, L3; 40 µs/cm, L4; 240 µs/cm and L5; 560 µs/cm. L3 has the lowest EC value while L5 has the highest.

The Expanded Durov gives a broader range of values for the ionic species and elemental composition of the water samples.

According to the expanded Durov diagram (Figure 5), it indicates the dominance of magnesium (Mg) in all water samples, and relatively moderate Cl and NO_3 values with minimal values of Na and T.Alkaline.

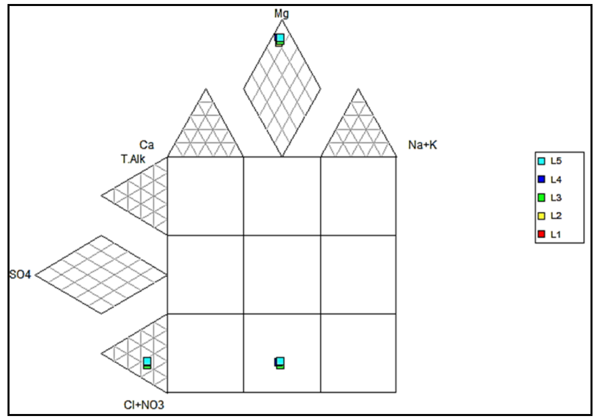

Figure 5: Expanded Durov Diagram of Ionic Species in Water Samples.

Stiff Diagrams

The stiff diagrams (Figure 6) show the proportion of each ion in the groundwater sample of the different locations. The Anions to the left of the plot and the cations are plotted to the right. All water samples show a high value of the Mg and $Cl^{+}NO_3$ specie. This could be probably due to increase in Mg from overlying rocks and Nitrate discharge into the groundwater source of the area from refuse dump sites and probably from the mining site. Ca shows a relatively low value and T.Alkaline is least present.

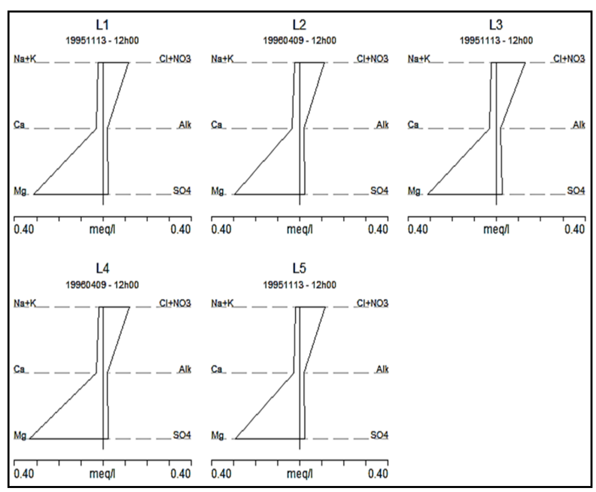

Figure 6: STIFF Diagrams for Hydrochemical Analysis of Water.

It was observed and suggested that mineral, elemental, metallic and ionic content of the analyzed water samples are majorly derived from geogenic factors (geology, topography, weather (climate) and rock influence on water chemistry) rather than anthropogenic (human, societal, industrial) influence. Groundwater interaction with the environment is the major influences of the hydrochemistry in this area.

Electrical Conductivity Plot

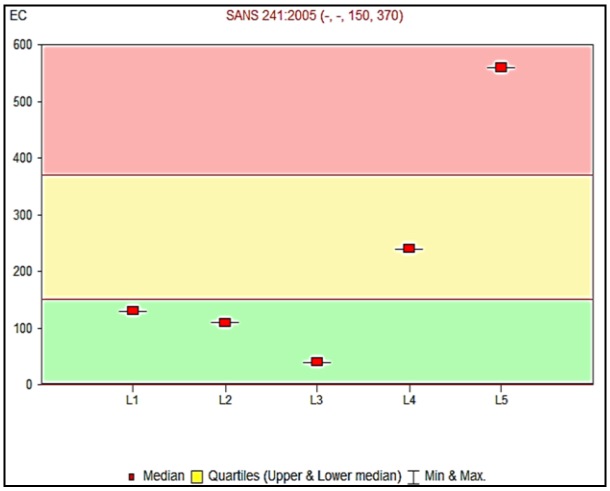

Figure 7: Electrical Conductivity Plot of the Water Sample.

The electrical conductivity plot (Figure 7) shows the rate of conduction of electricity of each samples analyzed from the five locations. Conductivity is plotted on the vertical axis against the locations on the horizontal axis.

Electrical Conductivity (EC) of the water sampled gives a range of between 40 and 560 µs/cm which is below the 2006 WHO desired conductivity of 1000 µs/cm. L1 has an EC value of 130 µs/cm, L2; 110 µs/cm, L3; 40 µs/cm, L4; 240 µs/cm and L5; 560 µs/cm. L3 has the lowest EC value while L5 has highest. Therefore implies that the water in this area is of low conductivity and contains little impurities in terms of dissolved metals and heavy elements.

Water Quality

The chemical character of any water determines its quality and usability. The quality is a function of the physical, chemical and biological parameters and could be subjective since it depends on a particular intended use (Tijani, 1994). The water quality indices evaluated from the data include, Sodium Absorption Ratio (SAR), and Total Hardness (TH).

Wilcox (SAR and Salinity Hazard) Diagram

The Wilcox diagram (Figure 8) shows values for both the Sodium Absorption Ratio (SAR) and salinity hazards. It is used to assess the suitability of water for irrigation purpose. The values for the Sodium Absorption Ratio (SAR) is relatively low (0 - 10), indicating abundant water for agriculture, if sodium is too much the water is not suitable for irrigation.

