TRACE ELEMENT ASSESSMENT OF ELEYELE UP STREAM LAKE, IBADAN, SOUTHWESTERN NIGERIA

ABSTRACT: This research work was carried out to assess the concentrations of selected trace elements in Eleyele upstream lake, Ibadan, South-Western, Nigeria. Nine water samples and eight sediment samples were analyzed for their physiochemical and trace element properties to quantify pollution of the lake by trace elements employing geochemical analytic tools such as ICP-MS, XRD, and XRF. The chemical index of alteration (C.I.A.) shows an average value of 75.21, 89.64, and 82.39, respectively, which shows zero to low affinity or similarities between C.I.A and the trace elements. The Chemical Index of weathering (CIW) value shows that the trace elements sources are related to the basement rock's chemical weathering. Plagioclase Index of Alteration (P.I.A.) shows that there are low to no similarities indicating the source of the selected trace element is not clay. The trace elements analyzed are As, Ca, Cd, Co, Ce, Cu, Ga, K, Li, Mo, Na, Ni, Sb and Zr. As, Ca, K, Na with a constant concentration of 0.5µg/l, 0.02µg/l, 0.1µg/l, and 0.2µg/l, respectively, Cd, Co, Ce, Cu, Ga, Li, Mo, Ni, Sb, and Zr have an average concentration value of 0.04µg/l, 0.67µg/l, 0.05µg/l, 1.01µg/l, 0.06µg/l, 0.72µg/l, 0.14µg/l, 0.79µg/l, 0.05µg/l and 0.03µg/l, respectively. The result analyses show that Cu has the highest concentration in the water and the trace element ranges in abundant from Cu> Ni> Li> As> Co> Mo> Ga> Cd> Sb> Cs> Zr> Ca> Na> K. Constant work is recommended for Eleyele Lake to protect the lake from an increase in the level of contamination.

Keywords. ***X- Ray Diffraction; X- Ray Fluorescence, Chemical Index of Alteration; Plagioclase Index of Alteration; Chemical Index of Weathering; Trace Elements***

1. Introduction

Water is essential to life. In the history of humanity, water has maintained its relevance. The quality of water lies in its ability to maintain optimum physical, chemical, and biological characteristics. Organisms, including humans, use water trace elements to live a healthy life. Trace elements assist in reducing the vitality of organisms. As a result of these characteristics, prominent trace elements such as As, Ag, and Cu, amongst others, are needed in considerable quantities for proper cell metabolism (Maune, 1973). However, trace elements may pose a significant threat to health. Essential trace elements are; Cu, Cr, Co, Fe, Mn, and Zn, some examples of non-essential trace elements, are As, Cd and Pb. The non-essential elements are more harmful to health as they induce some pathogens to cause deficiencies such as neurocognitive impairments, cardiovascular diseases, and cancer. Excess water consumption of significant trace elements may also be harmful (Calderon, 2000). Lakes with a high susceptibility to pollution and deterioration are located within the catchment region of artificial lakes. It is challenging for aquatic life to survive in artificial lakes because of the poor state of the water (Rosenberg et al., 2000). Most pollution in developed countries ends up in lakes because of the windward flow of water (Bernot & Dodds, 2005; Wetzel, 2001). Urban activities' Pollutants are increasingly affecting lakes' aquatic organisms (Magadza, 2003). An artificial lake, Eleyele lake serves both residential and commercial needs. Eleyele lake is located between the heavily populated and industrialized regions of Ibadan, Southwestern Nigeria (Olanrewaju et al., 2017).
Regulatory agencies built the dam to facilitate water distribution for household purposes (Akinyemi et al., 2014). Water quality in the lake is influenced by its many non-consumptive uses, including fishing, farming, religious activities, ceremonies, and irrigation (Olanrewaju et al., 2017). The lake has been contaminated by trace metals and some polychlorinated biphenyls, which originate from industrial and agricultural operations and are thought to contribute to health and environmental problems. (Dele & Daini, 2013). Thus, population increase and industrialization have significantly impacted the geochemistry of Eleyele lake's water. Heavy and trace metals, which are dangerous to human consumption, have increased in pollution due to the flood connected with Eleyele lake. Polychlorinated biphenyls in the catchment region are mainly deposited due to human activity. As Adeogun et al. (2016) point out, during the wet season in Ibadan city, torrential downpours wash metal pollutants from the streets and into the lake. Toxicity from hazardous substances in urban lakes and its consequences for aquatic life has been the subject of recent studies (Viera et al., 2011). It has been discovered that the accumulation of metallic elements has a cumulative effect on the organs of animals and humans, with various effects depending on the species and the level of exposure (Gaspi et al., 2011). The major element in the lake was investigated by Akinyemi et al. (2014), who elucidated its physicochemical properties. Although there are minor variances, Akinyemi et al. 2014 found that overall, the levels of the lakes' principal constituents are within WHO guidelines (Akinyemi et al., 2014).

Many studies have focused on the lake's abundance of metals and other vital elements. Domestic solid, liquid, and gaseous waste is the leading cause of pollution in Eleyele lake (Nriagu and Pacyna, 1998). Since sediment is a byproduct of sinks and can dissolve to impact water quality, sediment samples are crucial. This means that the sediment samples from Eleyele lake are essential for studying the trace elements there. Most research works on Eleyele lake are on the effects of heavy metals and elements on the water quality. There is a research gap as regards the trace elements constituents of the water and how it affects the water quality of Eleyele lake. Therefore, there is a need for detailed research work on the effects of trace elements in Eleyele lake, analyzing sediment and water samples taken from the catchment areas of the lake to determine the suitability of the water for domestic uses

This research work serves as a pedestal to further trace element investigation of the studied lake. This research aims to probe how some trace elements are distributed in the Eleyele upstream lake in Ibadan, South Western Nigeria, to predict the quality of the water and its suitability for domestic industrial by the analysis of both sediments and water samples are taken, as shown in figure 1

1. Location of The Study Area

Eleyele dam is located in the North-Eastern part of Ibadan, southwestern Nigeria, within longitude E 003° 52' 37" and E 003° 64' 40" and latitude N 07° 25' 14" and N 07° 26' 40". The Eleyele Dam is situated in the city of Ibadan within Geographical Coordinates: Longitude E 003° 51' 06" and E003° 52' 48" and latitude N 07° 25' 10" and N 07° 26' 48.5" and it also comprises of areas such as Idi Osan, Oniyere, Apete, Obaido, Oteru, Alakuta, Oluseyi. The dam is an earth dam constructed along the Ona River at the Eleyele community in 1942 to supply raw water for treatment at the Eleyele (Tijani et al., 2004). Waterworks to provide potable water for the city of Ibadan and act as flood control during high flow periods through its reservoir holding capacity. The reservoir has a catchment area of about 323.8 km^2, an impoundment area of 156.2 hectares, and a storage capacity of 29.5 million liters of water. Eleyele catchment has mean and median elevations of 88.0m and 87.6m (amsl), respectively.

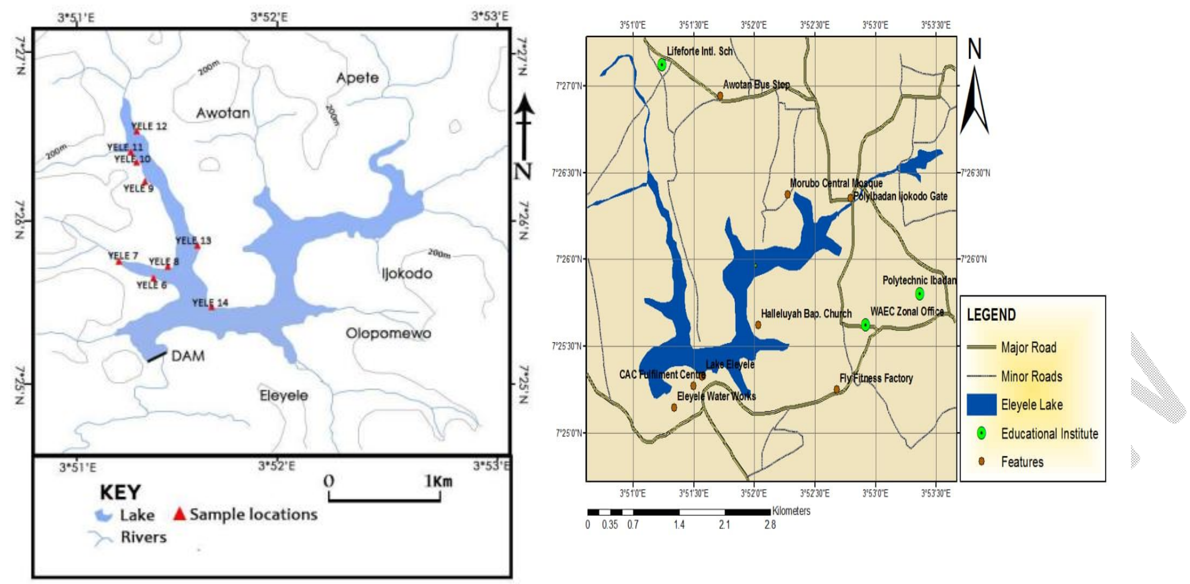

Fig 1: Map of the lake catchments showing sampling points.

