CONSTITUENT BUDGET AND POLLUTION MODELS OF NJABA RIVER AND ITS SEDIMENTS, SOUTHEASTERN NIGERIA

BY

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CERTIFICATION

This is to certify that this work "Constituent Budget and Pollution Models of Njaba River and its Sediments, Southeastern Nigeria" was carried out by Abiahu, Chidimma Maria Goretti, with Registration Number: 20174082358 in partial fulfillment for the award of the degree of M.Sc in Environmental Geology in the Department of Geology, Federal University of Technology, Owerri.

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DEDICATION

This research work is dedicated to God almighty that made all things possible.

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ABSTRACT

The physical, microbial, and geochemical properties of the Njaba River and its sediments were analyzed using Atomic Absorption Spectrophotometer (AAS), digital meters, and Total Plate Counts. A total of ten (10) surface water samples, five (5) soil samples, and five (5) sediment samples were obtained at five gauge stations (S1 to S5) designated at equal intervals of 2 km along the stretch of the river. The results of the water showed a slightly acidic to alkaline composition (6.44-6.77). This trend was also noticed in the soil samples within the river basin (6.24- 6.64) while the river sediment samples revealed pH values ranging between 6.30-6.52. The Odour of the water was unobjectionable while the appearance was slightly brownish. The presence of heavy metals such as Fe, Al, Si, and Zn was within the acceptable limits. On the other hand, the concentration of Hg which ranged between 0.001-0.071 mg/l and Pb with values between 0.060-0.23 mg/l were above acceptable limits of the FME Standard at most of the stations. The microbial assay of the water, soil, and sediments revealed the presence of organisms such as Ecoli bacteria, pseudomonas, fecal coliform, and fungi. The constituent budget of the Njaba River analyzed at Okwudor and Oguta over a period of eight years (2011 – 2019) and seven years (2012 – 2019) respectively revealed an increasing loading rate of the following constituents(Ca^{2+} 0.013, Mg^{2+} 0.70, Na^{+} 0.013, K^{+} 1.68, SO^{2-}_{4} 0.29, NO^{-}_{3} 0.15, Cl^{-} 2.97**,** and PO^{-3}_{4} 0.063) within the Njaba River with a decline in the concentration of HCO^{-}_{3} (-0.63) at Okwudor and a decline of NO^{-}_{3} (-0.03) at Oguta Lake. Pollution and ecological assessment models like Contamination Factor (CF), Pollution Load Index, Enrichment Factor, and Geoaccumulation Index(Igeo) were used to infer contamination levels of heavy metals in the soil and stream sediments. The CF results revealed Hg (0.46), Pb(2.35E-4 to 0.02), Al(ND), Zn (5.71E-4 to 1.2E-3)which shows low contamination factor in soil, the same trend was also found in the sediments with Hg (0.277), Pb (2.63E-6), Al (ND), Zn (3.64E-4 to 8.14E-4) and Fe(2.10E-6 to 2.63E-6) while the water samples have very high contamination factor for Pb (6.0 to 23), Hg revealed moderately contamination to very high contamination (0.1 to 7.1), Al (ND), Zn (0.192 to 0.403) and Fe (0.1 to 0.93). The I-geo revealed uncontaminated to moderately contaminated in the soil and stream sediment samples with Hg (0.28),>Pb(1.57E-4 to 0.01),>Zn(3.83E-4 to 8.04E-4), and Al(ND) for the soil samples while the stream sediments were in order of Hg (0.277),>Pb (1.15E-3 to 1.27E-3),>Zn (3.64E-4 to 8.14E-4) and Al (ND). The EF revealed low to minimal enrichment for the soil and stream sediment samples with Hg (0), Pb (0.303 to 1.000), Si (1.000 to 1.053), Zn (0.491 to 1.000) and Al (0) in soil and Hg (0), Pb (0.907 to 1.000), Si (1.000 to 1.282), Zn (0.051 to 0.114), Fe (0.800 to 1.000) and AL (ND) for stream sediments.The river water is however suitable for agricultural purposes based on the calculated SAR values with the dominant hydrogeochemical facies given as Na+K+Cl water type. In conclusion, there is a need for necessary treatment procedures which should be applied to raise the quality of the river water to the FME standards for safe drinking water for example the pH can be corrected (raised) using sodium bicarbonate (soda ash). The heavy metals can be treated using ascorbic or ion exchange methods while the microbial assay can be improved upon subjection to treatment using chlorine.

Keywords: Constituents Budget, Physico-chemical, Water Quality Index, Contamination Factor, Geo-accumulation Index

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Natural water resources such as lakes, streams, and rivers are of immense socio-economic value as they help to balance the natural ecosystem. Rivers are a delicate part of the environment which is an essential requirement for human and industrial development (Das & Acharya, 2003),. River water quality is the combination of numerous interconnected compounds, which are exposed to local and temporal variations and also affected by the volume of water flow (Mandal *et al.*, 2010). Water composition has always been influenced by natural (geogenic) and anthropogenic (human activities) factors (Karbassi & Pazoki, 2015). The changes in the physical and chemical characteristics of river water can cause great damage to the riverine bio-resources (Sinha, 2002). Moreover, river water has the capacity for self-purification; the level and quality of wastes and effluents discharged may be far beyond the purifying capacity (Agarwal *et al.*, 2000).

Physiochemical parameters such as temperature, turbidity, nutrients, hardness, alkalinity, dissolved oxygen, etc. are some of the factors that help the growth of living organisms in the water body(Smitha & Shivashankar.,2013). Water quality assessment, therefore, involves the analysis of physicochemical, and microbiological parameters that normally reflect the abiotic and biotic status of the ecosystem(Verma *et al.,* 2012). In essence, the pollution of a river first affects its chemical quality and then systematically destroys the community disrupting the delicate food web. The diverse uses of the rivers are seriously impaired due to pollution and even the polluters like industry suffer due to increased pollution of the rivers. River pollution has several dimensions and effective monitoring and control of river pollution require expertise from various disciplines (Verma et al., 2012). Contamination and pollution of the river is a global problem (Whitacre, 2008; Pandey*et al.*, 2014). The disposal of waste leads to contamination of rivers and lakes chronically affecting the flora and fauna (Patel*et al.*, 2019; Sonone*et al.*, 2020). According to surveys carried out on selected stretches of important rivers, it has been found that most of the rivers are grossly polluted (Joshi*et al.*, 2009; Matta*et al.*, 2017).

. For instance, domestic sewage discharged from a population of about 2 million can give rise to numerous water-borne diseases like typhoid, cholera, dysentery, poliomyelitis, and cysticercosis, thereby affecting human health and deterioration of the water quality (Smitha & Shivashankar, 2013). To this end, increased anthropogenic load on our aquatic ecosystem determines the necessity of investigations devoted to adverse effects of pollution and its potential risk for aquatic ecosystems.

Sediments in stream beds disrupt the natural food chain by destroying the habitat where the smallest stream organisms live and causing massive declines in the fish population. It can clog fish gills, reducing resistance to disease, lowering growth rates, and affecting fish egg and larvae development. Nutrients transported by sediments can activate blue-green algae that release toxins and can make swimmers sick. Sediments increase the cost of treating drinking water and can result in odor and taste problems.

Njaba River originated from Isu (Figure1.1) and flows through Okwudor, Awomanma, and empties into the Oguta Lake which is the largest fresh Lake in Southeastern Nigeria. Apart from the Njaba river serving as the major source for aggregates (sediments) and domestic water supply, the river and its watershed constitute a focal point for transport, fishing, sports, and tourism (Ahiarakwem & Onyekuru, 2011). The exploitation of aggregates at the banks of the Njaba River has lasted for over 40 years and it is being estimated that about 200 – 400 metric tons of laterite, gravel, and sand have been exploited from the banks of the river and used for various construction purposes(Ahiarakwem & Onyekuru, 2011).

Aside from sand excavation, other human activities such as washing and farming take place along the banks of the river hence chemicals from detergents and those used in agricultural lands surrounding the river flow into it during rainfall. Aside from providing fishing ground, the Njaba River also provides water for domestic purposes to the local population. The pressure on it increases during the dry season and festive periods (Ahiarakwem & Onyekuru 2011).

1.2 Statement of the Problem

The chemistry of surface water resources and their associated sediments is constantly being modified by activities (fishing, oil and natural gas exploration and exploitation, etc.) within and around it, thereby altering the resource status and usefulness. Apart from these, the activities also affect the influx of constituents (Mg, Ca, Cl, etc.) into the river thus affecting the constituent budget of the river. There is therefore a serious need for assessment of the chemistry of the river, stream sediment, and soil within its watershed of the Njaba River.

1.3 AIM AND OBJECTIVES

1.3.1 AIM

The main aim of this research is to carry out a constituent budget and pollution evaluation of the Njaba River and its sediments.

1.3.2 OBJECTIVES

1. To determine the physical and biochemical characteristics of Njaba River water to assess its quality.
2. To determine the constituent budget of the river at Okwudor and Oguta lake in order to determine the constituent loading rate over the period of (2011

– 2019) and (2012 – 2019) respectively.

3. To determine the Graphical methods of surface water interpretation (Piper, Stiff, Durov, Schoeller) of the Njaba river at strategic locations in order to determine the relationship of the constituents.
4. To determine the level of pollution of the Njaba River and its sediments using the pollution risk models like Contamination factor, Pollution load index, Geo-accumulation index, and Enrichment factor.

1.4 Justification of Study Area

There is a paucity of information on the chemistry of the Njaba River and its sediments as well as the soils within its watershed. There is also the need to update the constituent budget of the river from existing chemical data to determine the influx rate of the constituents into it. There is also a lack of information on some of the contamination indices such as Geo-accumulation index, Pollution land index as well as the Enrichment and Contamination factors. Therefore, this work will serve as a guide for prospective researchers and provide relevant of information for environmental management authorities on the influx of constituents and concentrations of heavy metals in sediments and soils through Anthropogenic activities within the Njaba watershed, thus providing remediation plans and reference for future research work.

1.5 Scope of the Study

This study involves hydrogeochemical, constituent budget, and microbial analysis of the Njaba River. A total of 20 samples were collected (10 water samples, 5 soil samples, and 5 stream sediment samples) at equal distances of 2kms along the stretch of the river.

A total of 31 parameters were analyzed including the physiochemical, heavy metals, and microbial analysis.

CHAPTER TWO

LITERATURE REVIEW

2.1 Location of the Study Area

Njaba River is located in the Niger Delta Basin of Nigeria. The section of the river under investigation in the basin is precisely located within Latitudes 5° 44' and 5° 47' North and Longitudes 6° 49' and 7° 03' East (Figure 2.1). The Njaba River has a shoreline length of 26.50 km, a mean depth of 4.50 m, and a mean specific discharge of 1700 m^3/h (Oteze, 2006). The area stands at an elevation of about 60 m above the mean sea level.

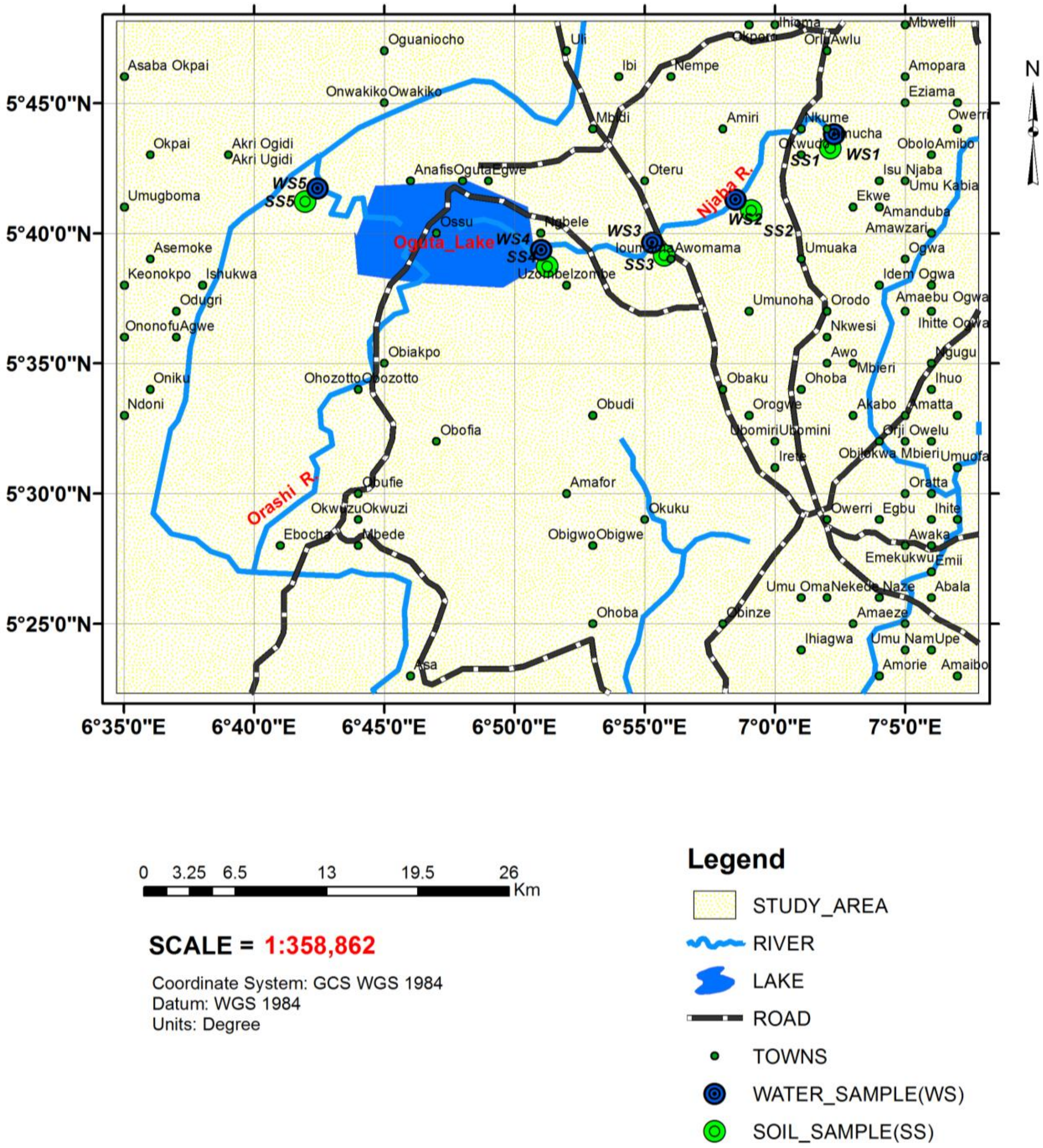

Figure 2.1: Location Map of the Study Area

2.2 Physiographic Setting and Hydrology

The Njaba River and its watershed are located within the equatorial climate belt of Nigeria, with a mean monthly temperature range of 25°C - 28.5°C, mean rainfall of about 2500 mm; most of which falls between May and October, (National Root Crop Research Institute, 2008), mean dept of 4.50 m and mean specific discharge of 1700 m^3/h (Oteze, 2006). The vegetation cover of the Njaba area is characterized by trees and shrubs of the rainforest belt of Nigeria. However, human activities such as agriculture, hydrocarbon exploration, and exploitation in the area have resulted in the deforestation of part of the study area.

The Njaba River originated from Amucha, Imo State, Nigeria, and flows in an almost east-western direction where it empties into the Oguta Lake (Figure 2.2). Oguta Lake is the largest freshwater resource of southeastern Nigeria. The Njaba River with a mean velocity of about 0.50 m/s contributes about 60% of the total channel inflow into Oguta Lake, (Ahiarakwem, 2007), The Njaba River on the other hand is adequately recharged by precipitation during the rainy season.