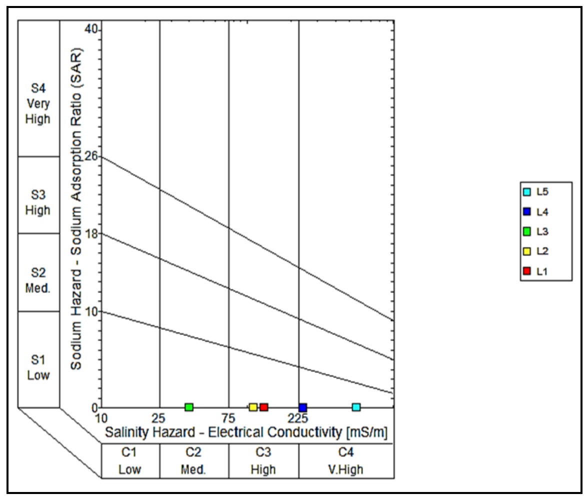

Figure 8: Wilcox Diagram of Water Parameters.

However, continual introduction of wastes emanating from different industrial resources development into the environment has great potentials to increase environmental toxicity, especially in the areas of water resources which could result to increase in the salinity hazards of the water and the adverse consequences of such wastes on crop-yielding potentials from groundwater need not be ignored.

From the SAR plot of the Wilcox diagram and according to classification made by Mandel and Shiftan 1991, based on SAR the water class is rated excellent for irrigation purpose and other domestic uses, although not so ideal for direct consumption.

Table 5: Classification of Water Based on SAR (After Mandel and Shiftan, 1991).

SAR (%)	WATER CLASS
<10	Excellent
10 – 18	Good
19 – 26	Fair
>26	Poor

Table 6: Hardness Classification according to Sawyer and McCarty, 1967.

INDEX RANGE	DESCRIPTION
>180	Very hard
120-180	Hard
60-120	Moderately Hard
<60	Soft

Water quality requirements for different purpose differ; hence standards have been developed to appraise water usability for the various purposes. Water is used predominantly for domestic, agricultural and industrial purposes; hence water quality in the study area is evaluated in terms of domestic, agricultural and industrial usage.

CONCLUSION

Magnesium ions were observed in highest proportion in the water samples. The concentration ranges from 85 mg/L to 97 mg/L. Magnesium may be derived from minerals like; olivine, biotite, hornblende, serpentine, talc and tremolite. Ca and Mg have higher values in the mafic rock; this could be attributed to the high amount of Mg and Ca in mafic minerals. Calcium may be derived from minerals, like amphibole, pyroxene and feldspar in the rocks. Metasedimentary rocks have the lowest value of Ca.

Potassium ions values that may be from feldspars (orthoclase and microcline) and some mica were observed to increase with magnesium ion values. Sodium does not occur as an essential constituent of many of the principal rock-forming minerals, plagioclase feldspar being an exception. Sodium ions were relatively low in the observed water samples.

The criteria for water portability are defined by Davies and DeWeist (1966) to include the absence of objectionable tastes, odors, color and substances of adverse health effects. A quantitative measure of these criteria is stipulated by WHO (2006). A comparison of the ionic and physical components of groundwater within Oke-Kusa area of Ijero-Ekiti with these standards shows that the water is accepted for domestic use. However, bacteriological analysis is still needed. The total hardness of the samples ranges within soft (< 60), this make the water suitable for laundry purposes. The pH of the water samples reveal very slightly acidic to neutral. Although the groundwater is portable, filtration, chlorination and perhaps boiling might be required to remove the color, slight taste from the water and turbidity of the water.

Water finds use in agriculture in two major ways; namely, livestock feeding and plant irrigation. The criteria for evaluation of water quality for agricultural use include; SAR (Salinity Hazard) and TDS**.** SAR is used to identity water suitable for irrigation, if sodium is too much the water is not suitable for irrigation. SAR values for all the water samples are very low and mostly at 0 level. According to Mandel and Shiftan (1981) water containing SAR 0 - 10 is applicable on all agricultural soils, while the water having SAR range of 18 - 26 may produce harmful effect, therefore good soil management is essential. Sodium Adsorption Ratio (SAR) ranges of 26 - 100 is unsuitable for irrigation purposes. Based on the above standards the waters from the study area can be utilized on all agricultural soils. The salinity hazard also expressed as electricity conductivity (EC) and total dissolved solids (TDS) is also considered in evaluation of water quality for irrigational practices.

The TDS is a major factor for determining the suitability of water for livestock farming. Based on the criteria of Jewell (1927) and Barber (1965) water with TDS of 0 - 300 ppm is suitable for all stock, while water with TDS of 3000 – 7000 ppm is suitable for sheep and grazing cattle in emergency cases. The above criteria indicate that the water from the study area is suitable for all stock as far as TDS is concerned.

In considering, the industrial use of the water parameters such as taste, odor, TDS, pH, total hardness (TH), iron and chloride. Water for industries should be odorless, colorless, and free from suspended matter, microorganisms and of low iron and manganese content. The quality guideline for industrial waters is given by American Water Works Association (1971). These include for most industries; taste and odor (none-low), TDS (50 - 1500 mg/L), total hardness (0 - 250 mg/L), pH (6.5 - 8.3), chlorides (20 - 250 mg/L), iron (0.1 - 1.0 mg/L) and manganese (0 - 0.5 mg/L). A comparison of the results as shown in Table 4 with the quality guidelines shows that groundwater in the study area would be suitable for use in most industries.

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