2. Geology and Geomorphology of the Studied Area

Eleyele lake can be found in the Precambrian basement complex in southern Nigeria. Migamatites, Biotite Gneiss, and certain metasediment rocks like quartzite and schist make up the bulk of the local geology. Quartz schist, a kind of schist, is the most common type in the places that have been examined. Medium- to coarse-grained soil samples were discovered in the research region. The city of Ibadan is geographically distinguished by its undulating terrain, framed by the nearby Inselberg and quartzites (Tijani *et al.*, 2004). The catchment region for Eleyele Lake is split into the wet and dry seasons. The rainy season, with an annual average rainfall of 1250 mm, is from March to October, whereas the dry season, also known as the harmattan, is from November to February (Tijani *et al.*, 2004). Apete is bounded to the north by Eleyele lake, to the south by Olopemewa, and to the northwest by both Ijokodo and Awotan. The hydrogeomorphic units in the study region range from high to low. From Apete in the north, island peaks and granites may be seen to the southeast corner of Ijokodo, down through the middle of Olopemewa, and up into the northwest corner of Awotan. The highlands have porphyritic relief, meaning they are above 140 meters in elevation. Lowlands covered by amphibolites and gneiss dominate the southern portion of the plotted region. Like many lakes in southern Nigeria, Eleyele lake has a dendritic drainage system and gets water from the rivers Ona and Alapata. Eleyele is found to be on top of the topsoil, laterites, Sandy clay, and worn crystalline rocks, according to geophysical data gathered using vertical electronic sounding. Fracture, weathering of the foundation rocks, and the thickness of the overburden all have a role in groundwater availability. Hydrogeochemical analyses have shown that the mapped region is somewhat acidic, with a composition of sodium, calcium, potassium, and bio-carbonate ions (Ajibade and Ogungbesan, 2013).

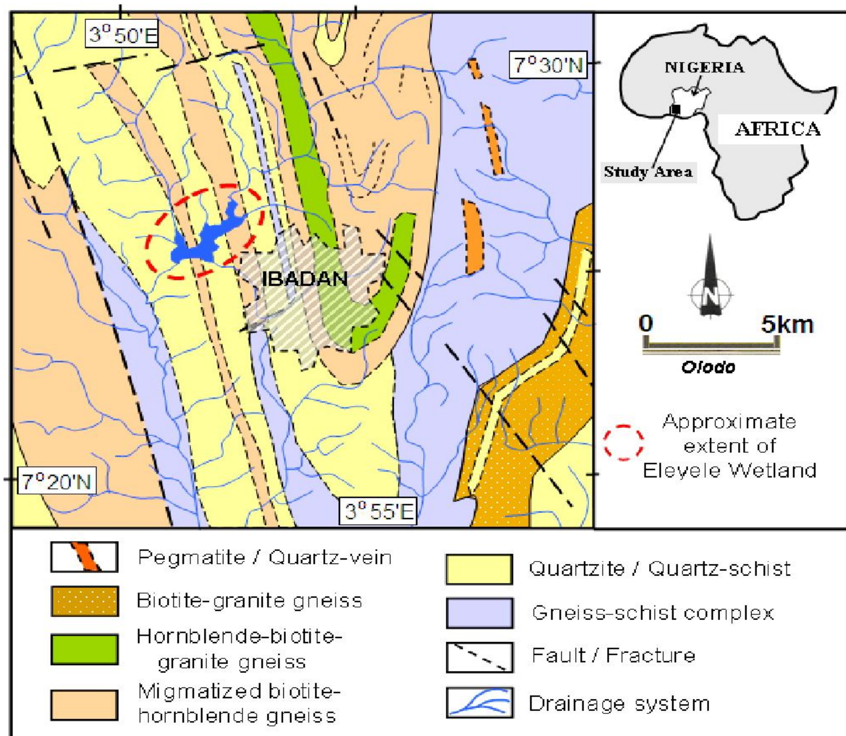

Figure 2.0 Geological map of Ibadan showing Eleyele wetland (Tijani *et al.*, 2012)

3. Methodology

The fieldwork was carried out at Eleyele, Ibadan, Oyo State, Southwestern Nigeria. Nine water samples and eight sediment samples were collected from the lake of the study area at different locations using a Geographic Positioning System (G.P.S.) to determine the position of different locations. A total of seventeen samples were collected from various parts of the lake. The Eleyele lake in Ibadan, southern Nigeria, has water and sediment samples taken from its catchment areas. The data was collected at the beginning, middle of the rainy season during a rain break, and end of the rainy season. In considering the expected drop in concentration and dilution rate, samples were taken in August, July, and November. It has been determined through regular lake monitoring that the lake's temperature remains stable throughout mine operations, hence preventing a possible temperature flip owing to elevated air pressure in the catchment regions (Akinyemi et al., 2014). Each sample was gathered from a depth of 1 meter using a 5-liter Ruttner sampler and then poured into a 500 ml sterile vial. The polyethylene bottles are stored until they are needed for laboratory testing. A Hanna portable meter and dissolved oxygen (D.O.) meter were used to test for total dissolved solids, pH, and turbidity.
Bottom sediments and water were collected in a polypropylene coring device measuring between 0.1 and 1 m in length and diameter to gather samples from the investigated region. The sediment samples were combined into one large sample and placed in a sealed, sterile plastic bag. In order to preserve the combined sediment samples for treatment trace elements analysis, they were stored in a refrigerator at 4 degrees before it was sent to ACME Laboratory, Vancouver, Canada, for trace element analysis using the ICP/MS method. Water sediments were analyzed at the civil engineering department of the University of Ilorin, Nigeria. The sediment was analyzed for grain size analysis. The sieve method was used to analyze the sediments. The sediments were thoroughly dried in the oven, after which they were pulverized using a mortal and pestle. The samples were then weighed before being sieved. Grain size analysis enables the statistical calculation of the sediments' mean, sorting, skewness and kurtosis following the standard (Folk and Ward, 1957).

During the mapping, the sampling was carried out during the dry season. Some physical parameters of water were determined, such as Total Dissolved Solids (T.D.S.) using the T.D.S. meter, Electrical Conductivity (E.C.) using the E.C. meter, alkalinity and Acidity of water using the P.H. meter, water temperature, and environmental temperature. Concentrated Nitric Acid (HNO_3) was added to the samples for cations to prevent cations' precipitations in the water sample before the water samples were analyzed for the various cations in ACME laboratory, Canada using ICP/MS method. They were then treated, packaged and stored before being sent to the laboratory for hydrochemical analysis. Laboratory analysis was done for X-ray Fluorescence and Diffraction analysis of sediment samples and determination of trace elements in water by Inductively Coupled Plasma-Mass Spectrometry.

4. Sediment Sample Discussion

The sediment samples were analyzed for their grain sizes, weathering indices, and trace elements using mesh, X-ray fluorescence, and X-ray diffraction analysis. Eight sediment samples from Eleyele upstream lake were used in this analysis. The cumulative weight percentage curves were prepared from the data obtained from the grain size analysis. From this curve, the phi ϕ values of the necessary percentile and quartiles such as ϕ5, ϕ16, ϕ25, ϕ50, ϕ64, ϕ75, ϕ84, and ϕ95 were obtained, and the quantitative graphical values were tabulated for each of the samples analyzed (Table 4 and 5). The corresponding graphic mean, sorting, skewness and kurtosis were calculated by Folk and Ward (1957). The corresponding mean, sorting, skewness, and kurtosis value for the sediment samples in the study area were computed in table 1 and interpreted in table 4. Table 5 shows that most of the sediment samples in the study area (Eleyele upstream lake) are coarse and poorly sorted, indicating that the source of deposition to the lake is close and there is high transportation energy in transporting coarse sediments. The poorly coarse sediment samples in the study area are positively or thinly distributed in 18YELE 8 and 18YELE 14, negatively or widely distributed in 18YELE 7, and are usually distributed in other samples.

5.1 Mean Size

Mean represents the average size of the total distribution of sediments. It serves as an indexto measure the nature as well as the depositional environment of the sediments. It is the function of the total amount of sediments available, the amount of energy imported to the sediments, and the transporting agent's nature. The most inclusive graphically derived value is that given by Folk (1968):

$$Mz = \frac{\varphi16 + \varphi50 + \varphi84}{3}$$

Where φ_{16} represents the size at 16% of the sample by weightΦ50
represents the size at 50% of the sample by weight
Φ84 represents the size at 84% of the sample by weight.