Njaba River is one of such surface water bodies in Nigeria that receive pollutants from floods aside from the ones introduced by man and nature. Njaba River originated from the north-western part of Isu at Isunjaba, flows south-westwards through Njaba and Oguta territories towards Oguta lake, passing through the southern parts of Ukworji, Umunnoha, and Oguta Local Government Areas. Njaba

River found in the Niger Delta basin of Nigeria lies within Latitudes 5°44' and 5°47' North and Longitudes 6°49' and 7°03' East (Atlas Map). The River has over the years seen a massive sand export that continues to erode its banks and gullies. Sand excavation businesses are carried out in the river for building construction and other purposes. The business is very sprawling and has over the years attracted some participants from other towns and villages. It is believed that the state (Imo State) and indeed the local government (Njaba L.G.A) also derive revenues from the sand excavation businesses.

Aside from sand excavation, other human activities such as washing and farming take place along the banks of the river hence chemicals from detergents and those used in agricultural lands surrounding the river flow into it during rainfall. Aside from providing fishing ground, the Njaba River also provides water for domestic purposes to the local population. The pressure on it increases during the dry season and festive periods.

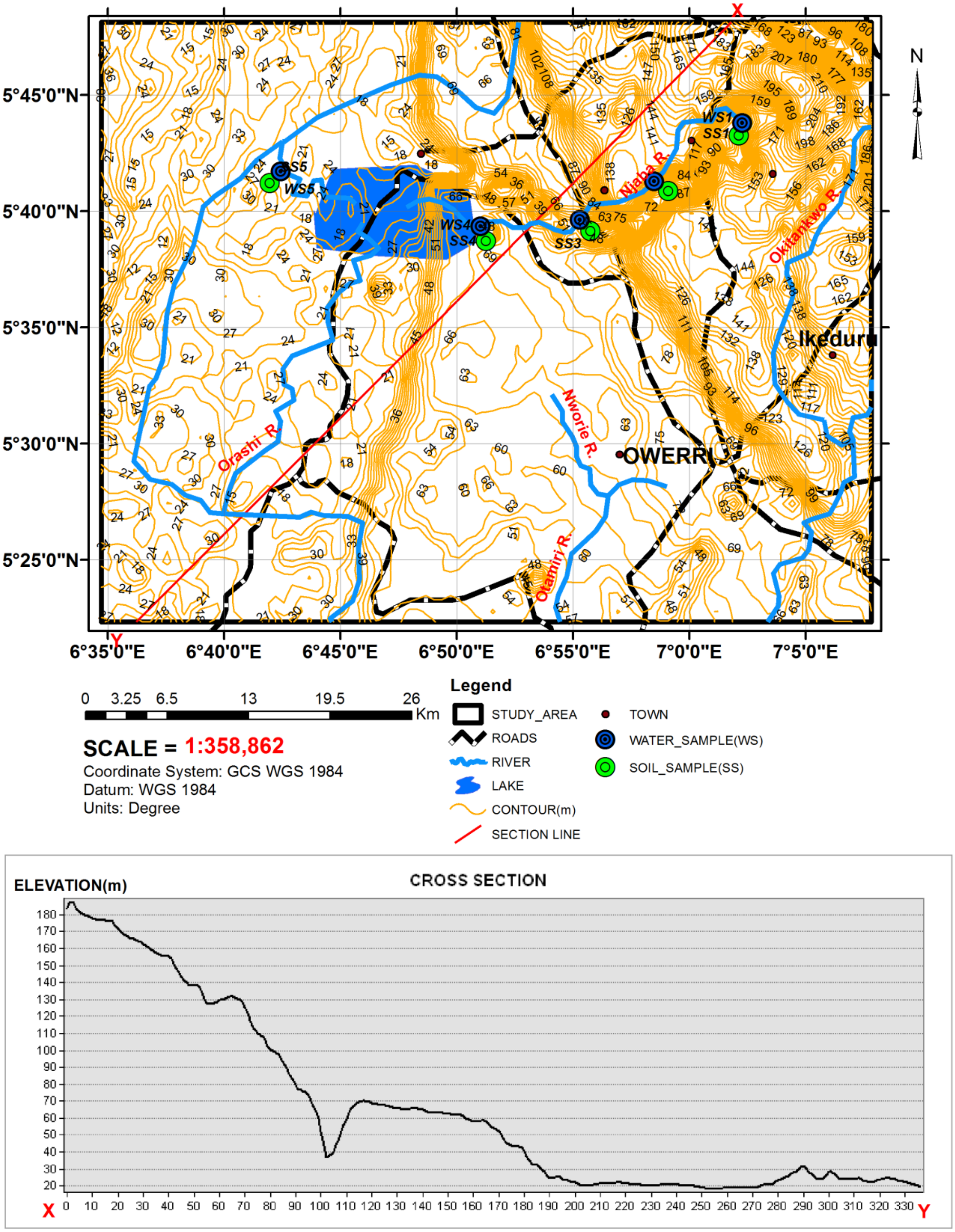

Figure 2.2: Topographical and Drainage Map of the Study Area

2.3 Geology of the Area

The study area is underlain by the Benin Formation (a major stratigraphic unit in the Niger Delta Basin which is the youngest after Agbada and Akata Formation the oldest according to stratigraphic records (Figure 2.3). The Benin Formation is made up of continental sands with lenses of clay/shale and some isolated units of gravel, conglomerate, and sandstones (Ananaba *et al.*, 1993). The Benin Formation is made up of high sand percentages ranging from 70–100% and forms the top layer of the Niger Delta depositional sequence (Obaje, 2009). The massive sands were deposited in a continental environment comprising the fluvial realms (braided and meandering systems) of the upper delta plain (Obaje, 2009).

The Formation is Pliocene to Miocene in terms of age and overlies the Agbada Formation which consists of sands and shale units. Odigi & Nwadiaro (1988) carried out a study on the surface geology of the Oguta Lake area using road cuts and low hills and observed that it consists of ferruginized sands which are occasionally massively bedded and pebbly. The sand units are majorly coarse-grained pebbly, poorly sorted, and contain lenses of fine-grained sands naturally as observed by Avbovbo (1978). The presence of the Benin Formation is a contributory factor to soil erosion, especially where they are exposed unprotected by vegetation (Ahiarakwem & Onunkwo, 2011).

The Benin Formation provides the aquifer for inhibition of groundwater storage.

The incidence of high porosity and permeability, as well as shallow water conditions, make the groundwater system in some parts of the area very vulnerable to pollution (Ibe *et al.*, 2003).

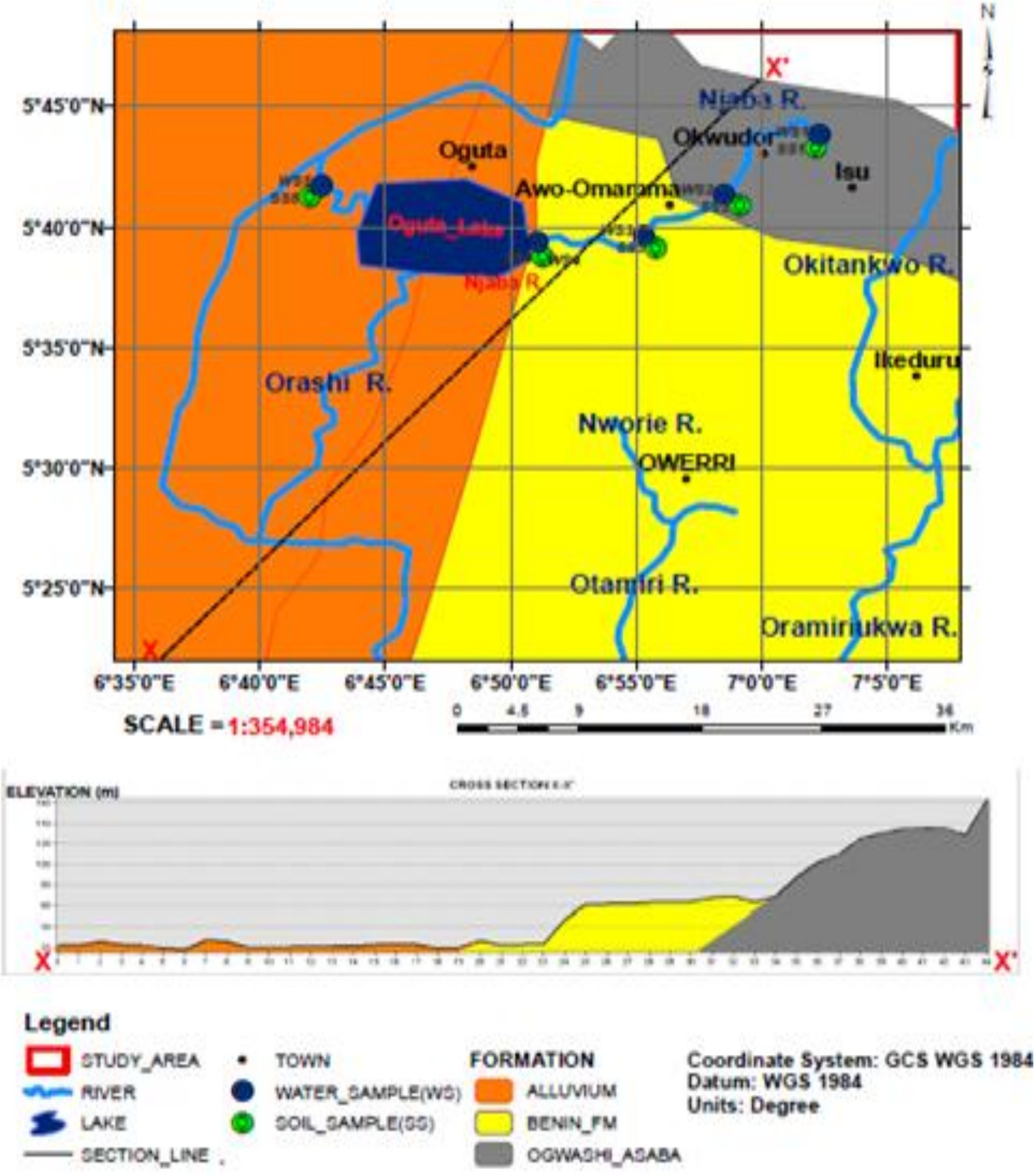

Figure 2. 3: Geologic Map and Cross-section of the Study Area

2.4 Previous Works

Several researchers have worked extensively on rivers and river basins in many parts of the world but few have worked on the constituent budget and pollution status of rivers in the study area.

According to Ogubanjo & Rolajo (2004), surface water resources are more vulnerably polluted than groundwater resources especially in developing countries where the heavy industrialization, increasing urbanization, and adaptation of modern agricultural practices play an important role in improving the living standard but at the same time it causes severe environmental impairment (Mulk *et al.,* 2015), and declining quality of life for many people (Pearce & Turner, 1990). Aquatic environmental deterioration is becoming a serious problem due to rapid urbanization and economic development, particularly in developing countries. As two important components of the aquatic environment, water quality and sediment pollution are widely considered to be concerns; however, they are considered separately in most cases (Peiru *et al.,* 2018). According to them, the relationship between water quality and sediment pollution with heavy metals has been little addressed. The water quality of the Njaba River was assessed using standard methods by Akubugwo *et al.* (2013). Constituent budget and flushing model of a tropical freshwater lake: case study of Oguta Lake, southeastern Nigeria was evaluated by Ahiarakwem *et al.* (2012). In their study that the highest annual maximally flushed constituent in the lake was bicarbonate while the lowest magnesium. According to them, the lake witnessed a low influx of nutrients (phosphate, nitrate, and dissolved silica) during their study period thus indicating a low level of eutrophication. Excessive flushing rate can cause nutrient imbalance and this can alter the resource status and usefulness of the lake. They concluded that the constituent budget and flushing model of the Oguta lake was therefore favorable for water supply, irrigation activities, and fisheries development.

In another study, Ahiarakwem & Onyekuru (2011) carried out a comparative assessment of the physicochemical and microbial trends in the Njaba River. They discovered that the generally decreasing low pH value and progressively increasing coliform counts and nutrient contents (although still low) were the major environmental problems observed in the Njaba River water. These problems are essentially associated with increased anthropogenic activities on the Njaba River Watershed within the period (2003 to 2008) in focus. In their work, they suggested that one approach that is required to maintain the resource status and usefulness of the Njaba River is the development of appropriate pollution preventive and mitigation strategies. This can be achieved through a well-programmed monitoring system that will involve a detailed periodic assessment of the physicochemical and bacteriological characteristics of the Njaba River ecosystem.

Ahiarakwem *et al.* (2012) assessed the physical and environmental aspects of the

Oguta Lake Watershed, Niger Delta Basin, Nigeria using the false colour composite technique. They displayed the study area into portions covered by vegetation as red; built-up areas around the lake as cyan; areas covered by sediments as blue/cyan and eutrophication, pale red. The result of the evaluation of some physical and environmental aspects of Oguta Lake using remote sensing/GIS techniques indicated that the water body covers an area of 61.2% while the degraded portions cover 38.8% of the surface area of Oguta Lake and its watershed. The degraded portion included areas under intense human activities (36.91%), areas covered by sediments (1.39%), and eutrophication (0.5%). They further concluded that there is a need for constant monitoring of the Oguta lake ecosystem using both biochemical as well as remote sensing/GIS approach. As well Government should set up machinery for proper land use and utilization to check the adverse effects of anthropogenic activities on the lake and its ecosystem. Also, Umunnakwe & Aharanwa (2014) assessed water quality and heavy metal levels of Fish Species in Oguta Lake. It deduced that the water body will sustain aquatic life taking cognizance of the values of DO and BOD which were within permissible limits. They further stated that the bioaccumulation of the heavy metals showed varying concentrations among the analyzed fish species with iron and cadmium having higher values than the others.

The geochemical characteristics of surface water and stream sediments in

Asprolakkas drainage basin, an area of Tertiary mineralization within amphibolite, located at NE Chalkidiki peninsula, Greece, was investigated by (Efstratios, 2012) to establish the geochemical baseline conditions before any type of new mining activities. The area represents the only example of active mining and processing of base metal sulfide ore in Greece and also includes an unmined porphyry Cu–Au ore deposit at Skouries. In a wider context, this research represents a pre-mining baseline geochemical study that can be used as an analog for similar metallogenetic provinces in areas with a Mediterranean-type climate.

In another study, Walla & Anmar (2015) calculated Enrichment Factor and Geo-accumulation Index to assess quantitatively the influences of human activities by heavy metals around Al Anbar Province in Iraq to identify the level of contamination in large industrial zones. Results of Er and shows a high to very high enrichment of Cd with significant enrichment of Pb, Cr, and Co while the Igeo shows high to very high pollution of Cd, Cu, and Pb with moderate to high pollution of Cr and Ni. They concluded that heavy metals assessment should be regular in industrial zones.

Likewise, (Verla *et al.*, 2017) applied Index models to the result of the heavy metals in surface soils around Port Harcourt city, Rivers State, Nigeria. Cf and Igeo results revealed Cd and Zn to be moderate to high contamination, that the source of the metals in the soils was largely from anthropogenic sources. The suggested that there is a need for regular monitoring of the study area for possible pollution as some of the metals show high concentrations.

More recently, water pollution scenario at river Uramurukwa flowing through Owerri metropolis, Imo state, Nigeria was investigated using water quality index (WQI), pollution load index (PLI), ecological risk factor (Er), and contamination factor (Cf) by Verla *et al.* (2018). Notably, these models help in the realization of the level of contamination and pollution level to know if necessary measures are required before any domestic use of the river water. WQI indicated unpolluted and safe for use while there was no indication Er except for Cd and Pb, so they concluded that the river is polluted with cadmium and lead.

Application of assessment models for pollution and health risk from effluent discharge into a tropical stream: a case study of Inyishi River, Southeastern Nigeria was carried out by Ibe *et al.* (2019). The aim was to examine the environmental health consequences of the release of wastewater effluent from the aluminum extrusion company on the Inyishi River. Contamination indexes and models like the pollution load index (PLI), water quality index (WQI), transfer factor (TF), ecological risk factor (Er), contamination factor (Cf), hazard index (HI), and hazard quotient (HQ) were used for assessment. Results show that Cd and Al have very high CF while TF were in decreasing order of Mn>Cd > Cr > Fe > Zn. For all the samples PLI was generally high while the river water sample generally shows high WQI and was thus classified as poor quality. Results also revealed that HQ and HI values were below unity (< 1), but might present a health risk to children in cases of long-term consumption according to their findings. They concluded that Inyishi River has an adverse effect by the wastewater effluent from the aluminium extrusion company and therefore needs proper treatment before consumption as long term usage of untreated water might present an unfavourable environmental health risk

Edori *et al.* (2019) conducted an investigation on the Silver River at Bayelsa to determine the levels of various physicochemical parameters in both sediment and water from the river. The findings of their work showed that the silver river (both water and sediment) were under human influence which if not handled immediately, can shortly constitute a major health risk to the entire environment.

Jannat *et al.* (2019) conducted a study to determine the water quality of Mokeshbeel, near the Gazipur industrial area of Bangladesh. The WQI showed that the water quality of Mokeshbeel is extremely poor and very unfit for human use. The study further reflects a very bad quality of water in the area. The results of their study pointed out the need to take necessary steps before discharging wastewater into the area and future policies by the responsive authority in terms of development of the environmental pollution control (Jannat *et al.,* 2019).

Saurabh & Amit (2021), evaluated River Narmada which is the fifth-largest holy river of Madhya Pradesh (M.P) flowing in the central part of India. The river receives a large quantity of untreated/partially treated wastewater enriched with heavy metals and supplementary toxic organic pollutants. Principal component analysis of data confirmed pollution in the river from both natural and anthropogenic sources (Saurabh & Amit, 2021). The strongest Pearson correlation coefficient between Cu-Pb (0.998) and Zn-Cu (0.986) indicated that the input of wastewater in the river was probably from electroplating industriesSaurabh & Amit (2021). They further found out that the river water is unsuitable for human intake. They suggested that the government should control the direct flow of wastewater into the river to restore ecological health (Saurabh & Amit, 2021).

2.5 Graphical Methods of Surface Water Analysis

A variety of graphical and multivariate statistical techniques have been devised since the early 1920s to facilitate the classification of waters with the ultimate goal of dividing a group of samples into similar homogeneous groups (each representing a hydrogeochemical facies). Several commonly used graphical methods and multivariate statistical techniques are available including Collins bar diagram, pie diagram, Stiff pattern diagram, Schoeller semi-logarithmic diagram, Piper diagram, Q-mode hierarchical cluster analysis (HCA), K-means clustering (KMC), Principal components analysis (PCA), and Fuzzy k-means clustering (FKM). This work utilizes a relatively large data set to review these techniques and compare their ease of use and ability to sort water chemistry samples into groups. But for this study, only the following techniques were used vis: Stiff Diagram, Piper Diagram, Schoeller Diagram, and Durov Diagram.

All the graphical methods use a limited number of parameters, usually a subset of the available data, unlike the statistical methods that can utilize all the available parameters. The fundamental aim of the techniques compared here is to identify the chemical relationships between water samples. Samples with similar chemical characteristics often have similar hydrologic histories, similar recharge areas, infiltration pathways, and flow paths in terms of climate, mineralogy, and residence time.

2.5.1 Stiff Diagram

The Stiff pattern is a polygon that is created from three (or four) parallel horizontal axes extending on either side of a vertical zero axes (Stiff, 1951). In this diagram, cations are plotted on the left of the axes, and anions are plotted on the right in units of milliequivalents per liter (meq L-1). The Stiff diagram is usually plotted without the labeled axis and is useful for making visual comparisons of waters with different characteristics. The patterns tend to maintain their shape upon concentration or dilution, thus visually allowing us to trace the flow paths on maps (Stiff, 1951).

2.5.2 Piper Diagram

This is a graphical representation of the chemistry of a water sample or samples. The cations and anions are shown by separate ternary plots. The apexes of the cation plot are calcium, magnesium, and sodium plus potassium cations. The apexes of the anion plot are sulphate, chloride, and carbonate plus bicarbonate anions. The two ternary plots are then projected up into a diamond. The diamond is a matrix transformation of a graph of the anions and cations. Unlike the Stiff diagram, the Piper diagram concentration is expressed in %meq/l. Many analyses can be plotted on the same diagram and are useful in classifying waters by hydrochemical facies. Piper diagram is convenient to identify the mixing of waters and can track changes through space and time. Its disadvantages are concentrations are renormalized and it cannot easily accommodate other cations or anions may be significant.

2.5.3 Schoeller Diagram

Schoeller diagram is a semi-logarithmic diagram of the concentration of the main ionic constituents in water (SO_4, HCO_3, Mg, Ca, and Na/K) in equivalent per million per kg of solution (meq/kg). An equivalent is the amount of an anion or cation species needed to add or remove one mole of electrons from a system. The concentration of each ion in each sample is represented by points are connected by a line. The diagram gives absolute concentration but the line also gives the ratio between two ions in the same sample. The Schoeller semi-logarithmic diagram (Schoeller, 1955 &1962) allows the major ions of many samples to be represented on a single graph, in which samples with similar patterns can easily be discriminated. The Schoeller diagram shows the total concentration of major ions in log-scale.

2.5.4 Durov Diagram

Durov diagram in AquaChem is an alternative to the Piper diagram. The Durov diagram plots the major ions as percentages of mill-equivalents in two base triangles. The total cations and the total anions are set equal to 100% and the data points in the two triangles are projected onto a square grid that lies perpendicular to the third axis in each triangle. The plot reveals useful properties for large sample groups. The main purpose of the Durov diagram is to show the clustering of data points to indicate samples that have similar compositions. The Durov diagram can be used to plot all samples in the open database or selected sample groups.

2.6 Sodium Adsorption Ratio (SAR)

SAR is an expression that is used for characterizing the sodium hazard of irrigation water. SAR value is used to calculate the degree to which irrigation water tends to enter into the cation exchange section in the soil. The main problem with high sodium concentration is its effect on soil permeability. Sodium also contributes directly to the total salinity of the water and maybe toxic to sensitive crops such as fruits trees.

Table 2.1: Classification of Water Based on Sodium Absorption Ratio (SAR) (After The U.S Department of Agric, 1965)

SAR	WATER CLASS
0-10	Excellent
10-18	Good
18-26	Fair
>26	Poor

2.7 Ecological Risk and Pollution Models

2.7.1 Assessment of soil and sediment contamination

The levels of contamination in soil and sediments in the present study have been quantitatively assessed using environmental indices like geo-accumulation index (I_{geo}), and enrichment factor (EF). These indexes are methods widely used for the assessment of the impacts of anthropogenic activities on soils and sediments which involves calculating the contamination factors for the heavy metal concentrations against uncontaminated background levels (Lin *et al.,* 2016). These indexes have been extensively used in different studies (for example, Bonnail *et al,*2016, Wang *et al.,* 2015) and are discussed in detail in the following section.

2.7.2 Geo-accumulation Index (I_{geo})

The geo-accumulation Index (I_{geo}) was introduced by Muller (1969). This approach involves comparing the current concentration of heavy metal in a system to pre-industrial concentrations. The method has been commonly used to evaluate heavy metal contamination in urban soils and sediments. Index of Geoaccumulation can be calculated using the equation:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \tag{3.8}$$

Where C_n is the measured concentration of an element in question measured at a certain site, B_n is the geochemical background value in the soil (Muller, 1979). In the present work, the global Earth's shale values (Pb = 20; Mn = 900; Cu = 45; Cd = 0.3; Ni = 68; Cr = 90; Zn = 95 mg /kg dry weight) for heavy metals as documented by Turekian & Wedepohl (1961) were used as background values for metals and was employed in calculating I_{geo} values.

The constant 1.5 was used in the $\mathbf{I_{geo}}$ equation to reduce the possible effects of varying background values which may have resulted from varying soil and sediment lithology (Lu *et al.*, 2010). The geo-accumulation index has been subdivided into classes that range from practically uncontaminated, to moderately and heavily contaminated based on their values (Huu & Damme,2010; Muller, 1969). These classes are given in Table 2.2.

Table 2.2: Classification of index of geoaccumulation (Huu & Damme, 2010; Muller, 1969)

I_{geo} class	I_{geo} value	Category
0	<0	Practically unpolluted
1	0-1	Uncontaminated to moderately polluted
2	1-2	Moderately polluted
3	2-3	Moderately to heavily polluted
4	3-4	Heavily polluted
5	4-5	Heavily to extremely polluted
6	>6	Extremely polluted

2.7.3 Contamination Factor (CF)

Contamination factor is a method used to assess the extent of contamination of each heavy metal in soils and sediments to the background concentrations (Rastmanesh*et al.*, 2010). The C^i_f is derived by dividing the concentration of each metal in the soil or sediments by the background value (Bonnail *et al.*, 2016), and is calculated by the equation:

$$C^i_f = \frac{C^i_{o-1}}{C^i_n} \qquad \textbf{(3.9)}$$

where C^i_f is the contamination factor of the element of interest, C^i_{o-1} is the concentration of the element in the sample, C^i_n is the background concentration. In this study, the continental crustal averages have been used (Taylor & Meclenan, 1985). C^i_f is defined according to four categories (see Table 2.3).

Table 2.3: Description of Contamination Factor (After Bonnail *et al.*, 2016; Hakanson, 1980).

C_f Value	Category
<1	Low contamination factor indicating low contamination
1 -3	Moderate contamination factor
3-6	Considerable contamination factor
>6	Very high contamination factor

2.7.4 Enrichment Factor

Enrichment factor which was put forward by Zoller *et al.*(1974) and Ravichandran *et al.* (1995) is a method for estimating the anthropogenic impact on soil and sediments by calculating differences between the metals originating from human activities and those from natural provenance or the mixed source of the metals (Ravichandran *et al.*, 1995). The EF calculation seeks to reduce the metal variability associated with variations in soil and sediment ratios. The EF method normalizes the measured heavy metal content for a sample reference metal such as Fe or Al (Muller, 1968). In this study, we use Fe as a sample reference metal to calculating the enrichment factor since Fe was considered that the distribution of Fe was not related to other heavy metals and usually has a relatively high concentration in the earth. The background value taken for Fe is considered from the world average value in shale (47200 mg/kg) (Verla *et. al.,* 2017). The FE is calculated by the following equation:

$$EF = M_x \ X \ Fe_b \ / \ M_b \ X \ Fe_x \qquad \textbf{(3.10)}$$

Where; Mx and Fe_x are the soil/sediment sample concentrations of the heavy metal and Fe (or other normalizing elements, e.g Al), while M_b and Fe_b are their concentrations in a suitable background or baseline reference material (Salomons &Förstner, 1984).

Five contamination categories are recognized based on the enrichment factor as shown in Table 3.4. Values of EF lower than 1.5 (García *et al.*, 2008) or <2 (Abreu *et al.*, 2016) indicate that the metal is entirely from crustal materials or natural processes, while EF values higher than 1.5 or 2 suggest an increasing portion of the anthropogenic sources (Abreu *et al.*, 2016).

Table 2.4: Description of Enrichment Factor (Yongming *et al.*, 2006; Kartal *et al.*, 2006)

EF Value	Category
<2	Deficiency to minimal enrichment
2-5	Moderate enrichment
5- 20	Significant enrichment
20-40	Very high enrichment
>40	Extremely high enrichment

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The following table shows the list of materials used during the fieldwork and laboratory analysis.

Table 3.1: Materials and Equipment used

S/N	FIELD TOOLS	LABORATORY TOOLS	REAGENTS	SOFTWARES USED
1	Topographic map	pH meter	Sabourand Dextrose Agar	Microsoft office suite
2	Global positioning system (etrex GPS)	Glassware	Nutrient agar	Grapher 4
3	Sample bottles and sample bags	Hanna Hi 83200 photometer	Distilled Water	SCHLUMBERGER aqua V.1
4	Hand Auger	Hox box oven	Mineral Salts Agar (medium)	
5		Burrette	Nitric acid	
6		Conical flask	Perchloric acid	
7		Pipettes	Sulphuric acid	
8		Atomic Absorption Spectrophotometer	Air oxidant gas	
9.		Crucibles	Acetylene gas	
10.		Incubator	E.D.TA	
11.		Autoclave	Sodium hydroxide	
12.		Bunsen burner	Solochrome	
13		Petric dishes	Moedant Black	
14.		Test tubes	FAS	

3.2 Methods

3.2.1 Field Work and Sample Collection

The use of a Global Positioning System (GPS) was used in geo-referencing points of interest.

A total of ten (10) surface water samples, five (5) soil samples, and five (5) sediment samples were obtained at five gauge stations designated (WS1, SS1 to WS5, SS5) (Figure 1.1 and 1.2) located at equal distances of 2 km along the stretch of the river. The water samples were obtained with the aid of a sterilized 1.5 plastic bottle; the sample bottles were corked under water immediately after collection to prevent oxidation of the constituents. The sediment samples were obtained with the aid of a dredging machine around the river using well-labeled sample bags. The soil samples were collected using the hand auger around the study area. The samples were all sent to the laboratory within 24 hours of collection.

3.3 Laboratory Analysis

The sample bottles used for water samples were sent to the laboratory for analysis of major cations and anions using the Atomic Absorption Spectrophotometer (AAS) while total alkalinity was analyzed in-situ using digital meters.

Calculations

The concentrations of the major constituent cations and anions in milligram/liter (mg/l) were converted to milliequivalent/liter (meq/l) and Percentage equivalent mass (% epm) using the equation 3.1 developed by Todd (1980)

$$\left.\begin{array}{l}\text{Mean equivalent mass} = \dfrac{\text{Atomic weight}}{\text{Valency}} \\[2ex] \text{Concentrations (meq/l)} = \dfrac{\text{Concentrations (mg/l)}}{\text{Equivalentmass}} \\[2ex] \%\ \text{epm} = \dfrac{\text{Concentrations (meq/l)}}{\textit{Total Cation or Anion}} \times 100\end{array}\right\} \qquad \textbf{(3.1)}$$

The concentrations in meq/l were used to prepare Piper trilinear, Schoeller, Durov, and Stiff diagrams as well as calculation of Sodium Adsorption Ratio (SAR).

The SAR was determined using equation 3.2 (Wilcox, 1955).

$$\textbf{SAR} = \frac{Na^{+}}{\sqrt{\dfrac{Ca^{2+} + Mg^{2+}}{2}}} \qquad \textbf{(3.2)}$$

The total hardness as ($CaCO_3$) of the Njaba River water was determined using equation 3.3 developed by Todd (1980). Total hardness as

$$\mathbf{CaCO_3\ mg/l = 2.5\ [Ca^{2+}] + 4.1\ [Mg^{2+}]} \qquad \textbf{(3.3)}$$

The concentration of pH, total alkalinity, total dissolved solids (TDS), total hardness, sulphate, and chloride in mg/l were used to determine the pollution index (PI) of the water samples. This was done using the method below;

The parameters considered for the determination of the pollution index (PI) of the Njaba River water samples were pH, Total Alkalinity, Total Hardness, Total dissolved solids (TDS), sulphate, and chloride. The PI was calculated using equation 3.4 developed by Horton (1965).

$$\mathbf{PI} = \sqrt{\frac{\left(\frac{maxCij}{Lij}\right)^2 + \left(\frac{meanCij}{Lij}\right)^2}{2}} \qquad \mathbf{(3.4)}$$

Where:

Ci = concentration of chemical parameters

Lj = World Health Organization (2011) permissible limit.

The Constituent Budget of the river was determined using the method described by Clark *et al.* (1972). A single conceptual model structure for a single constituent (I) is expressed as:

$$Cu - Co = \Delta Cic/\Delta t \qquad \mathbf{(3.5)}$$

Where Cu = Constituent input into the system per unit time

Co = Constituent output from the system per unit time

ΔCic = Cu − Co (Change in concentrations of constituent storage within the system).

Δt = Time Interval ($t_2 - t_1$)

In this study, equation 5 was simplified as follows:

Cu − Co = Change in mean constituent concentrations (Conc2011 – Conc.2019)/8 and 7 **(3.6)**

The change in mean constituent concentrations (Cu − Co) is equivalent to the constituent loading rate.