Mean is also measured in phi units and is the most widely compared parameter

5.2 Sorting

Sorting is the degree of uniformity of grain size. The degree of sorting depends upon howmuch transport the sediment has undergone. The sorting can be quantified using the Inclusive Graphic Standard Deviation. Folk (1968) introduced the "inclusive graphic standard deviation", which is calculated as follows:

$$\sigma i = \frac{\varphi84 - \varphi16}{4} + \frac{\varphi95 - \varphi5}{6.6}$$

Table 1 Classification Scale for sorting (Folk, 1968)

Values from	To	Equal
0.00	0.35 φ	Very well sorted
0.35	0.50 φ	Well sorted
0.50	0.71 φ	Moderately well sorted
0.71	1.00 φ	Moderately sorted
1.00	2.00 φ	Poorly sorted
2.00	4.00 φ	Very poorly sorted
4.00	Φ	Extremely poorly sorted

5.3 Skewness

Skewness measures the degree to which a cumulative curve approaches symmetry. Two samples may have the same average grain size and sorting but differ in their degrees of symmetry. Folk's "inclusive graphic skewness" (1968) is determined by the equation:

$$Ski = \frac{\varphi 16+\varphi 64-2\varphi 50}{2(\varphi 84+\varphi 16)} + \frac{\varphi 5+\varphi 95-2\varphi 50}{2(\varphi 95-\varphi 5)}$$

Where the phi values represent the exact percentages as those used for sorting, this formula includes a measure of the "tails" of the cumulative curve and the central portion.

Table 2: Classification scale for skewed (Folk 1968)

Values from	To	Mathematically	Graphically skewed to the phi value:
+1.00	+0.30	Strongly positive skewed	Very negative phi value, coarse
+0.30	+0.10	Positive skewed	Negative phi value
+0.10	-0.10	Near symmetrical	Symmetrical
-0.10	-0.30	Negative skewed	Positive phi value
-0.30	+1.0	Strongly negative skewed	Very positive phi value, fine

5.4 Kurtosis

Kurtosis is a measure of "peakness" in a curve. Folk's (1968) formula for kurtosis is:

$$KG = \frac{\varphi 95 - \varphi 5}{2.44(\varphi 75-\varphi 25)}$$

Where the phi values represent the exact percentages used for sorting, a standard Gaussian distribution has a kurtosis of 1.00, a curve with the sorting in the tails equal to the sorting in the central portion. If a sample curve is better sorted in the central part than in the tails, the curve is said to be excessively peaked or leptokurtic, but if the sample curve is better sorted in the tails than in the central portion, the curve is flat peaked or platykurtic. For standard curves = 1.00, leptokurtic curves have >1.00, and platykurtic curves have < 1.00.

Table 3: Classification Scale Value for Kurtosis (Folk 1968)

Values from	**To**	**Equal**
0.41	0.67	Very platykurtic
0.67	0.90	Platykurtic
0.90	1.10	Mesokurtic
1.10	1.50	Leptokurtic
1.50	3.00	Very leptokurtic
3.00		Extremely leptokurtic

Table 4: Statistical analysis of grain size in Eleyele upstream lake

Sample no.	**Mean ($M_{Z.}$)**	**Sorting (Ơi)**	**Skewness (Ski)**	**Kurtosis ($K_{G.}$)**
18YELE 6	0.97	1.72	-0.94	0.92
18YELE 7	0.80	2.48	-0.10	0.59
18YELE 8	0.67	1.57	-0.12	1.11
18YELE 9	1.23	1.40	-0.16	1.09
18YELE 10	1.23	1.58	-0.35	1.09
18YELE 11	1.67	1.37	-0.35	0.96
18YELE 13	0.50	1.77	-0.45	0.92
18YELE 14	0.47	1.68	-0.81	1.13

Table 5: Statistical analysis interpretation of grain size in Eleyele upstream lake

Sample no.	**Mean ($M_{.Z.}$)**	**Sorting (Ơi)**	**Skewness (Ski)**	**Kurtosis ($K_{.G.}$)**
18YELE 6	Coarse sand	Poorly sorted	Strongly coarse skewed	Mesokurtic
18YELE 7	Coarse sand	Very poorly sorted	Negative coarse skewed	Platykurtic
18YELE 8	Coarse sand	Poorly sorted	Negative coarse skewed	Leptokurtic
18YELE 9	Medium sand	Poorly sorted	Negative coarse skewed	Mesokurtic
18YELE 10	Medium sand	Poorly sorted	Strongly coarse skewed	Mesokurtic
18YELE 11	Medium sand	Poorly sorted	Strongly coarse skewed	Mesokurtic
18YELE 13	Coarse sand	Poorly sorted	Strongly coarse skewed	Mesokurtic
18YELE 14	Coarse sand	Poorly sorted	Strongly coarse skewed	Leptokurtic

5.5 Weathering Indication

Chemical and/or physical/mechanical activities may disintegrate a whole body of rock into sediment particles (rock fragments, soils, etc). The sedimentdistribution, presence of feldspathic soils and geometric orientation of sediments are high indicators of weathering activities. In the process of weathering, sediments are associated with elements other than the rock's original constituent, which alter (chemically) the original composition. These elements are said to be sourced from anthropogenic source (Nesbitt and Young, 1982). For this study, the chemical index of weathering (CIW), chemical index of alteration (C.I.A.) and the plagioclase index of alteration (P.I.A.) are the indices used in this study.

5.5.1 Chemical Index of Alteration

C.I.A. is the measure of the extent of conversion of feldspars (which dominate the upper crust) to clays such as Kaolinite (Nesbit and young 1984, 1989; Fedo et al., 1995). In this study, CaO was corrected with the subsequent methodology proposed by McLennan et al., (1993), in which CaO values are accepted only if $CaO<Na_2O$ and when $CaO>Na_2O$, it is assumed that the concentration of CaO equals that of Na_2O. High C.I.A. values reflect the removal of mobile or stable cations (Ca, Na, K) relative to highly immobile or stable residual constituents (Al, Ti) during weathering (Nesbitt and Young, 1982). Conversely, low C.I.A. values near absence of chemical alteration and consequently may reflect cold and/or arid conditions (Nesbitt and Young, 1982, 1989). CIA= 5060 indicates an incipient weathering, C.I.A. = 60-80 an intermediate weathering and C.I.A.>80 extreme weathering (Nesbitt and Young, 1982).

The formula is given below:

$$C.I.A = \frac{Al_2O_3}{Al_2O_3+CaO*+Na_2O+K_2O}) * 100$$

Table 6: summary of the chemical index of alteration (after Nesbit and Young, 1982)

Index	Optimum fresh value	Optimum value weathered	Increase in weathering
C.I.A.	Less than or equal to 50%	100%	Positive

5.5.2 Chemical Index of Weathering

Harnois (1988) developed the chemical index of weathering (CIW). The index is identical to the C.I.A., except that it eliminates K_2O from the equation. The CIW does not account for aluminum associated with K-feldspar. It may yield very high for K- feldspar-rich rocks, whether chemically weathered or not (Fedo et al., 1995). Like C.I.A., the CIW is also essentially a measure of the extent of conversion of feldsparsto clays (Nesbit and young, 1984, 1989; Fedo et al., 1995).

The formula is given by: $C.I.W = \frac{Al_2O_3}{Al_2O_3+CaO*+Na_2O}) * 100$

Table7: Summary of the chemical index of weathering (after Harnois, 1988)

Index	Optimum fresh value	Optimum value weathered	Increase in weathering
CIW	Less than or equal to 50%	100%	Positive

5.5.3 Plagioclase Index of Alteration

Fedo *et al.,* (1995) proposed the plagioclase index of the alteration as an alternative to the chemical index of weathering because plagioclase is abundant in silicate rocks and dissolves relatively rapidly. The P.I.A. may be used when plagioclase needs to be monitored. High P.I.A. values (>84) would indicate intense chemical weathering, while lower values (~50) are characteristic of fresh rock samples.
The formula is given as

$$P.I.A = \frac{Al_2O_3 - K_2O}{Al_2O_3 + CaO* + Na_2O - K_2O}) *100$$

Table 8: summary of plagioclase index of alteration (Fedo et al., 1995)

Index	Optimum fresh value	Optimum value weathered	Increase in weathering
P.I.A.	Less than or equal to 50%	100%	Positive

The Chemical index of alteration (C.I.A.) computed value shows the minimum, maximum and average values of 75.21, 89.64, and 82.39, respectively. The Chemical index of alteration measures the chemical weathering of feldspar to clay minerals, which releases stable cations such as Ca, Na, and K related to stable residual constituents such as Al and Ti during weathering McLennanet al., (1993). The value of the C.I.A. is correlated with the concentration of selected trace elements to establish the similarities or affinity between the earlier mentioned stable cations released during chemical weathering and the trace elements of the study area (Nesbit and young 1984; Fedo et al., 1995). The correlation between them is shown in table 12. The correlation matrix between the C.I.A. and the trace elements shows no to low affinity or similarities between C.I.A. and the trace elements. The computed value of the Chemical Index of Weathering (CIW) was calculated as suggested by (Nesbit and young 1984, 1989; Fedo et al., 1995). The recorded values in table 9 show the minimum, maximum and average values of 87.02, 94.54, and 91.41, respectively. The result indicates moderately to chemically weathered sediment from the surrounding basement rock. The correlation of the CIW value with the selected trace elements shows that there are low similarities, which implies that the trace elements' sources are related to the basement rock's chemical weathering and anthropogenic sources.