The accuracy test or the error test shows the major cations and anions in their respective summations in mili equivalent per liter (Meq/L). The accuracy test is used to know the state of equilibrium of the water samples. The error can be estimated using the following formulae;

$$\text{Error} = \frac{\sum A - \sum C}{\sum A + \sum C} \times \frac{100}{1} \qquad \textbf{(3.7)}$$

Determination of pH (ISO: 3025 Electrometric Method)

The pH meter was switched on for at least 30 minutes before the test. Preparation of buffer solution to 4.0, 7.0, and 9.0. The pH meter calibrates to 9.2 using the buffer and by adjusting the calibration knob. Then calibrated the pH meter to 7.0 using the buffer and by adjusting the calibration knob. The pH meter was calibrated to 4.0 using the buffer and by adjusting the calibration knob**.** Read the pH meter by inserting the sample.

Determination of Turbidity

Turbidity was determined by the photometric method using HACH DR/2010 spectrometer at a wavelength of 860 nm and program number 750. 250 ml of the filtered de-ionized water is poured into a 25 ml sample cell bottle as blank. The blank is to zero the spectrophotometer, then the sample is vigorously shaken and 25mL of the sample is poured into another 25 ml sample cell bottle. The sample is put into the light shield and closed after the blank is removed and a button is pressed to read the result. The value is digitally displayed in mg/l

Determination of Conductivity/ Total Dissolved Solid

Conductivity was determined using handheld conductivity meter model HI98302 (HANNA). The meter was first rinsed in distilled water. The conductivity was then calibrated using conductivity solution at 25ºC it was then switched on and inserted into the 50ml water sample conductivity was recorded in µs/cm when the reading became stable.

Determination of Nitrate

Nitrate was determined by the Cadmium reduction method using Hanna HI 83200 multi-parameter bench photometer at a wavelength of 525 nm. 10 ml of the sample was poured into two separate sample cell bottles. One (1) was used as blank to zero the photometer and one (1) sachet of Nitrate reagent powder pillow was added to the second sample cell bottle and was inserted into the cell compartment and time for 4 minutes and 30 seconds. At the end of the countdown, the READ button was pressed to display the result in mg/L of Nitrate and Nitrate – Nitrogen.

Determination of Phosphate

Phosphate was determined by Amino Acid methods using HI 83200 multi-parameter bench photometer at a wavelength of 525 nm. 10 ml of the sample was poured into two (2) separate sample cells. One was used for blank to zero the photometer and 10 drops of HI 93717 A-0 molybdate Reagent, then the content of one packet of HI 93717 B-0 phosphate HR reagent B was added to the curette. It was shaken gently to dissolve and was inserted into cell comportment and time for 5 minutes. At the end of the countdown, the READ button was pressed to display the result in mg/l of phosphate phosphorus and phosphate (P_2O_s)

Determination of Chlorides (Cl^-): (Argentometric Titration Method, APHA 1998)

In 100ml of the sample, 1ml of K_2CrO_4 indicator was added and titrated against 0.02N $AgNO_3$ till brick red precipitates were formed.

Determination of Bi-Carbonate (Titration Method)

This is determined by the titration method. Add 50 ml or 100 ml of the water sample in a clean flask and add a slight excess of Barium Chloride solution to precipitate the carbonate which does not affect the bicarbonate. Add two (2) drops of phenolphthalein indicator to the solution. Shake and titrate to the endpoint with 0.02 M standard HCl (hydrochloric Acid). Record the volume of acid use.

Determination of Sulphate

100 to 400ml of the sample was taken, filtered when necessary. Added 1:1 HCL in drops until acid to litmus added three drops in excess and evaporate to 50ml. Boiled the solution and added boiling Barium chloride solution until all the sulphate was precipitated. Digested on a water bath until the precipitate settled. Dried a sintered-glass crucible to constant weight. Connected the filtering equipment to the vacuum

pump and filtered the precipitate through the sintered-glass crucible. Washed several times with hot water until the filtrate was chloride-free ($AgNO_3$ test). Then dried the crucible precipitate in an oven at 103- 105ºC to constant weight. The weight of the precipitate alone was known by difference.

Determination of Heavy Metals Using Atomic Absorption Spectrometer

Water Digestion for Heavy Metal Analysis

50ml of the sample was digested in a 250mL conical flask by adding 10mL of aqua regia and heated on a hot plate until the volume remains about 7-12mL. The digest was filtered using what-man filter paper and the volume made up to the mark in a 50mL volumetric flask and was then stored in a plastic container for AAS analysis.

Principles of Atomic Absorption Spectrophotometer

Working principles: Atomic absorption spectrometer's working principles are based on the sample being aspirated into flame and atomized when the AAS's light beam is directed through the flame into a monochromator, and onto the detector that measures the amount of light absorbed by the atomized element in the flame. Since metals have their characteristic absorption wavelength a source lamp composed of that element is used, making the method relatively free from spectral or radiational interferences. The amount of energy of the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample.

Procedure

The sample is thoroughly mixed by shaking and 100mL of it is transferred into a glass beaker of 250mL volume. The sample is aspirated into the oxidizing air-acetylene flame or nitrous oxide acetylene flame. When the aqueous sample is aspirated, the sensitivity for 1% absorption is observed.

Microbiology for Water Samples Serial Dilution (Spread Plate/Pour Plate Method)

Inoculation

1ml of each water sample was pipetted into a test tube containing 9mls of sterile distilled water.10-fold serial dilution of the water sample was prepared using sterile distilled water as the diluents. Aliquots (0.1ml) of each (10^{-2}, 10^{-3}, $10^{-4,}$ or 10^{-5}) of the test tube were inoculated in a Nutrient agar plate, Sabouraud dextrose agar, and Mineral Salt Agar by spread plate technique and incubated at 37°C for 24hrs for bacteria and 25°C for 78hrs-96hrs for fungi on the incubator. After incubation, colonies were observed on a different plate and was counted and recorded.

Media Preparation

A) **Nutrient agar:** This is a basic media mostly used for culturing, subculturing, and for the total viable bacterial count.

B) **Sabourand Dextrose Agar:** For cultivation of yeast mould and acidic microorganisms.

Mac-Conkey Agar: This is a differential medium best for total coliform counts.

CHAPTER FOUR

RESULTS AND DISCUSSION

The results of the Constituents budget, physical and biochemical characteristics of Njaba River at five gauge stations (**AMUCHA, OKWUDOR, AWOMMAMMA 1, AWOMMAMMA 2 and OGUTA LAKE**) with soil and sediments are shown in Tables 4.1, 4.7, and 4.8 respectively while the Sodium Adsorption Ratio (SAR), Pollution Index (PI) and Constituents budget are shown in Table 4.2, 4.3, 4.4 and 4.5 respectively.

The table below shows the entire physical and biochemical characteristics of Njaba river water at five stations. It depicts the standards in terms of comparison based on the mean and range.

Table 4.1: Physical and Biochemical Characteristics of Njaba Water

PARAMETER	FMEnv. Std 1999	Amucha water (Njaba Source)		Mean	Njaba River (Okwudor)		Mean	Njaba River (Awommamma 1)		Mean	Njaba River (Awommamma 2)		Mean	Njaba River (Oguta Lake)		Mean
Coordinates		N $5^{0}697^{l}$ E 7^{0} 060^{l}			N $5^{0}714^{l}$ E 7^{0} 001^{l}			N $5^{0}680^{l}$ E 7^{0} 938^{l}			N $5^{0}690^{l}$ E 7^{0} 505^{l}			N $5^{0}705^{l}$ E 6^{0} 808^{l}		
pH	6.50 -8.50	6.76	6.78	6.77	6.43	6.45	6.44	6.55	6.76	6.65	6.68	6.55	6.61	6.76	6.76	6.76
Odour	Unobjectionable	Unobjectionable			Unobjectionable			Unobjectionable			Unobjectionable			Unobjectionable		
Appearance	Clear	Slightly brownish			Slightly brownish			Slightly brownish			Slightly brownish			Slightly brownish		
Total Dissolved Solid, mg/l TDS	500.00	18.00	18.50	19.00	6.50	7.50	7.00	6.50	19.50	13.00	31.00	39.50	35.25	18.00	19.50	18.75
Conductivity, µS/cm	1000.00	30.00	30.00	30.00	12.50	11.50	12.00	10.00	30.00	20.00	65.00	60.00	62.25	30.00	32.00	31.00
Turbidity, NTU	10.00	9.30	9.20	9.25	6.28	6.28	6.28	7.28	9.30	8.29	6.28	9.30	7.79	9.30	9.30	9.30
Total chloride, mg/l Cl^{-}	250.00	29.50	31.50	30.00	24.97	25.95	25.36	27.19	27.00	27.09	27.70	29.94	28.47	27.18	26.04	26.61
Total hardness, mg/l $CaCO_3$	200.00	46.34	45.58	45.96	40.46	42.46	41.46	39.46	46.36	42.91	41.46	46.34	43.39	46.34	46.34	46.34
Calcium Hardness, mg/l $CaCO_3$	150.00	17.07	17.88	17.47	33.85	34.45	34.15	35.25	19.17	27.21	34.15	27.07	30.61	16.84	17.64	17.24
Magnesium Hardness, mg/l $MgCO_3$	150.00	29.27	30.27	29.77	7.31	7.31	7.31	10.31	27.27	18.79	7.31	29.27	18.29	29.27	29.27	29.27
Iron, mg/l Fe	1.00	0.27	0.29	0.28	0.03	0.03	0.03	0.03	0.27	0.15	0.03	0.27	0.15	0.27	0.27	0.27
Calcium, mg/l Ca	250.00	5.79	5.99	5.89	4.49	4.51	4.50	4.80	5.80	5.30	11.77	9.89	10.83	6.89	5.95	6.92
Magnesium, mg/l Mg	100.00	7.24	7.00	7.12	5.88	5.68	5.78	5.48	5.52	5.50	5.78	8.12	6.95	5.42	5.45	5.43
Carbonate mg/l CO^{-}_{3}	150.00	8.50	7.50	8.00	17.00	15.00	16.00	16.00	19.00	17.50	16.00	8.00	12.00	10.00	11.00	10.50
Mercury, mg/l	0.001	0.001	0.001	0.001	0.071	0.071	0.071	0.001	0.001	0.001	0.071	0.001	0.035	0.001	0.001	0.001

Hg																
Bi-carbonate, mg/l HCO$_3^-$	30.00	41.00	44.00	42.50	20.00	19.00	19.50	38.00	34.00	36.00	41.00	40.00	40.50	39.00	38.00	38.50
Nitrate, mg/l NO$_3^-$	50.00	4.30	1.60	1.20	1.40	1.40	1.40	4.40	3.50	3.95	1.40	1.33	1.36	1.29	1.23	1.26
Phosphate, mg/l PO$_4^{-3}$	<5.00	1.26	1.24	1.25	0.70	0.70	0.70	0.70	1.20	0.95	0.70	1.20	0.95	1.18	1.10	1.14
Sulphate, mg/l SO$_4^-$	200.00-400.00	8.90	11.10	10.00	4.50	4.50	4.50	4.80	4.96	4.88	9.00	10.00	9.50	10.00	10.00	10.00
Sodium, mg/l Na	200.00	6.14	6.00	6.07	5.46	5.46	6.50	5.46	6.07	5.76	6.46	7.09	6.77	8.07	7.32	7.69
Potassium, mg/l K	10.00	14.00	16.00	15.00	15.00	15.00	15.00	16.50	16.00	16.25	15.90	16.23	16.06	17.00	17.21	17.11
Lead , mg/l Pb	0.01	0.167	0.167	0.167	0.064	0.064	0.064	0.054	0.067	0.060	0.064	0.167	0.23	0.167	0.167	0.167
Aluminium, mg/l Al	1.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Silicon, mg/l Si	NS	1.38	1.38	1.38	1.42	1.42	1.42	1.42	1.38	1.40	1.55	1.28	1.41	1.38	1.38	1.38
Zinc, mg/l Zn	3.00	0.403	0.403	0.403	0.192	0.192	0.192	0.182	0.303	0.242	0.192	0.403	0.297	0.403	0.403	0.403
Total Bacteria count, cfu/ml	0-30	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6	1.4 x 10^6
Total Coliform Count, cfu/ml	0-10	2.4 x 10^4	2.4 x 10^4	2.4 x 10^4	5.8 x 10^5	5.8 x 10^5	5.8 x 10^5	5.8 x 10^5	2.4 x 10^4	3.02 x 10^5	5.8 x 10^5	2.4 x 10^4	2.4 x 10^4	2.4 x 10^4	2.4 x 10^4	2.4 x 10^4
Total E. Coli Count, cfu/ml	0	6.6 x 10^4	6.6 x 10^4	6.6 x 10^4	5.8 x 10^5	5.8 x 10^5	5.8 x 10^5	5.8 x 10^5	6.6 x 10^4	6.6 x 10^4	5.8 x 10^5	5.8 x 10^5	5.8 x 10^5	6.6 x 10^4	6.6 x 10^4	6.6 x 10^4
Pseudomonas, cfu/ml	0	1.8 x 10^5	1.8 x 10^5	1.8 x 10^5	1.6 x 10^4	1.6 x 10^4	1.6 x 10^4	1.6 x 10^4	1.8 x 10^5	1.8 x 10^5	1.6 x 10^4	1.6 x 10^4	1.6 x 10^4	1.8 x 10^5	1.8 x 10^5	1.8 x 10^5
Total vibro bacterial count, cfu/ml	0	2.8 x 10^4	2.8 x 10^4	2.8 x 10^4	6.0 x 10^5	6.0 x 10^5	6.0 x 10^5	6.0 x 10	2.8 x 10^4	2.8 x 10^4	6.0 x 10^5	6.0 x 10^5	6.0 x 10^5	2.8 x 10^4	2.8 x 10^4	2.8 x 10^4
Total Fungi Count, cfu/ml	0	NG	NG	NG	NG	NG	NG	NG	NG	NG	NG	NG	NG	NG	NG	NG

4.1 WATER SAMPLES RESULTS

4.1.1 Physical Parameters of the Njaba River

The mean concentrations of pH at the five stations range from 6.44 to 6.77 respectively (Figure 4.1). Electrical conductivity is a measure of the capacity of water to conduct electric current. As much of the salts on the water present in the ionic form are responsible to conduct electric current (Gunasekar & Suthakar, 2015). The values for Electrical Conductivity range from 12.00 to 62.25 µS/cm respectively (Figure 4.2). The Odour at the five stations was unobjectionable while the Appearance was slightly brownish respectively. The values for Total Dissolved Solid range from 7.00 to 35.25 mg/l respectively. The Turbidity values range from 6.28 to 9.30 NTU respectively. Except for some slightly acidic values of pH, the Electrical Conductivity values were within the permissive limit of the Federal Ministry of Environment (1999) standard for water. The odour correlated with the permissible limit of the Federal Ministry of Environment. In the same vein, the Total Dissolved Solids, and Turbidity of the five stations were in the limit of the FME (1999) standard for water. The appearance of the river did not conform to the FME (1999) standard for water.

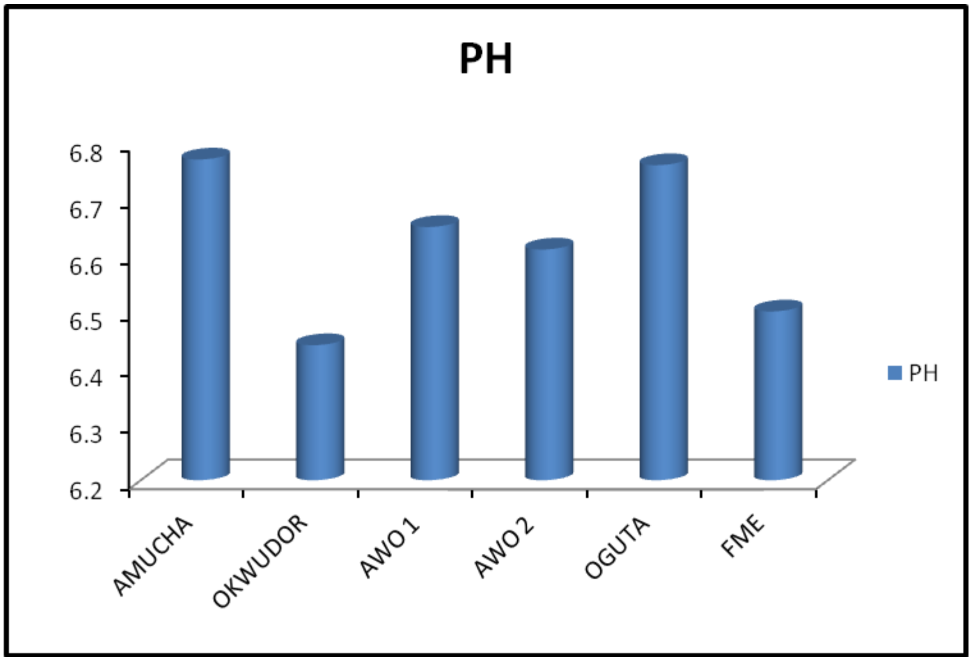

Figure 4.1: pH levels for water samples

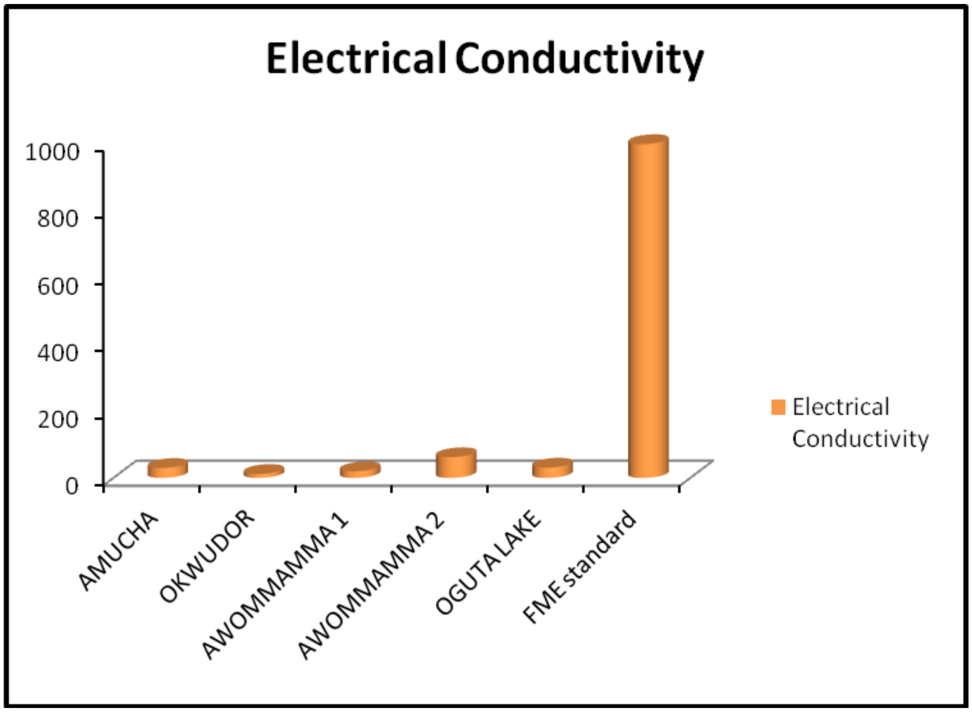

Figure 4.2: Electrical Conductivity for water samples

4.1.2 Chemical Parameters of the Njaba River

Total hardness, Calcium Hardness, and Magnesium Hardness

The soap-consuming capacity and scale-forming tendencies of water are measured using water hardness (Ray *et al.,* 1992). According to Gray (1994), water with a hardness value of less than 50 mg/l is classified as soft and moderately soft when the hardness value is between 50-100mg/l.The mean concentrations of Total hardness at the five stations range from 41.46 to 46.34 mg/l respectively while the values for Calcium Hardness ranges from 17.47 to 34.45mg/l respectively and that of Magnesium Hardness ranges from 7.31 to 29.27 mg/l respectively. The values all conform to the FME (1999) standard for water (Figure 4.3).

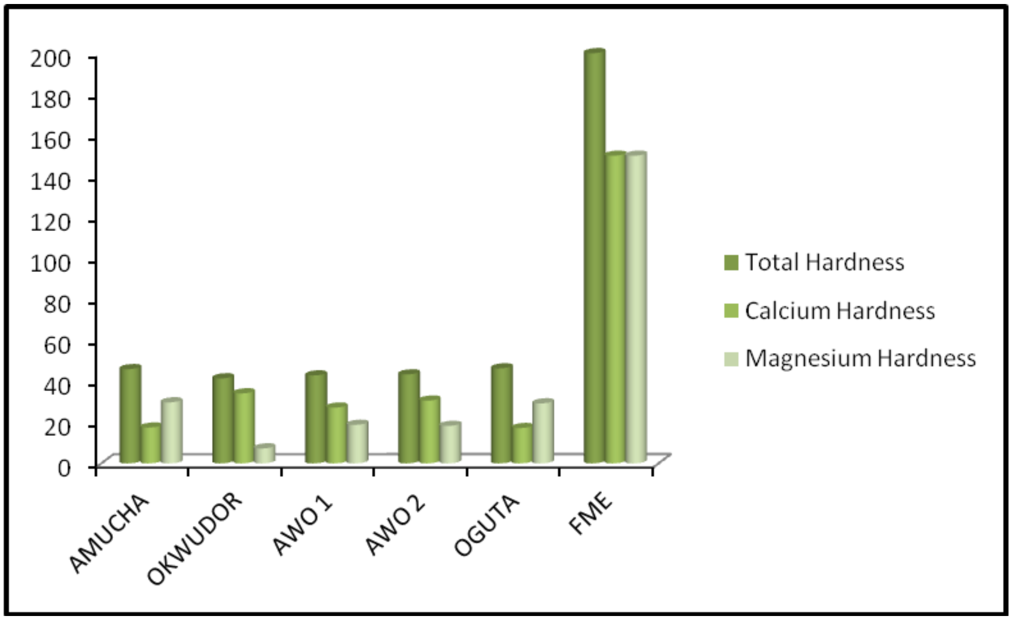

Figure 4.3: The variations of Total Hardness, Calcium Hardness, and Magnesium Hardness in water samples

Major Cations and Anions for water samples

The mean concentrations for Ca^{2+} range from 4.50 to 10.83 mg/l respectively. Magnesium is an important constituent of chlorophyll, so it is a presiding need for phytoplankton for their productivity (Round, 1970). The values of Mg^{2+}ranges from 5.43 to 7.12 mg/l respectively. The concentration values of Na^{+}ranges from 5.76 to 7.69 mg/l respectively while the values for K^{+} ranges from 15.00 to 17.11 mg/l respectively. Except for K^{+} which exceeded the permissible limit, the values of Ca^{2+}, Mg^{2+}, and Na^{+} all conform to the FME (1999) standard for water.

The mean concentration values for HCO^{-}_{3}ranges from 19.50 to 40.50 mg/l respectively. Except for the concentration at the Okwudor station, the remaining four stations did not conform to the FME (1999) standard for HCO_3. Bouwman *et al.* (2005) estimated that on a global scale half of the riverine Nitrogen is derived from anthropogenic activities. The mean values for NO^{-}_{3} range from 1.20 to 3.95mg/l. The values of Cl^{-} ranges from 25.36 to 28.47 mg/l respectively. The values for SO^{-}_{4} range from 4.50 to 10.00 mg/l. The role of phosphate in biological productivity is citable; Phosphate is one of the indispensable nutrients for the growth and development of flora in any ecosystem (Gunasekar & Suthakar, 2015). The values for PO^{3-}_{4} range from0.70 to 1.25mg/l and CO^{-}_{3} range from 8.00 to 17.50, mg/l respectively. The concentrations of NO^{-}_{3}, Cl^{-}, SO^{-}_{4} and CO^{-}_{3} all conformed to the FME (1999) standard for water.

4.1.3 Heavy Metals

The mean concentrations of heavy metals at the five stations for Fe range from 0.03 to 0.28mg/l respectively (Figure 4.4). The values for Hg range from 0.001 to 0.071 mg/l. This is a very toxic element, the hazards of which are magnified by the accumulation of organo-mercury compounds in fish. When humans take this fish it can cause cancer. Pb values ranges from 0.060 to 0.23 mg/l respectively (Figure 4.4). Lead exposure may cause neurological deficits such as mental retardation in children and kidney disease such as interstitial nephritis in adults. According to WHO (2011), exposure to lead may also contribute to hypertension and cardiovascular disease. Lead tends to accumulate in bone and lie dormant for years, and then pose a threat later in life during events such as pregnancy, lactation, osteoporosis, and hyperthyroidism, and hyperparathyroidism, which mobilizes stores of lead ion bones (WHO, 2011). Some of the known effects on higher plants include dark green leaves, stunted foliage mid increased amounts of shoots (Ferguson, 1990). It is not known to be of any known function in the human body (Essa, 1999). The inorganic forms of lead in soil have the same toxic endpoints (National Environmental Policy Institute, 2000).

The values for Si range from 1.38 to 1.42 mg/l. The values for Zn ranges from0.192 to 0.403mg/l while that of Aluminum at the five stations were Not Detected. Zinc has been shown to exert an adverse reproductive biochemical, physiological and behavioral effect on a variety of aquatic organisms as concentrations exceed 20µg/l. This is characterized by symptoms of irritability, muscular stiffness and pain, loss of appetite, and nausea. The concentrations of Fe and Zn conform to the FME (1999) standard for water while that of Hg and Pb did not conform to the FME (1999) standard for water (Figure 4.4).

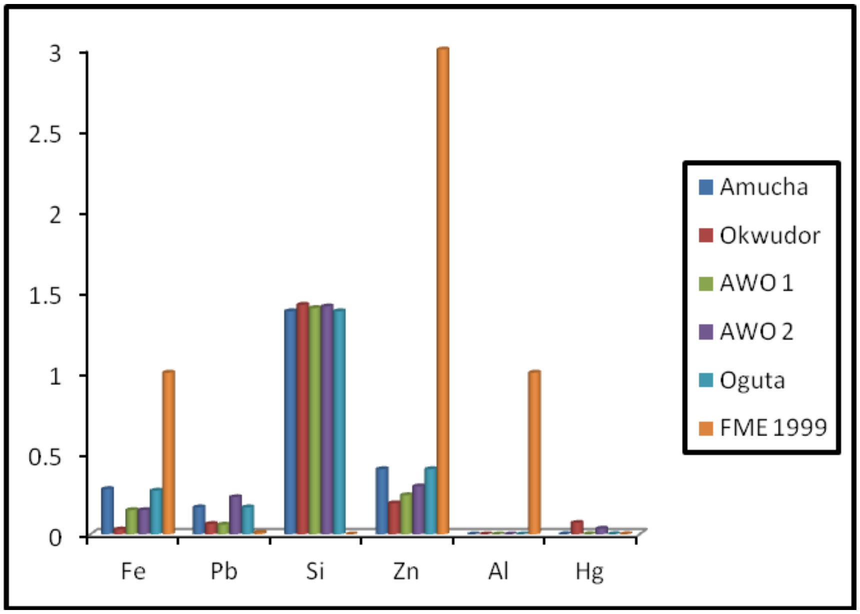

Figure 4.4: Mean Concentration of Heavy Metals in Njaba River

4.1.4 Microbial Assay

Microbial presence in a water body is an index of biological pollution (Pipes, 1981). The Total Bacteria Count at the five stations was all1.4 x 10^6, 1.4 cfu/ml respectively. The presence of faecal coliform in the studied water samples further indicated faecal contamination of the river. The Total Coliform Count ranges from2.4 x 10^4 to 5.8 x 10^5, cfu/ml. The Total E. Coli Count ranges from 5.8 x 10^5 to

6.6×10^4 cfu/ml. The Pseudomonas ranges from 1.6×10^4 to 1.8×10^5, cfu/ml. The Total Vibro Bacterial Count was from 2.8×10^4 to 6.0×10^5 cfu/ml respectively. The Total Fungi Count was Not Detected at all stations. The values for all the parameters exceeded the FME (1999) standard for water.

Therefore, the poor microbial assay of the river is typical of most surface water resources in the tropics. According to Ahiarakwem & Onyekuru (2011), the bacteriological quality of most of the stream waters in the tropics is poor, mainly due to pollution from widespread and indiscriminate human and animal defecation and very poor waste disposal practices. This condition is a major cause of diseases such as cholera, dysentery, and typhoid, among others in the area (Ahiarakwem & Onyekuru, 2011).

4.1.5 Sodium Adsorption Ratio (SAR)

The table below depicts the sodium absorption ratio (SAR) values of the five stations in the study area. Sodium content is used to classify water quality for agricultural purposes because its reaction with soil reduces soil permeability.

Table 4.2: Sodium Absorption Ratio (SAR) of Njaba River

Sample	**Na^+, mg/l**	**Mg^+, mg/l**	**Ca^+, mg/l**	**SAR**
Amucha	0.264	0.584	0.295	0.39
Okwudor	0.283	0.474	0.225	0.48
AWO 1	0.250	0.450	0.265	0.42
AWO 2	0.294	0.569	0.542	0.39
Oguta	0.334	0.445	0.346	0.58

The computed SAR ratio values at the five stations range from 0.39 to 0.58 respectively (Table 4.2). According to the United States department of agriculture (1965), water with SAR value of 1 to 10 is classified as excellent for irrigation purposes while those with SAR values above 26 are considered poor. (see table 2.1) Thus, the SAR values of the five stations were within the range of 1-10 which is excellent for irrigation purposes.

4.1.6 Pollution Index (PI)

The table below shows the pollution index of the Njaba River according to water samples evaluated at the five stations. The pollution index is an index number system for rating water quality developed by Houston (1965).

Table 4.3: Pollution Index of Njaba River

		Mean Concentration (C_{ij})					**(C_{ij}/L_{ij})**				
Parameters	**L_{ij}**	**Amucha**	**Okwudor**	**Awommamma 1**	**Awommamma 2**	**Oguta**	**Amucha**	**Okwudor**	**Awommamma 1**	**Awommamma 2**	**Oguta**
Ph	8.5	6.77	6.44	6.65	6.61	6.76	0.77	0.79	0.78	0.78	0.79
TDS mg/l	500.00	19.00	7.00	13.00	35.25	18.75	0.038	0.014	0.026	0.071	0.038
Total Chloride	250.00	30.00	25.36	27.09	28.47	26.61	0.12	0.10	0.11	0.11	0.11
HCO_3^- mg/l	30.00	42.50	19.50	36.00	40.50	38.50	1.417	0.650	1.200	1.350	1.283
SO_4^- mg/l	400.00	10.00	4.50	4.88	9.50	10.00	0.025	0.011	0.012	0.024	0.025
Total							2.37	1.57	2.13	2.34	2.25
Mean							0.47	0.31	0.43	0.47	0.45
PI							1.06	0.60	0.90	1.00	0.96

The mean Pollution Indices (PI) of the Njaba River at the five stations ranges from 0.60 to 1.06 respectively (Table 4.3). It has been shown that the critical value of the Pollution Index is 1; hence, a pollution index of more than 1 indicates a very high degree of pollution (Horton, 1965). Although the values of Amucha and Awommamma 2 stations are at a critical value which is indicative of a high rate of degradation of the river resource especially through the high influx of wastes disposal along the river channel. However, there is a need to monitor the PI value of Awommamma 1 and Oguta stations since they are already tending to the critical value of 1.

4.1.7 Constituent Budget

The tables below show the constituent budget of Njaba River at Okwudor and Oguta for eight and seven years respectively.