The computed value of the Plagioclase Index of Alteration (P.I.A) was recorded in table 8, showing the minimum, maximum and average values of 84.62, 94.22, and 90.14, respectively. The result indicates moderate to chemical weathering of the basement rock. PIA is modified from CIA to monitor plagioclase. The chemical weathering of basement rock to plagioclase is being monitored by Fedo *et al.* (1995). The correlation matrix shows that there are low to no similarities indicating the source of the selected trace element is not clay.

Table 9: Shows average weathering indication parameters

Sample No	CIA	CIW	PIA
18 YELE 02	84.31	92.49	91.69
18 YELE 05	86.71	93.21	92.66
18 YELE 06	89.64	94.54	94.22
18 YELE 12	76.10	89.78	87.53
18 YELE F1	75.21	87.02	84.62
AVERAGE	82.39	91.41	90.14

The X-Ray diffraction (XRD) results of the studied samples as shown in figures 3.0 and 4.0. The corresponding major, minor and trace elements were identified. The major, minor, and trace minerals in 18YELE 06 sediment sample are quartz, Kaolinite, muscovite, and goethite, respectively, where Kaolinite and muscovite are the minor minerals present. The minerals in the sediment samples tell the source of trace elements in the water, indicating that weathering of the surrounding rock, like Cal-silicate rock and migmatite gneiss, has occurred. Kaolinite indicates that clay and clay minerals are mainly sourced from feldspar minerals; muscovite, however, is a feldspar-rich mineral, which is the process of weathering that gives rise to Kaolinite in the sediment. The presence of goethite in this sediment is indicative of iron. Iron is mainly sourced from the weathering of iron-rich minerals such as magnetite, apatite, hematite, etc. However, non-of of these minerals are present, but irons are also sourced from rusting of metals. The result suggests that the presence of goethite in this sediment sample may result from human activities by the disposal of metallic materials, which will rust over time, thereby contributing to the mineral constituent of the sediment. The central, minor, and trace elements in 18YELE 12 sediment samples are quartz, Kaolinite, and albite as minor and zircon and rutile as trace minerals, respectively.

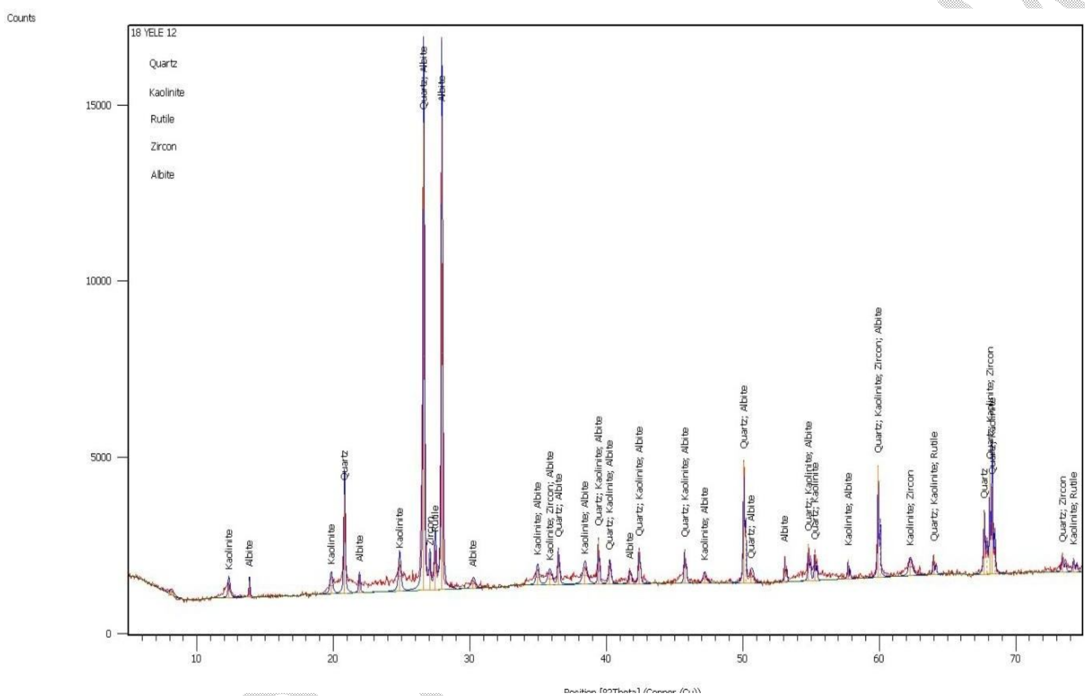

Fig 3.0: X-Ray Diffraction of sediment sample 18YELE 12 showing variation of minerals a different position

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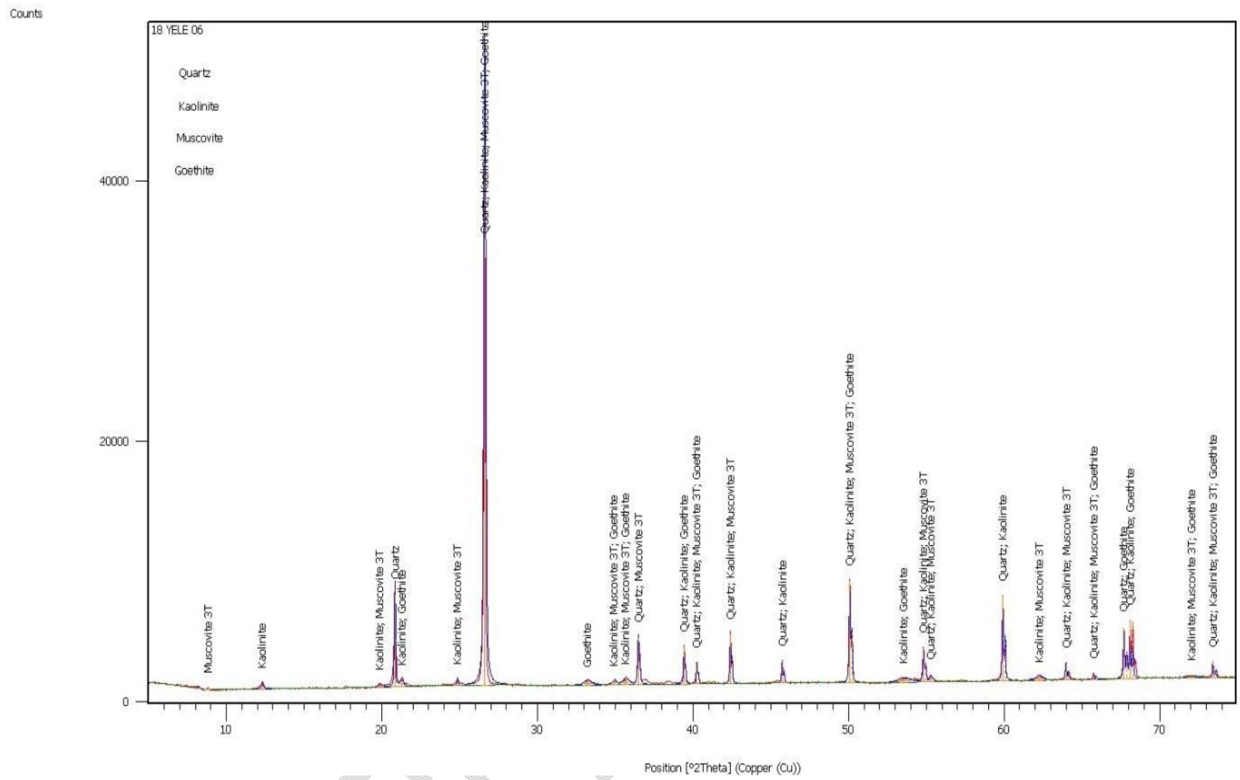

Fig 4.0: X-Ray Diffraction of sediment sample 18YELE 6 showing the variation of minerals in a different position

5. Hydrochemical Analysis

The analysis of water samples shows the variation in concentration (ppb) of trace elements in 18YELE samples. Table 9 illustrate their variation in the sample from 18YELE 6 to 18YELE 14, making a total of 9 samples. The table below shows the variation in the concentration of trace elements. The result of the hydrochemical analysis of trace elements (As, Ca, Cd, Co, Cs, Cu, Ga, K, Li, Mo, Na, Ni, Sb, and Zr) in Eleyele lake was presented graphically in table 9 to show the variation in concentration of trace element. The results revealed that Copper has the highest concentration in the samples and that the 18YELE 7 sample has the highest concentration of trace elements. However, they are all in part per billion ppb, i.e., in small quantities but have a signature in the water samples.

Add unit of trace elements concentration in the Table 2.1: Corrected in table 10

Table 10: Presentation of concentration of trace element present in the study area in (**PPB**)

Sample no	As	Ca	Cd	Co	Cs	Cu	Ga	K	Li	Mo	Na	Ni	Sb	Zr
18YELE 6	0.5	0.02	0.05	0.45	0.04	1.4	0.05	0.01	0.6	0.2	0.02	1.1	0.05	0.02
18YELE 7	0.5	0.02	0.07	2.73	0.11	2.7	0.14	0.01	0.9	0.1	0.02	1.5	0.06	0.12
18YELE 8	0.5	0.02	0.05	0.43	0.04	0.8	0.05	0.01	0.6	0.2	0.02	0.8	0.05	0.02
18YELE 9	0.5	0.02	0.05	0.28	0.03	0.5	0.05	0.01	0.8	0.2	0.02	0.4	0.05	0.02
18YELE 10	0.5	0.02	0.05	0.3	0.04	0.8	0.05	0.01	0.8	0.1	0.02	0.7	0.05	0.02
18YELE 11	0.5	0.02	0.05	0.27	0.03	0.5	0.05	0.01	0.8	0.1	0.02	0.5	0.05	0.02
18YELE 12	0.5	0.02	0.05	0.41	0.04	0.9	0.05	0.01	0.7	0.1	0.02	0.5	0.05	0.02
18YELE 13	0.5	0.02	0.05	0.66	0.04	0.7	0.05	0.01	0.6	0.2	0.02	0.8	0.05	0.02
18YELE 14	0.5	0.02	0.05	0.52	0.05	0.8	0.05	0.01	0.7	0.1	0.02	0.8	0.05	0.02

The concentration of arsenic in all the sample locations is constant throughout, which is less significant or has no effect on the water. The concentration of arsenic in the waterfalls is within the permissible value of the World Health Organization of 10ppb. The presence of arsenic in the water may result from the occupational activities in the area, like mechanical engineering work and the insecticide used by the farmers on their farmland. The calcium concentrations are constant throughout the study area and are minimal, i.e., less significant and have no effect on the body of the lake. The possible sources of calcium in the water may be due to geogenic sources from the weathering of surrounding Cal-silicate rock in the study area. Cadmium falls between the ranges of 0.05 to 0.07 ppb with its average mean value of 0.04 ppb, which falls within the permissible value of WHO of 3pbb. The WHO value makes it suitable for the standard for drinking purposes. The anomaly in 18YELE 7 may be due to the area's closeness to the surrounding where the waste product has been discharged from the industries and an individual. Cobalt falls between 0.27 to 2.73pbb with an average value of 0.67pbb, which is very minute or has no effect on the body of water and is within the standard daily intake of cobalt is 1ppm.

An anomaly occurs in location 18YELE 7 because of the closeness to the surrounding river and the transfer of cobalt minerals from the surrounding rock. Cesium value falls between 0.03 to 0.11pbb with an average value of 0.05pbb from the samples. Therefore, the possible source of cesium in the water bodies is from a zone of pegmatite ore bodies formed by the process of magma crystallization. Copper in Eleyele lake is a minor trace element in terms of the concentration in the water. The mean value of the concentration in Eleyele lake is 1.01ppb which implies it is a minority, it is highest in the 18YELE 7 water sample, which may be due to anthropogenic sources or human activities because of the location at the edge of the lake. The possible source of Copper in the lake is due to the weathering of copper-like minerals from the surrounding basement rock, anthropogenic factors affecting the area like the activities of humans occurring in that location like farming and disposal of domestic and industrial waste.

Gallium in the study area is also one of the minor trace elements in terms of the concentration in Eleyele upstream lake. The mean value of the concentration in the study area is 0.06ppb which implies its minority. It is highest in 18YELE 7 which is 0.14pbb, possibly due to anthropogenic sources or human activities in the surrounding area. Potassium is the least among the trace elements present in the study area in terms of concentration in the lake. It is constant throughout the location of the study area, which is of no effect on the water and may result from geogenic sources like weathering the surrounding cal-silicate rock. Gallium occurs in drinking water at concentrations well below those of health concern. Lithium in the study area is one of the major trace elements in terms of concentration in the body of the lake. It falls under the ranges of 0.6 to 0.9pbb with an average mean of 0.72pbb. The anomaly in 18YELE 7 may be due to geogenic sources like the transfer of weathering material from the surrounding rock to the water. Molybdenum is one of the minor trace elements present in the study in terms of concentration, with an average value of 0.14pbb. The results show it is a minority in the lake and less significant to the water. It normally occurs in drinking water at concentrations well below those of health concern. It's possible to the source. As a result transfer of surrounding sediment contains a deposit of molybdenum, indicating its geogenic source. Sodium concentrations are also one of the minor trace elements present in the study area in terms of concentrations. It is geogenic, possibly due to weathering surrounding silicate rock in the study area. Not of health concern at levels found in drinkingwater.

Nickel is the second major trace element in the study area in terms of concentrationwithin the body of the lake. It ranges from 0.4 to 1.5ppb, with an average value of 0.79ppb, which falls within the WHO permissible value of 70ppb. Therefore it is suitable for standard drinking water. Antimony is also one of the minor trace elements present in Eleyele Lake, and it do not affect the water. The concentration value of antimony is constant throughout the location except in location 18YELE 7 where there is an anomaly that may be of the geogenic or anthropogenic source. It also falls within WHO permissible value of 0.02ppm. Zirconium is also one of the minor trace elements present in Eleyele Lake, which falls within the range of 0.02 to 0.12pbb with an average value of 0.03pbb, which shows it is a minorityin the water and maybe a result of the geogenic source.

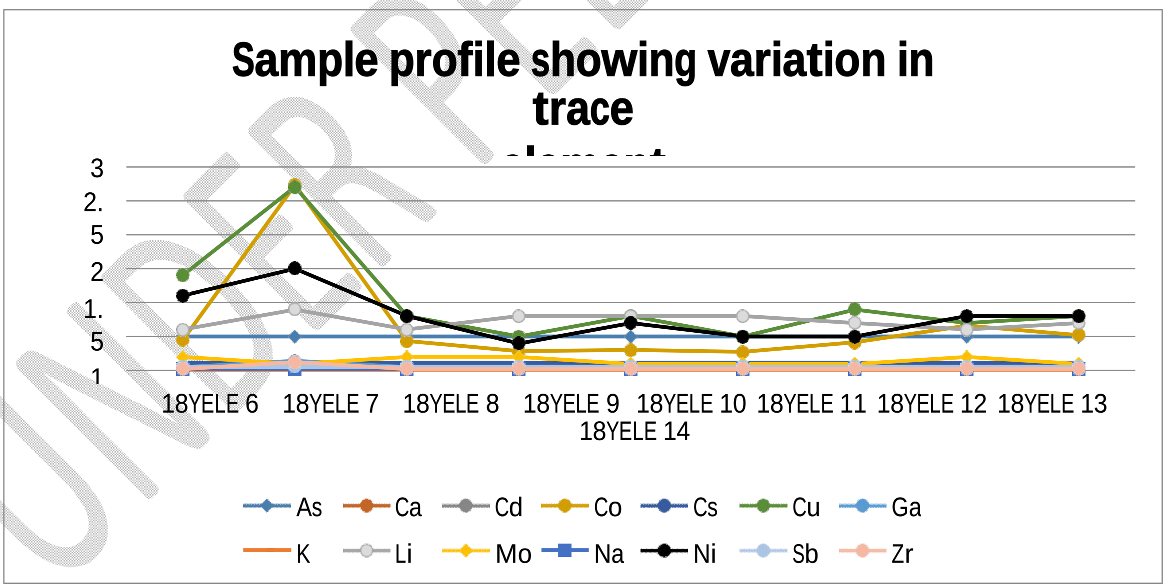

Figure 5.0: Profile showing variation in trace element

7.0 Results of Physiochemical Parameters and Interpretation

The results of the physiochemical parameters such as electrical conductivity, total dissolved solids, pH Concentration and temperature of the water samples in the investigated study area are presented in Table 1.10. The electrical conductivity of the study area shows a constant value throughout, which is 200µS/cm with a mean value of 200µS/cm. While Total Dissolved Solid of the study area Eleyele upstream lake ranges from 120 to 130ppm with an average value of 126ppm. pH values range from 7.8 to 8.3, with an average of 8.07, which is the pH value of neutral water, indicatingthat the water is a non-acidic value. The anomaly may be due to human activities in the area, such as farming and mechanical workshop. The water body temperature in the study area ranges from 30 to 34°C with an average value of 31.8°C.