Table 4.4: Constituent Budget of Njaba River at Okwudor

Parameters	2011 (A)	2019 (B)	Time Interval (Δt)	B-A (ΔC_{ic})	$\Delta C_{ic}/\Delta t$	Percentage Increase	Percentage Decrease
Ca^{2+} (mg/l)	4.4	4.50	8	0.10	0.013	2.27	
Mg^{2+} (mg/l)	0.18	5.78	8	5.60	0.70	3111	
Na^{+} (mg/l)	6.40	6.50	8	0.10	0.013	1.56	
K^{+} (mg/l)	1.60	15.00	8	13.40	1.68	837	
HCO^{-}_{3} (mg/l)	24.50	19.50	8	-5.0	-0.63		-20.41
SO^{2-}_{4}(mg/l)	4.20	6.50	8	2.30	0.29	54.76	
NO^{-}_{3} (mg/l)	0.22	1.40	8	1.18	0.15	536	
Cl^{-}(mg/l)	1.60	25.36	8	23.73	2.97	1485	
PO^{-3}_{4}(mg/l)	0.20	0.70	8	0.50	0.063	10	

Table 4.5: Constituent Budget of Oguta Lake

Parameters	**2012 (A)**	**2019 (B)**	**Time Interval (Δt)**	**B-A (ΔC_{ic})**	**$\Delta C_{ic}/\Delta t$**	**Percentage Increase**	**Percentage Decrease**
Ca^{2+} (mg/l)	2.91	6.92	7	4.010	0.57	137.80	
Mg^{2+} (mg/l)	1.12	5.43	7	4.310	0.62	384.82	
Na^{+} (mg/l)	4.60	7.69	7	3.090	0.44	67.17	
K^{+} (mg/l)	1.62	17.11	7	15.49	2.21	956.17	
HCO^{-}_{3} (mg/l)	17.90	38.50	7	20.60	2.94	115.08	
SO^{2-}_{4} (mg/l)	3.39	10.00	7	6.610	0.94	194.98	
NO^{-}_{3} (mg/l)	1.49	1.26	7	-0.23	-0.03		-15.44
Cl^{-} (mg/l)	1.09	26.61	7	25.52	3.64	2341	
PO^{3-}_{4} (mg/l)	0.19	1.14	7	0.950	0.14	500	

The constituent budget of the river Okwudor and Oguta over the period of eight and seven years (2011 – 2019) and (2012 – 2019) respectively (Tables 4.3 and 4.4) indicates continuous loading in the concentrations of the following constituents (**Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO^{2-}_4, NO^{-}_3, Cl^{-}** and **PO^{3-}_4**) into the Njaba river at Okwudor with their values ranging from 0.013 to 2.97 mg/l respectively (Table 4.3) and the following constituents (**Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO^{-}_3, SO^{2-}_4, Cl^{-}** and **PO^{3-}_4**) with values ranging from 0.44 to 3.64 mg/l respectively at Oguta lake (Table 4.4).

However, there is a decline in the concentration of bicarbonate(-0.6 mg/l) at Okwudor and Nitrate(-0.03 mg/l) at Oguta lake (Table 4.3 and 4.4) respectively. Chloride has the highest loading rate at Okwudor and Oguta lake (2.97mg/l and 3.64mg/l) respectively while the lowest loading rate at Okwudor were bicarbonate (-0.63mg/l) at Okwudor and nitrate (-0.03mg/l) at Oguta lake. The constituent budget also shows that the percentage increase of the following constituents (**Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO^{2-}_4, NO^{-}_3, Cl^{-}** and **PO^{3-}_4**) at Okwudor were 2.27, 3111, 1.56, 837, 54.76, 536, 1485 and 10% respectively while **HCO^{-}_3** had a percentage decrease of -20.41% at Okwudor (Figures 4.5 and 4.6). At Oguta lake, the percentage increase of the following constituents (**Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO^{-}_3, SO^{2-}_4, Cl^{-}** and **PO^{3-}_4**) were 137.80, 384.82, 67.17, 956.17, 115.08, 194.98, 2341 and 500% respectively while **NO^{-}_3** had a percentage decrease of -15.44% at Oguta lake. (Figures 4.7 and 4.8)

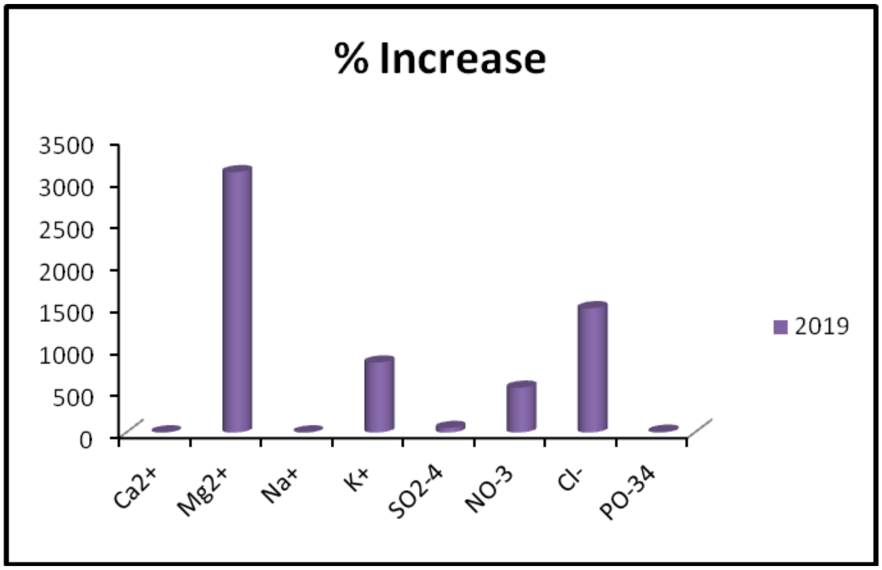

Figure 4.5: Percentage increase of constituents of Njaba River at Okwudor

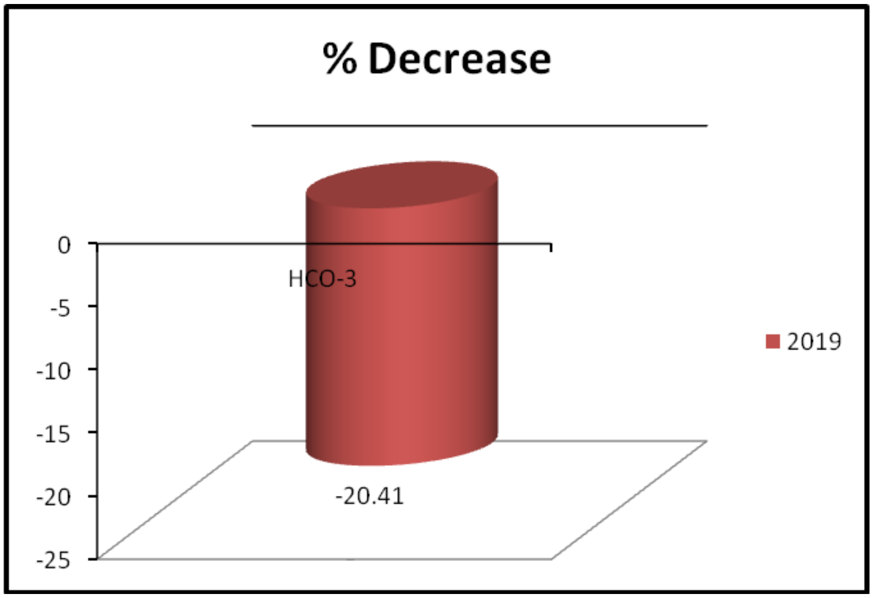

Figure 4.6: Percentage decrease of constituents of Njaba River at Okwudor

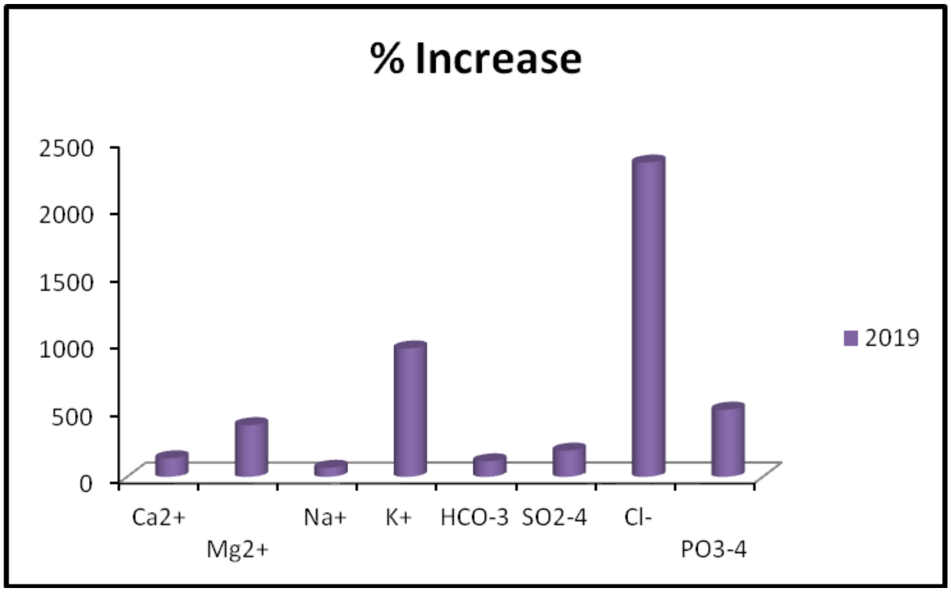

Figure 4.7: Percentage increase of constituents of Oguta

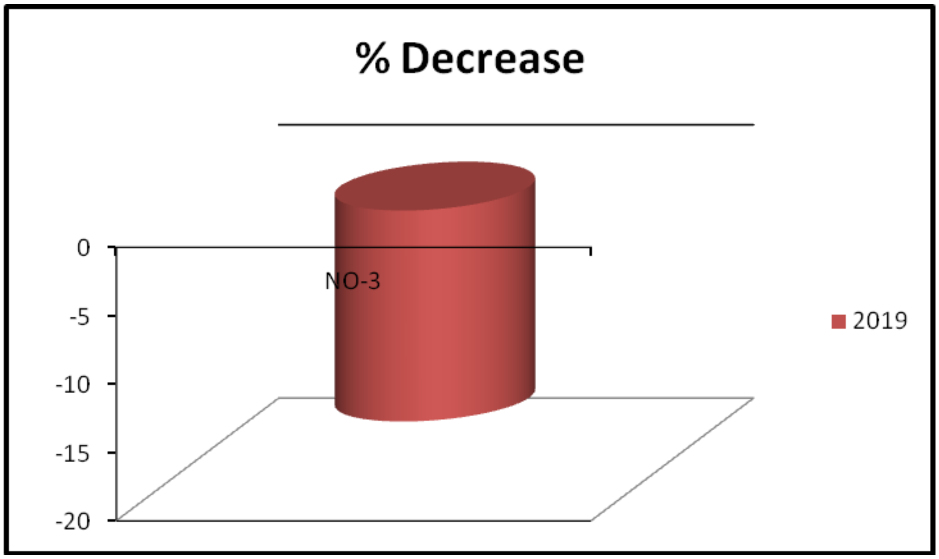

Figure 4.8: Percentage decrease of constituents of Oguta

The constituent budget indicates continuous loading of constituents into the river but at a very slow rate. Since the majority of the constituents are increasing and few are decreasing, the loading trend is therefore said to be erratic. The continuous loading of constituents was a result of chemical reactions and activities such as waste disposal and other anthropogenic activities within and around the Njaba watersheds. Generally, the constituent loading and constituent peak risk did not affect the water quality as all the constituents conform to the Federal Ministry of Environment (FME, 1999) standard for safe drinking water.

Table 4.6: The Mean Concentrations of Constituents of Njaba River in Milliequivalent/Liter (meq/l)

Parameters	Equivalent mass	**Amucha**		**Okwudor**		**Awommamma 1**		**Awommamma 2**		**Oguta**		**Amucha**	**Okwudor**	**Awommamma 1**	**Awommamma 2**	**Oguta**
		Mean (mg/l)	**Mean (meq/l)**	**Mean (mg/l)**	**Mean (meq/l)**	**Mean (mg/l)**	**Mean (meq/l)**	**Mean (mg/l)**	**Mean (meq/l)**	**Mean (mg/l)**	**Mean (meq/l)**	**% epm**	**% epm**	**% epm**	**% epm**	**% epm**
Ca	20	5.89	0.295	4.50	0.225	5.30	0.265	10.83	0.542	6.93	0.346	19.32	16.47	19.20	29.85	22.15
Mg	12.2	7.12	0.584	5.78	0.474	5.50	0.450	6.95	0.569	5.43	0.445	38.24	34.69	32.61	31.33	28.49
Na	23	6.07	0.264	6.50	0.283	5.76	0.250	6.77	0.294	7.69	0.334	17.29	20.72	18.12	16.19	21.38
K	39.1	15.00	0.384	15.00	0.384	16.25	0.415	16.06	0.411	17.11	0.437	25.15	28.11	30.07	22.63	27.98
TOTAL CATIONS (meq/l)			**1.527**		**1.366**		1.380		**1.816**		**1.562**	**100**	**100**	**100**	**100**	**100**
HCO_3^-	61	42.50	0.697	19.50	0.319	36.00	0.590	40.50	0.664	38.50	0.631	39.40	32.45	44.19	25.17	36.43
SO_4^{2-}	48	10.00	0.208	4.50	0.093	4.88	0.102	9.50	0.198	10.00	0.208	11.76	9.460	7.640	7.505	12.01
NO_3	62	1.20	0.019	1.40	0.223	3.95	0.064	1.36	0.022	1.26	0.020	1.074	22.69	4.794	0.834	1.155
Cl^-	35.5	30.00	0.845	12.00	0.348	20.00	0.579	62.25	1.754	31.00	0.873	47.77	35.40	43.37	66.49	50.40
TOTAL ANIONS (meq/l)			**1.769**		**0.983**		**1.335**		**2.638**		**1.732**	**100**	**100**	**100**	**100**	**100**
SAR			**0.39**		**0.48**		**0.42**		**0.39**		**0.58**					

4.1.8 Graphical Methods of Geochemical Interpretation

The graphical methods of geochemical interpretation shed light on the various types of water regimes to which the five sampling stations belong. They are briefly described below according to the charts.

Piper Diagram

This is a graphical representation of the chemistry of a water sample or samples (Piper, 1944 &1953). Many analyses can be plotted on the same diagram and are useful in classifying waters by hydrochemical facies. Piper diagram is convenient to identify the mixing of waters and can track changes through space and time (Ghoraba and Khan, 2013).

From the plots, it is seen that the majority of water samples of the five stations fall within the right side indicating that they are saline water which is typical of marine and deep ancient waters (Ghoraba and Khan, 2013). They further fall within the potable water zone of the diamond portion of the Piper diagram (Figure 4.9).