Table 11: Summary of water samples and their physiochemical parameters

Sample No	Coordinates(Long/lat)	T.D.S. (ppm)	E.C. (µs/cm)	pH	TEMP (°C)
YELE 6	07° 25' 41.3" 003° 51' 14.9"	130	200	8.3	30
18YELE 7	07° 25' 46" 003° 51' 06"	120	200	8.2	30
18YELE 8	07° 25' 44.5" 003° 51' 19.5"	130	200	8.0	31
18YELE 9	07° 26' 06" 003° 51' 17"	120	200	8.2	32
18YELE 10	07° 26' 13.9" 003° 51' 16.4"	120	200	8.1	32
18YELE 11	07° 26' 20.7" 003° 51' 11.4"	130	200	8.2	31
18YELE 12	07° 26' 20.4" 003° 51' 13.9"	120	200	8.0	32
18YELE 13	07° 25' 53.4" 003° 51' 26.6"	130	200	7.8	34
18YELE 14	07° 25' 29.8" 003° 51' 31"	130	200	7.8	34
MINIMUM VAUE		120	200	7.8	30
MAXIMUM VALUE		130	200	8.3	34
AVERAGE VALUE		126	200	8.07	31.8

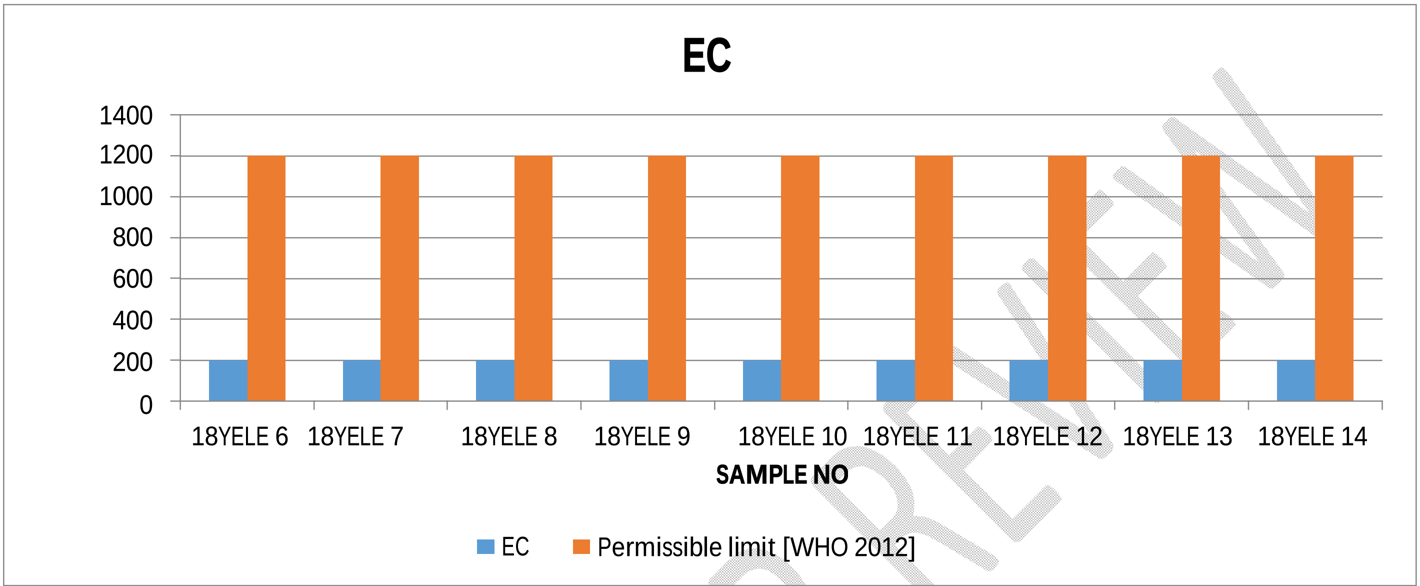

Figure 6.0: profiling showing the E.C. variation of the study area (Eleyele upstream lake) compared with WHO (2012) permissible limit for E.C.

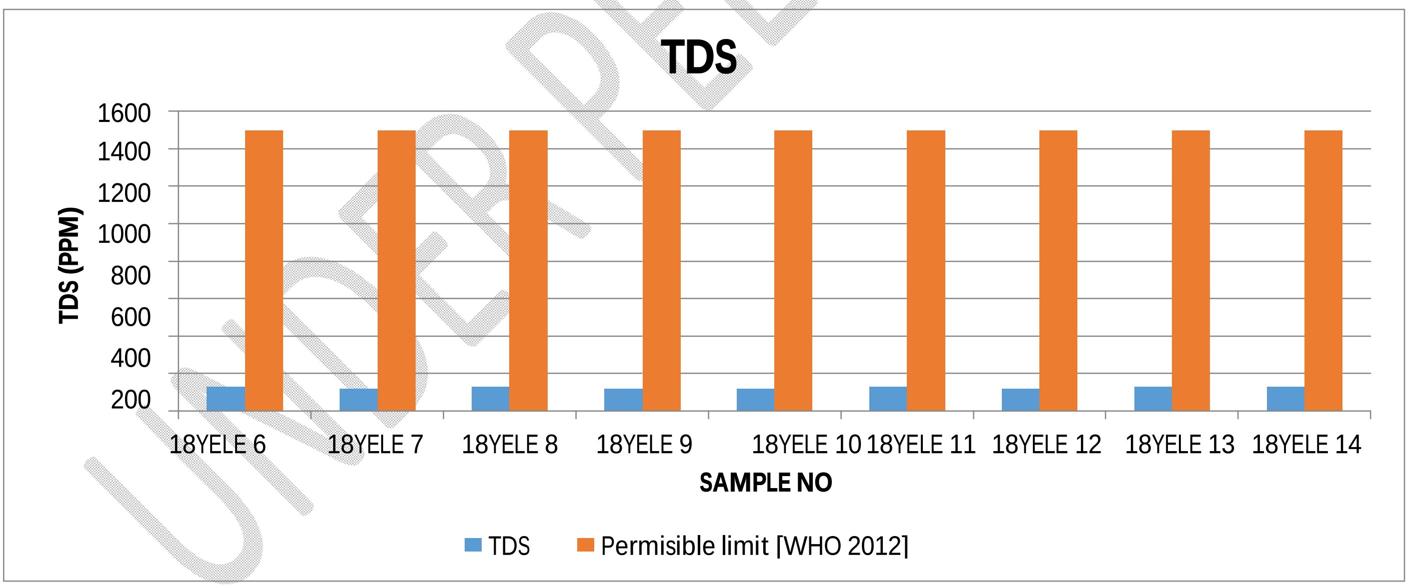

Figure 7.0: profiling showing the Total Dissolved Solid variation of the study area (Eleyele upstream lake) compared with WHO (2012) permissible limit for Total Dissolved Solid.

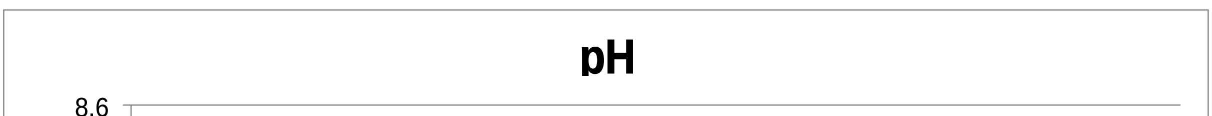

Figure 8.0: Profile of the pH variation of the study area Eleyele upstream lake

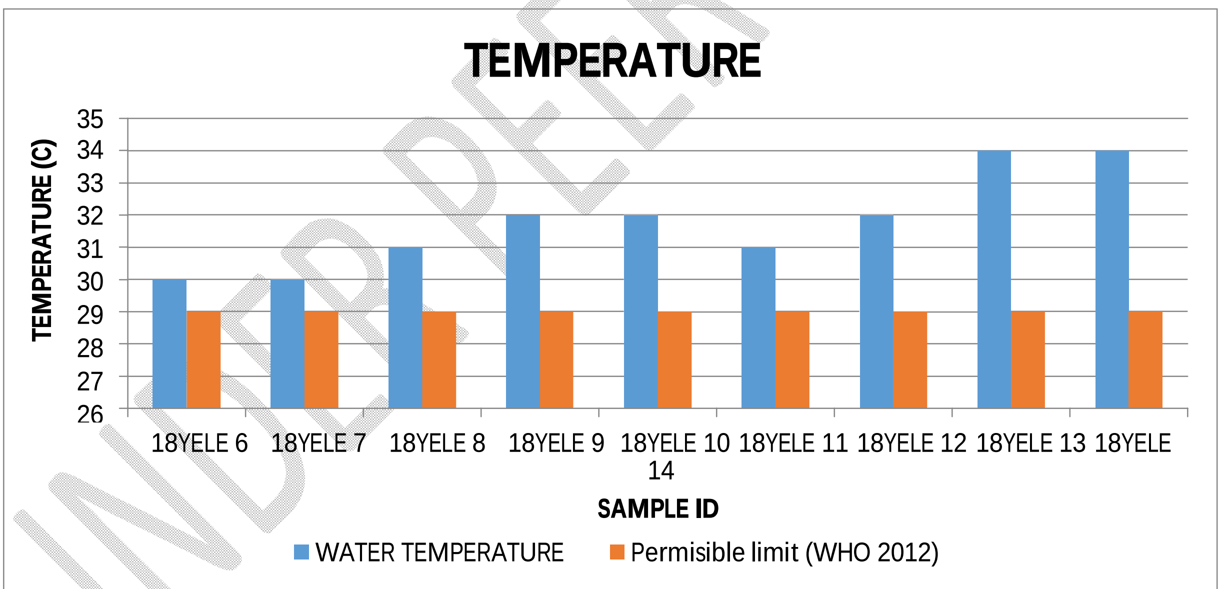

Figure 9.0: Profile of the pH variation of the study area Eleyele upstream lake

The correlation matrix of chemical data of the study area is presented and analyzed. The correlation matrix was useful because it can point out the association ofindividual chemical parameters with several influence factors. The correlation table is shown in table 5.2, using the baseline of variables having r=0.9-1.00 has a very high correlation, r=0.7-0.89 has a high correlation, r=0.5-0.69 has moderate correlation, r=0.3-0.49 has low correlation and r=0.00-0.29 have little or negligible correlation according to Guildford's rule of thumb (Nura *et al.;* 2013). The correlation matrix shows that there are very high positive correlation existing between Cd-Co (r=0.987), Cd-Cs (r=0.970), Cd-Cu (r=0.923), Cd-Ga (r=1.000), Cd-Sb (r=1.000), Cd-Zr (r=1.000), Co-Cs (r=0.982), Co-Cu (r=0.929), Co-Ga (r=0.987),Co-Sb (r=0.987), Co-Zr (r=0.987), Cs-Cu (r=0.939), Cs-Ga (r=0.970), Cd-Li (r=0.610), Cd-Ni (r=0.783), Cs- Ni (r=0.949), Cs-Sb (r=0.970), Cs-Zr (r=0.970), Cu-Ga (r=0.9923), Cu-Li (r=0. Cu-Ni (r=0.915), Cu-Sb (r=0.923), Cu-Zr (r=0.923), Ga-Sb (r=1.000), Ga-Zr (r=1.000) and Sb- Zr (1.000). The very high positive correlation between these trace elements implies that they are from common sources. The source is suggested to be from weathering of dominant minerals in the basement rock found in the study area, which depict its origin in the water as from geogenic origin. A high positive correlation occurs between these trace elements, Co-Ni (=0.829), Ga-Ni (r=0.783), Ni-Sb (r=0.783), and Ni-Zr (0.783), which also come from geogenic sources. Co-Li (r=0.501), -Li (r=0.610 Li-Sb (r=0.610) and Li-Zr (r=0.610)have moderate correlation, Cs-Li (r=0.498) have low correlation and Cd-Mo (r= -0.316), Co-Mo (r= -0.264), Cs-Mo (r= -0.355), Cu-Mo (r= -0.223), Ga-Mo (r= -0.316), Li-Mo (r= -0.627), Mo-Ni (r= -0.039), Mo-Sb (r= -0.316) and Mo-Zr (r= -0.316) have negative correlation

Table 12: Correlation matrix between the physiochemical parameters and hydrochemical result analysis

	T.D.S.	pH	T	Cd	Co	Cs	Cu	Ga	Li	Mo	Ni	Sb	Zr
TDS	1.000												
pH	-0.307	1.000											
T	0.178	-0.874	1.000										
Cd	-0.395	0.277	-0.450	1.000									
Co	-0.313	0.161	-0.362	0.987	1.000								
Cs	-0.323	0.113	-0.333	0.970	0.982	1.000							
Cu	-0.296	0.337	-0.550	0.923	0.929	0.939	1.000						
Ga	-0.395	0.277	-0.450	1.000	0.987	0.970	0.923	1.000					
Li	-0.675	0.423	-0.275	0.610	0.501	0.498	0.380	0.610	1.000				
Mo	0.350	0.044	-0.018	-0.316	-0.264	-0.355	-0.223	-0.316	-0.627	1.000			
Ni	0.039	0.176	-0.426	0.783	0.829	0.849	0.915	0.783	0.108	-0.039	1.000		
Sb	-0.395	0.277	-0.450	1.000	0.987	0.970	0.923	1.000	0.610	-0.316	0.783	1.000	
Zr	-0.395	0.277	-0.450	1.000	0.987	0.970	0.923	1.000	0.610	-0.316	0.783	1.000	1.000

7.1 Assessment of Contamination

Contamination Factor

To assess the extent of contamination of water, contamination factor and degree of contamination has been used (Rastanesh et al., 2010). The C.F. is the single element index which is determined by the relation:

$CF= C^{i}o\text{-}1/C^{i}n$. Where C.F. is the contamination factor of the element of interest, C^{i} 0-1 is the concentration of the element in the sample, $C^{i}n$ is the background concentration in the study. C.F. is defined according to four categories: <1 low contamination factor 1-3 moderate contamination factor 3-6 important contamination factor and >6 very high contamination factor. The contamination factor <1 signifies geogenic sources while the contamination factor >1 signify anthropogenic sources.

Degree of Contamination

The sum of all the contamination factors of all the elements in the sample gives the degreeof contamination as indicated in the equation below:

$Cdeg = \Sigma CF$

Four categories have been defined for the degree of contamination as follows;
<8 low degrees of contamination,
8-16 moderate degrees of contamination,
16-32 considerable degree of contamination and
>32 very high degree of contamination.

Enrichment Factor

The enrichment factor (E.F.) of an element in the studied samples is based on standardizing a measured element against a reference element. A reference element is often the characterized by low occurrence variability. It is used to differentiate heavy metals originating from anthropogenic activities and those of geogenic sources. The element usedfor normalization is Al. This is determined by the relation:

$$EF_x = (Xs/Es_{(ref)})/ (XC/Ec_{(ref)})$$

Where EFx is the enrichment factor for the element X, Xs is the concentration of the element of interest in sample. $Es_{(ref)}$ is the concentration of the reference element used fornormalization in the sample, Xc is the concentration of element in the crust, and $Ec_{(ref)}$ is the concentration of the element used for normalization in the crust (Taylor and Meclenan, 1985). Five contamination categories are recognized based on the enrichment factor:
When E.F. is <2, states deficiency to minimal enrichment. When
E.F. is 2-5, moderate enrichment
When E.F. is 5-20, significant enrichment When E.F.
is 20-40 very high enrichment and
When E.F. is >40, extremely high enrichment (Yongming *et al*., 2006; Kartal *et al*., 2006).

7.2 Discussion on the contamination of the water samples in the studied area

Contamination Factor

The contamination factor for each element and presented in table 1.12. Low contamination factor was obtained for As, Ca, Cd, Li Mo, Na and Sb in all locations, which means they are from a geogenic source. Important contamination factor was obtained for Co 18YELE 13 and 18YELE 14, and moderate contamination factor for other location samples. A very high contamination factor was obtained for Cs in 18YELE 7, moderate contamination in 18YELE 9 and 18YELE 11 and an essential factor for the rest locations. A low contamination factor was obtained for Cu in all locations except 18YELE 7, which is moderately contaminated. Moderate contamination factor was obtained for both Ga and K in all location except in 18YELE 7 where Ga have an important contamination factor. Low contamination was obtained for Ni 18YELE 9, 18YELE 10, 18YELE 11, 18YELE 12, and moderate contamination factor for the rest locations. Low contamination was obtained for Zr in all locations except in18YELE 7 where it is moderately contaminated.