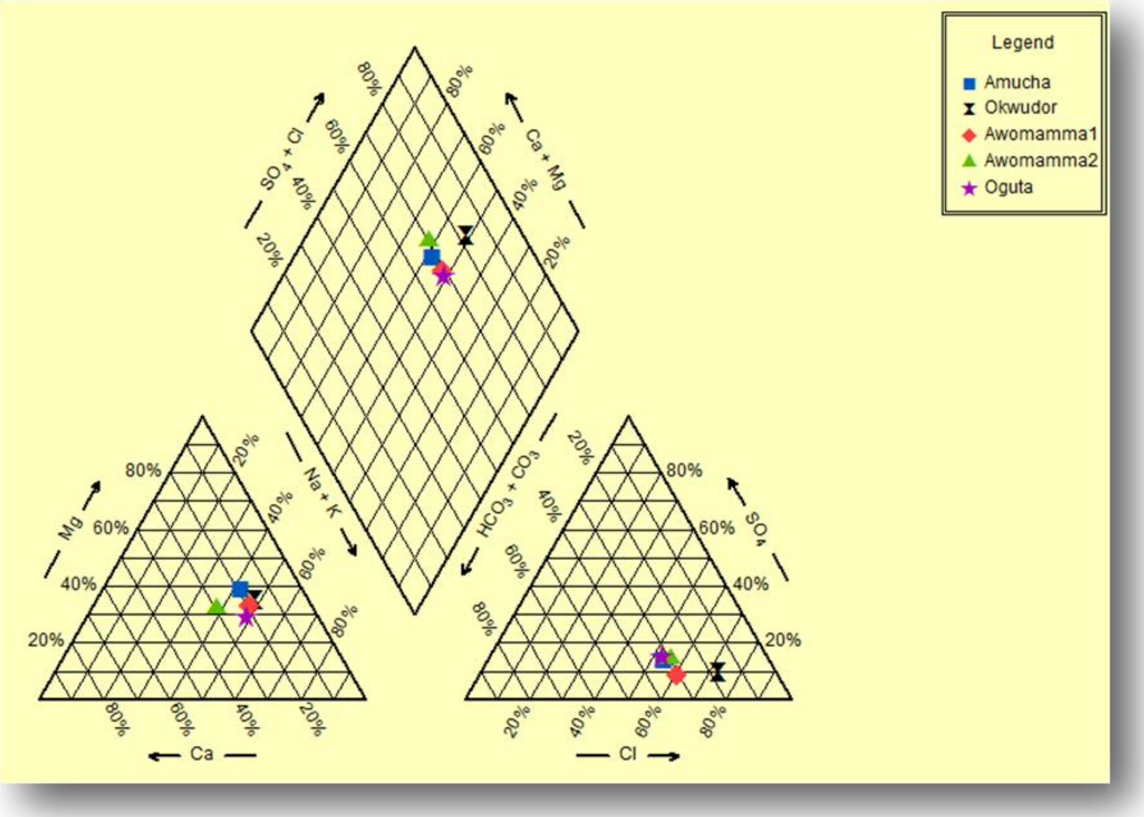

Figure 4.9: Piper Diagram

Durov Diagram

The plot reveals useful properties for large sample groups (Durov, 1948). The main purpose of the Durov diagram is to show the clustering of data points to indicate samples that have similar compositions (Durov, 1948; Ghoraba and Khan, 2013). The Durov diagram can be used to plot all samples in the open database or selected sample groups (Yousef et al., 2009).

The pH part of the plot reveals that water in the river is slightly acidic which is not good for drinking. The electrical conductivity of the river lies in the range of FME (1999) standard for drinking water (Figure 4.10).

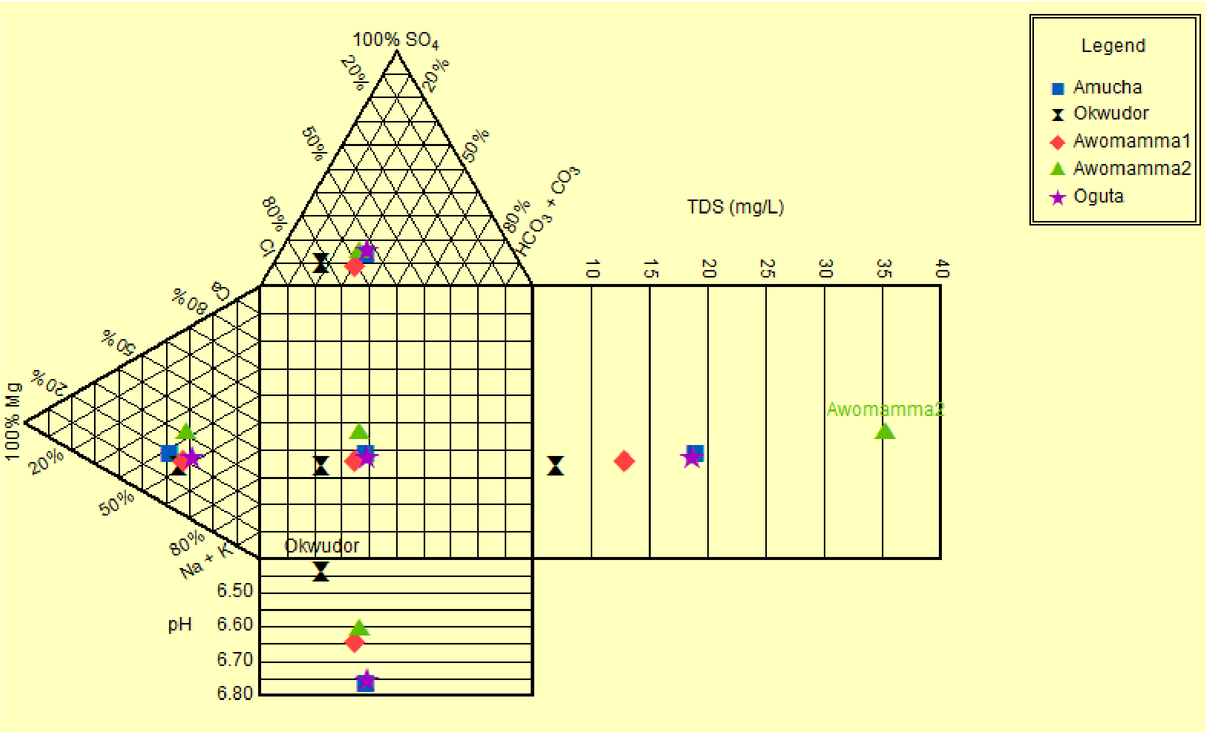

Figure 4.10: Durov Diagram

Schoeller Diagram

The diagram gives absolute concentration but the line also gives the ratio between two ions in the same sample. The Schoeller semi-logarithmic diagram (Schoeller, 1960 &1977) allows the major ions of many samples to be represented on a single graph, in which samples with similar patterns can easily be discriminated. The Schoeller diagram shows the total concentration of major ions in log-scale (Ghoraba and Khan, 2013).

The Schoeller diagram of the study area shows all the main ionic constituents in the water samples (Figure 4.11). The relative tendency of ions in mg/l shows $Cl^- > Na^+ K^+ > HCO_3^- > Mg^{2+} > Ca^{2+} > SO_4^{2-}$. The hydrogeochemical facies identified in the study area is mainly the water type Na^+ $K\text{-}Cl^-$ water type.

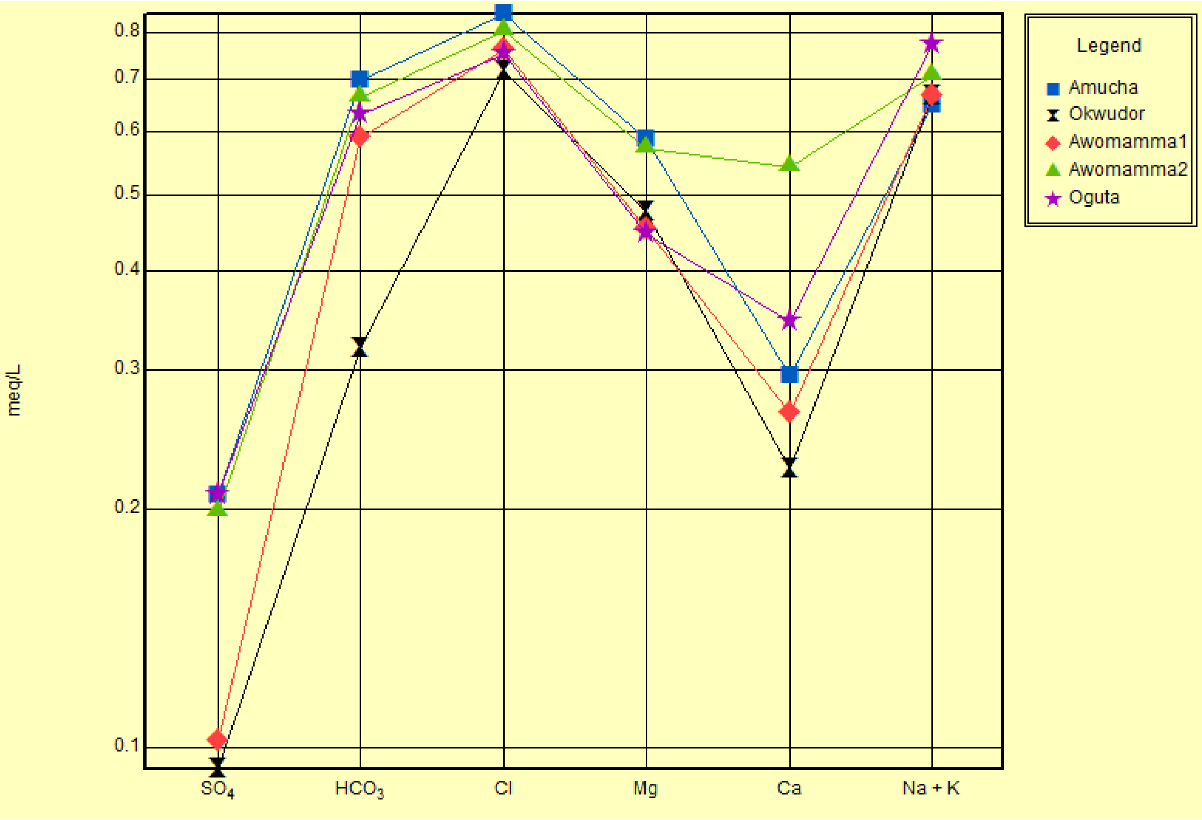

Figure 4.11: Schoeller Diagram

Stiff Diagram

The Stiff pattern is a polygon that is created from three (or four) parallel horizontal axes extending on either side of a vertical zero axes (Stiff, 1951; Ghoraba and Khan, 2013). The patterns tend to maintain their shape upon concentration or dilution, thus visually allowing us to trace the flow paths on maps (Stiff, 1951).

The Stiff diagram at the five stations reveals a similar shape which depicts Na^+ $K\text{-}Cl^-$ water type (Figure 4.12, 4.13, 4.14, 4.15, and 4.16).

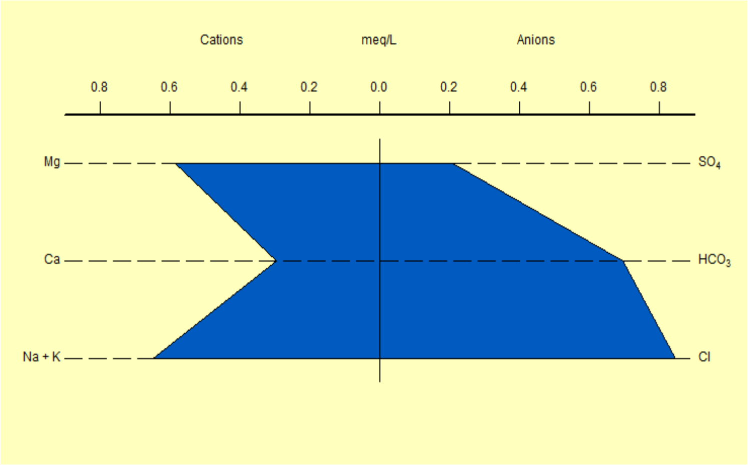

Figure 4.12: Stiff diagram for Amucha

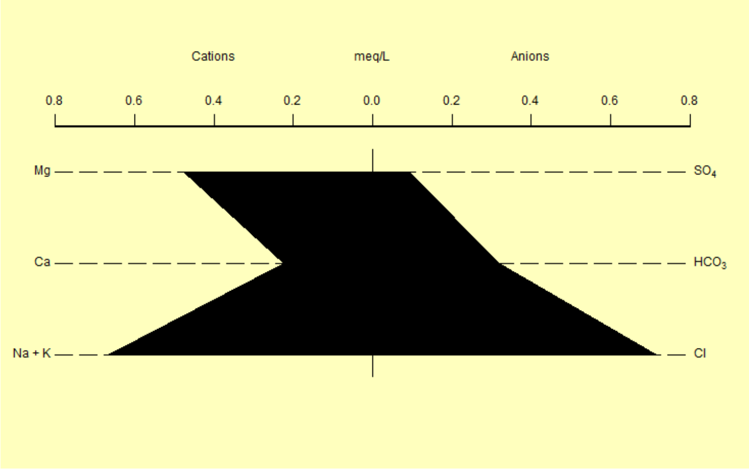

Figure 4.13: Stiff diagram for Okwudor

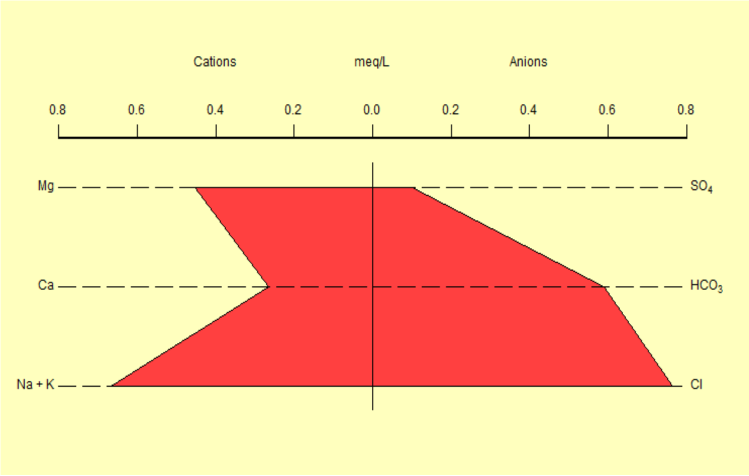

Figure 4.14: Stiff diagram for Awomamma 1

Figure 4.15: Stiff diagram for Awomamma 2

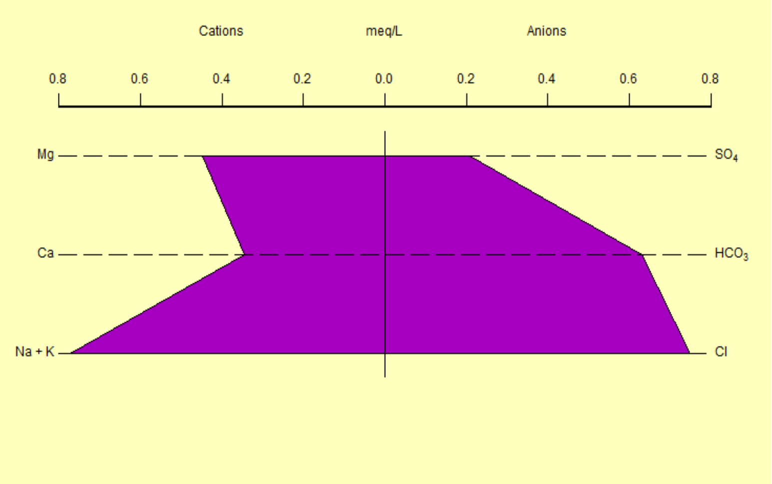

Figure 4.16: Stiff diagram for Oguta

Ionic Balance

This shows the balance of both cation and anion in the water sample from the river at various stations respectively (Figure 4.17-4.21). For Amucha, anions were higher than cations, at Okwudor cations was higher than anions, at Awomamma 1, anions were higher than cations, at Awomamma 2 cations were higher than anions while at Oguta anions was slightly higher than cations. This depicts that the ions are well balanced with the river at the five stations.