Degree of Contamination

The degree of contamination (Cdeg) for each sample is shown in table 5.6. 18YELE 6, 18YELE 8, 18YELE 10, 18YELE 11, 18YELE 12, 18YELE 13 and 18YELE 14 have considerable degree of contamination, 18YELE 9 and18YELE 11 have moderate degree

of contamination while there is a very high degree of contamination spotted in 18YELE 7 which may be due to the ongoing activities in the study area.

7.3 Geo Accumulation Index

The computed results of the geo accumulation index of the selected trace elements are presented in table 1.12. The result shows that the value for As, Ca, Cd, Li, Mo, Na, Ni, and Sb are practically unpolluted. Cu and Zr are practically unpolluted in all location samplesexcept in 18YELE 7, unpolluted to moderately polluted. Co is strongly polluted in 18YELE 7, moderately polluted in 18YELE 13 and 18YELE 14 and practically unpolluted in all other location samples. Cs is between moderately polluted and strong polluted. Ga and K are unpolluted to moderately pollute in all location samples.

Table 13: Presentation of contamination factor of trace element in the study area

Sample no	As	Ca	Cd	Co	Cs	Cu	Ga	K	Li	Mo	Na	Ni	Sb	Zr
18YELE 6	0.81	0.58	0.63	3.0	4	0.95	1.67	2.86	0.33	0.48	0.66	1.38	0.71	0.5
18YELE 7	0.81	0.58	0.88	18.2	11	1.82	4.67	2.86	0.49	0.24	0.66	1.88	0.86	3
18YELE 8	0.81	0.58	0.63	2.9	4	0.54	1.67	2.86	0.33	0.48	0.66	1.00	0.71	0.5
18YELE 9	0.81	0.58	0.63	1.9	3	0.34	1.67	2.86	0.43	0.48	0.66	0.50	0.71	0.5
18YELE 10	0.81	0.58	0.63	2.0	4	0.54	1.67	2.86	0.43	0.24	0.66	0.88	0.71	0.5
18YELE 11	0.81	0.58	0.63	1.8	3	0.34	1.67	2.86	0.43	0.24	0.66	0.63	0.71	0.5
18YELE 12	0.81	0.58	0.63	2.7	4	0.61	1.67	2.86	0.38	0.24	0.66	0.63	0.71	0.5
18YELE 13	0.81	0.58	0.63	4.4	4	0.47	1.67	2.86	0.33	0.48	0.66	1.00	0.71	0.5
18YELE 14	0.81	0.58	0.63	3.5	5	0.54	1.67	2.86	0.38	0.24	0.66	1.00	0.71	0.5

Table 14: source interpretation of selected trace element in Eleyele upstream lake

Trace elements	Average contamination factor	Sources interpretation
As	0.81	Geogenic source
Ca	0.51	Geogenic source
Cd	0.66	Geogenic source
Co	4.49	Anthropogenic source
Cs	4.67	Anthropogenic source
Cu	0.68	Geogenic source
Ga	2.00	Anthropogenic source
K	2.86	Anthropogenic source
Li	0.39	Geogenic source
Mo	0.35	Geogenic source
Na	0.66	Geogenic source
Ni	0.99	Geogenic source
Sb	0.73	Geogenic source
Zr	0.78	Geogenic source

NOTE; C.F. <1 is Geogenic and C.F.>1 is Anthropogenic

Table 15: degree of contamination

Sample no.	Degree of Contamination	Interpretation
18YELE 6	18.56	Considerable degree of contamination
18YELE 7	47.95	Very high degree of contamination
18YELE 8	17.67	Considerable degree of contamination
18YELE 9	15.07	Moderate degree of contamination
18YELE 10	16.51	Considerable degree of contamination
18YELE 11	14.86	Moderate degree of contamination
18YELE 12	16.98	Considerable degree of contamination
18YELE 13	19.1	Considerable degree of contamination
18YELE 14	19.08	Considerable degree of contamination

Table 16: enrichment factor of the trace elements in the study area

Sample no	As	Ca	Cd	Co	Cs	Cu	Ga	K	Li	Mo	Na	Ni	Sb	Zr
18YELE 6	0.59	0.42	0.45	2.18	2.91	0.69	1.21	2.08	0.24	0.35	0.48	1.00	0.52	0.36
18YELE 7	0.07	0.05	0.08	1.68	1.01	0.17	0.43	0.26	0.05	0.02	0.06	0.17	0.08	0.28
18YELE 8	1.03	0.74	0.80	3.67	5.12	0.69	2.13	3.66	0.42	0.61	0.85	1.28	0.91	0.64
18YELE 9	1.84	1.32	1.43	4.27	6.86	0.77	3.81	6.53	0.99	1.09	1.51	1.14	1.63	1.14
18YELE 10	0.96	0.69	0.74	2.37	4.74	0.64	1.98	3.39	0.52	0.28	0.78	1.04	0.85	0.59
18YELE 11	2.35	1.68	1.82	5.24	8.73	0.98	4.85	8.31	1.26	0.69	1.93	1.82	2.08	1.45
18YELE 12	1.72	1.23	1.33	5.83	8.53	1.30	3.56	6.10	0.81	0.51	1.41	1.33	1.52	1.07
18YELE 13	0.89	0.64	0.69	4.86	4.41	0.52	1.84	3.15	0.36	0.53	0.73	1.10	0.79	0.55
18YELE 14	0.46	0.33	0.36	1.98	2.86	0.31	0.95	1.63	0.22	0.14	0.38	0.57	0.41	0.29

Table 17: Geo-accumulation index of the trace elements in the study area

Sample no	As	Ca	Cd	Co	Cs	Cu	Ga	K	Li	Mo	Na	Ni	Sb	Zr
18YELE 6	-0.9	-1.4	-1.3	1.0	1.4	-0.7	0.2	0.9	-2.2	-1.7	-1.2	-0.1	-1.1	-1.6
18YELE 7	-0.9	-1.4	-0.8	3.6	2.9	0.3	1.6	0.9	-1.6	-2.7	-1.2	0.3	-0.8	1.0
18YELE 8	-0.9	-1.4	-1.3	0.9	1.4	-1.5	0.2	0.9	-2.2	-1.7	-1.2	-0.6	-1.1	-1.6
18YELE 9	-0.9	-1.4	-1.3	0.3	1.0	-2.2	0.2	0.9	-1.8	-1.7	-1.2	-1.6	-1.1	-1.6
18YELE 10	-0.9	-1.4	-1.3	0.4	1.4	-1.5	0.2	0.9	-1.8	-2.7	-1.2	-0.8	-1.1	-1.6
18YELE 11	-0.9	-1.4	-1.3	0.3	1.0	-2.2	0.2	0.9	-1.8	-2.7	-1.2	-1.3	-1.1	-1.6
18YELE 12	-0.9	-1.4	-1.3	0.9	1.4	-1.3	0.2	0.9	-2.0	-2.7	-1.2	-1.3	-1.1	-1.6
18YELE 13	-0.9	-1.4	-1.3	1.6	1.4	-1.7	0.2	0.9	-2.2	-1.7	-1.2	-0.6	-1.1	-1.6
18YELE 14	-0.9	-1.4	-1.3	1.2	1.7	-1.5	0.2	0.9	-2.0	-2.7	-1.2	-0.6	-1.1	-1.6

8.0 Conclusion

This research aimed to conduct hydrochemical analyses of selected trace element levels in the upstream lake of Eleyele in Ibadan, Southwestern Nigeria. Water and sediment trace element concentrations were measured using various methods, including physiochemical parameters (such as T.D.S. and E.C. meters, pH and temperature metres, and thermometers), ICP-MS methodology, XRF analysis, and XRD analysis. The average total dissolved solids concentration (T.D.S.) is 126 ppm, and the average effective conductivity (E.C.) is 200 s/cm, both of which indicate that the water is fresh and suitable for drinking and other specific purposes; the pH ranges from 7.8 to 8.3, with an average of 8.07, indicating that the water is alkaline; the temperature ranges from 30 to 340 C, with an average of 31.8^{0} C, indicating that the water is warm and The level of the selected trace element in the water is consistent with the World Health Organization's guidelines for safe intake. As, Ca, Cd, Cu, Li, Mo, Na, Ni, Sb, and Zr all have contamination indices below 1, indicating that they originate from geological processes such weathering of the local basement complex rock, while K, Ga, Cs, and Co all have contamination indices above 1. There is a high to medium level of contamination in the water.

It is recommended that sewage and rubbish disposal facilities be made available to the general population. There should be regulations placed on the use of certain pesticides, manures, and fertilisers in fishing and farming because these things are harmful to aquatic life and make their way into the food chain in an indirect manner. Additional research should include microbial investigations and isotopic compositions in order to ascertain other quality parameters and hence prescribe the necessary treatment methods. Because the lake is a supply of water for the region, the lake should be included in the research.

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