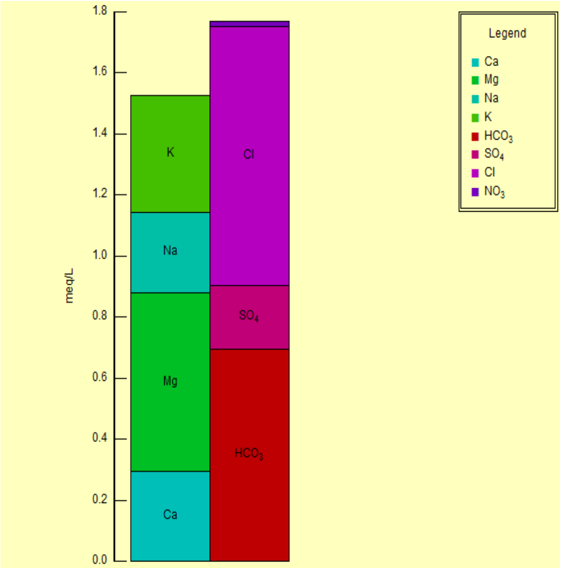

Figure 4.17: Ionic balance for Amucha

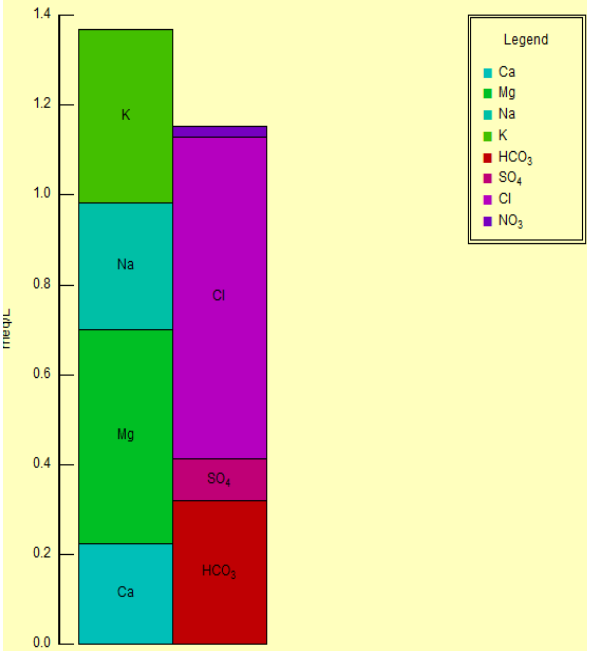

Figure 4.18: Ionic balance Okwudor

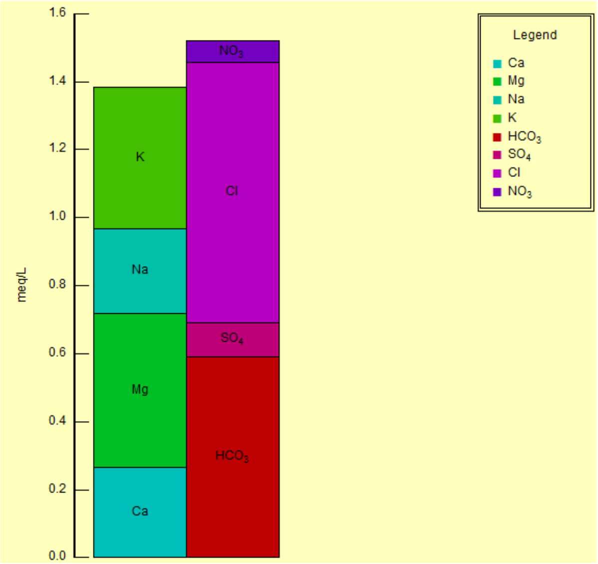

Figure 4.19: Ionic balance Awomamma 1

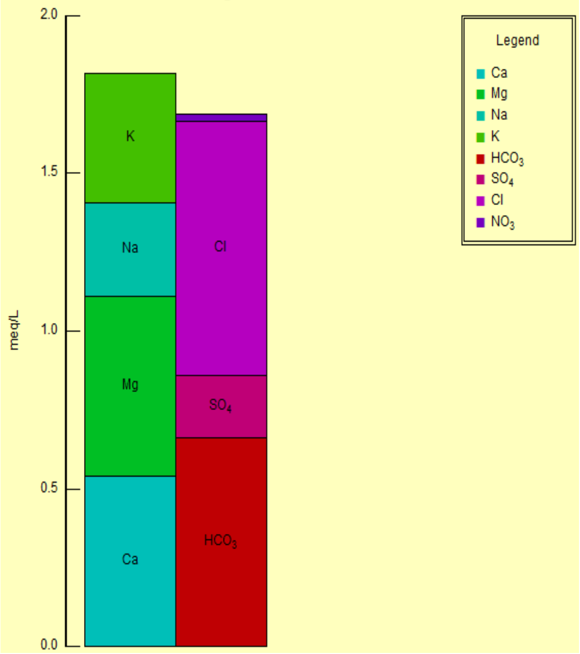

Figure 4.20: Ionic balance Awomamma 2

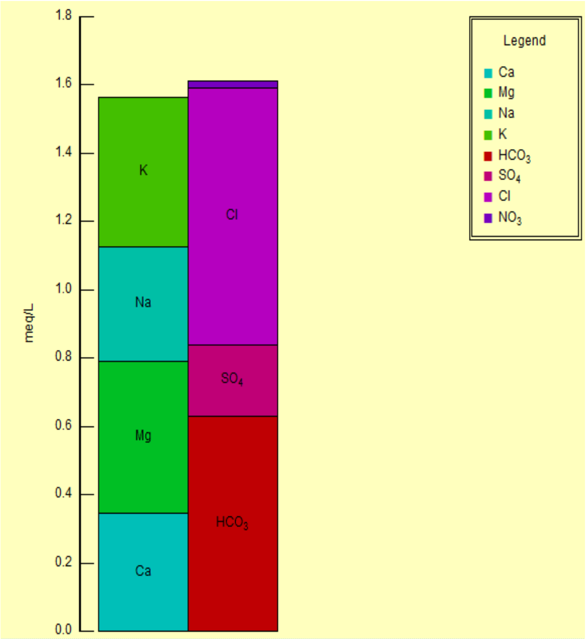

Figure4.21:IonicbalanceOguta

The table below depicts the physicochemical and biological characteristics of soil samples around the five stations of the Njaba River. It also shows the entire result of the soil data collected and processed for results interpretation with the outlined standard for comparison.

Table 4.7: Results of Soil Samples

PARAMETER	**FME STD. 2006**	**AMUCHA SOIL**	**OKWUDOR SOIL**	**AWOMMAMMA**	**AWOMMAMMA 2**	**OGUTA**
Coordinates		N 5^0 697^l E 7^0 060^l	N 5^0 714^l E 7^0 001^l	N 5^0 680^l E 7^0 938^l	N 5^0 690^l E 7^0 505^l	N 5^0 705^l E 6^0 808^l
Ph	6.50	6.24	6.64	6.64	6.24	6.24
Conductivity, µS/cm	100.00	ND	10.00	10.00	ND	ND
Total chloride, mg/kg Cl^-	250.00	139.96	126.96	126.96	139.96	139.96
Calcium, mg/kg Ca	200.00	4.21	4.21	4.21	4.21	4.21
Magnesium, mg/kg Mg	100.00	6.53	6.53	6.53	6.53	6.53
Carbonate, mg/kg CO^-_3	150.00	17.8	19.9	19.9	17.8	17.8
Total Nitrogen, % N	NS	0.25	0.34	0.34	0.25	0.25
Mercury, mg/kg Hg	0.001	ND	0.415	0.415	ND	ND
Nitrate, mg/kg NO^-_3	20.00	25.50	22.80	22.80	25.50	25.50
Phosphate, mg/kg PO^{-3}_4	>100.00	1.90	1.40	1.40	1.90	1.90
Sulphate, mg/kg SO^-_4	100.00	ND	5.00	5.00	ND	ND
Sodium, mg/kg Na	NS	5.60	7.41	7.41	5.60	5.60
Potassium, mg/kg K	>100.00	40.00	15.00	15.00	40.00	40.00
Lead, mg/kg Pb	0.05	0.066	0.020	0.020	0.066	0.066
Silicon, mg/kg Si	NS	0.38	0.40	0.40	0.38	0.38
Aluminium, mg/kg Al	<0.01	ND	ND	ND	ND	ND
Zinc, mg/kg Zn	5.00	0.163	0.080	0.080	0.163	0.163
Total Bacteria Count, cfu/g	NS	8.7×10^5	1.3×10^6	1.3×10^6	8.7×10^5	8.7×10^5
Total Coliform Count, cfu/g	NS	1.4×10^5	2.5×10^5	2.5×10^5	1.4×10^5	1.4×10^5

Total E. Coli Count, cfu/g	NS	1.2 x 10^4	1.4 x 10^5	1.4 x 10^5	1.2 x 10^4	1.2 x 10^4
Pseudomonas,cfu/g	NS	NG	1.0 x 10^4	1.0 x 10^4	NG	NG
Total Vibro-bacterial count, cfu/g	NS	4.0 x 10^3	7.0 x 10^4	7.0 x 10^4	4.0 x 10^3	4.0 x 10^3
Total Fungi, cfu/g	NS	NG	NG	NG	NG	NG

4.2 SOIL SAMPLES

4.2.1 Physical Parameters of the Njaba Soil

The mean concentrations of pH at the five stations range from 6.24 to 6.64 respectively (Table 4.7 and Figure 4.22). While the values for Electrical Conductivity were not detected at Amucha, Awommamma 2, and Oguta stations, the values for the remaining two stations Okwudor and Awommamma 1 were 10.00, 10.00 b µS/cm respectively (Table 4.7 and Figure 4.23). The pH values indicated conformity to the FME (2006) Standard for soil even though they were all slightly acidic. The Electrical Conductivity also conformed to the FME standard at the stations detected.

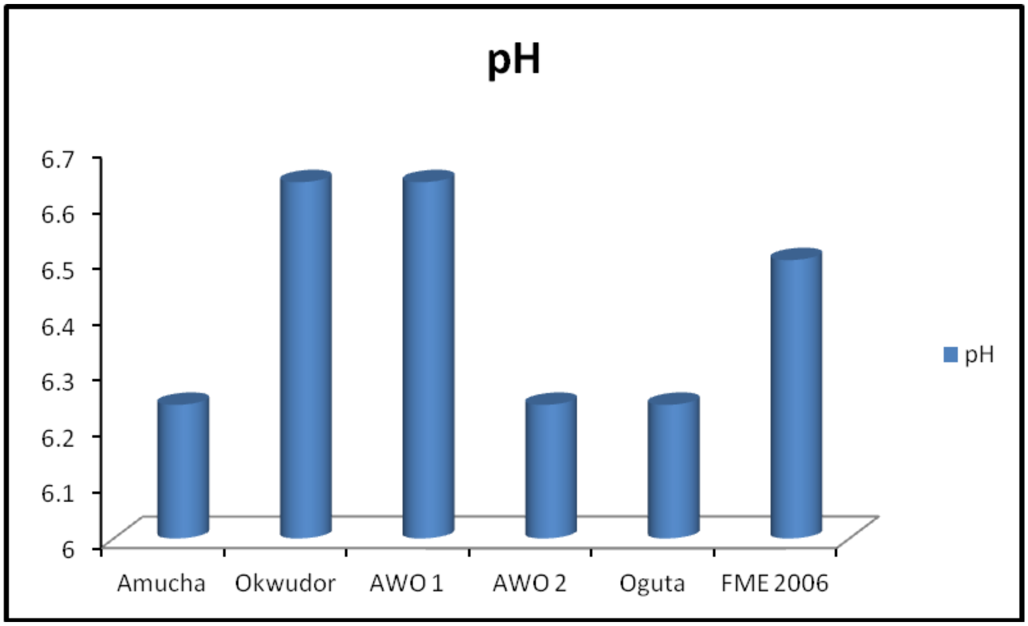

Figure 4.22: Mean pH Values for Njaba Soil

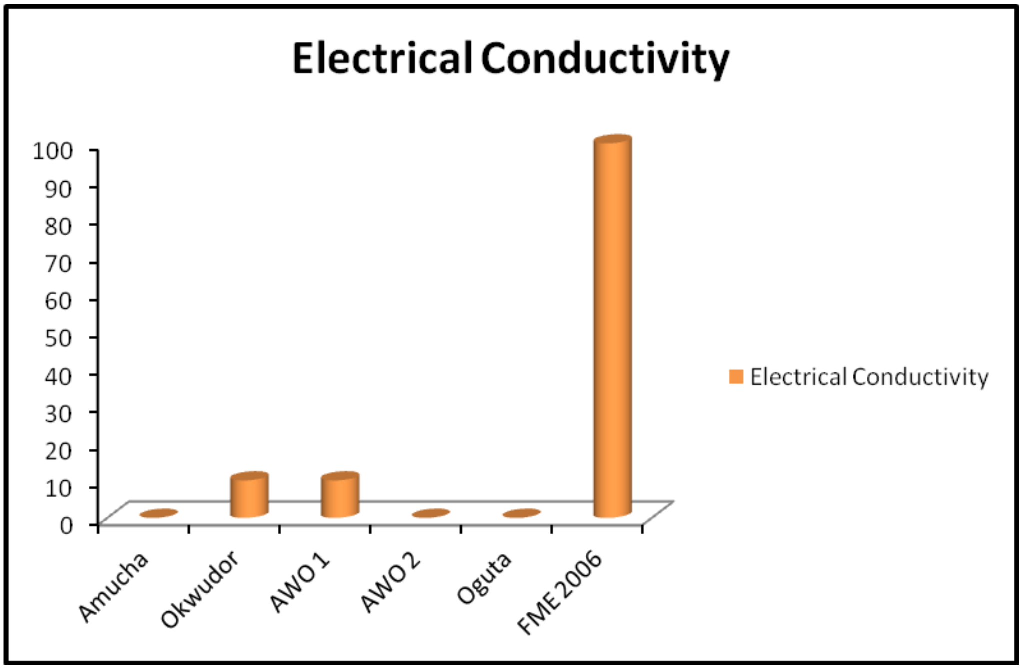

Figure 4.23: Mean Electrical Conductivity Values for Njaba Soil

4.2.2 Chemical Parameters of the Njaba Soil

Major Cations and Anions

The mean concentrations for Ca^{2+} were all 4.21 mg/kg respectively. The values of Mg^{2+} were all 6.53 mg/kg respectively. The concentration values of Na^{+} range from5.60 to 7.41 mg/kg while the values for K^{+} were 15.00 to 40.00 mg/kg respectively. The values for N ranges from 0.25 to 0.34 mg/kg. The values for the major cations such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and N conformed to the FME (2006) Standard for soil.

The mean concentration values for NO^{-}_{3} ranges from 25.50 to 25.50 mg/kg. The values of Cl^{-} range from126.96 to 139.96 mg/kg respectively. The values for SO^{-}_{4} at **Amucha, Awommamma 2**, and **Oguta** stations were not detected but the values for the remaining stations were 5.00 and 5.00 mg/kg respectively while the values for PO^{3-}_4 range from 1.40 to 1.90mg/kg and CO^{-}_3 ranges from 17.8 to 19.9.mg/kg respectively. Except for $NO^{-}_3$the values for other major anions such as Cl^{-},SO^{-}_4, $PO^{3-}_{4,}$ and CO^{-}_3 did conform to the FME (2006) Standard for soil.

4.2.3 Heavy Metals

The mean concentrations for Hg at **Amucha, Awommamma 2**, and **Oguta** were not detected but the values of the remaining two stations were 0.415 and 0.415 Mg/kg respectively (Figure 4.24). The values for Pb ranges from 0.020 to 0.066 Mg/kg respectively. The values for Si ranges from 0.38 to 0.40Mg/kg. The values for Zn from 0.080 to 0.163 Mg/kg while that of Aluminum at the five stations were Not Detected. Except for Hg and Pb which exceeded the permissible limit which invariably indicates pollution, the values of the other heavy metals such as Zn, Al, and Si were within the permissible limit of FME (2006) Standard for soil (Figure 4.24). According to Hinojosa et al. (2004), soil contamination by heavy metals is the most important apprehension throughout the industrialized world. Heavy metal pollution not only results in adverse effects on various parameters relating to plant quality and yield but also causes changes in the size, composition, and activity of the microbial community (Yao *et al.*,2003; Singh & Kalamdhad, 2011). Therefore, heavy metals are considered one of the major sources of soil pollution. Heavy metal pollution of the soil is caused by various metals especially Cu, Ni, Cd, Zn, Cr, and

Pb (Hinojosa *et al.*, 2004). Heavy metals indirectly affect soil enzymatic activities by shifting the microbial community which synthesizes enzymes (Shun-hong *et al.*, 2009). Heavy metals exhibit toxic effects on soil biota by affecting key microbial processes and decrease the number and activity of soil microorganisms (Singh & Kalamdhad, 2011).

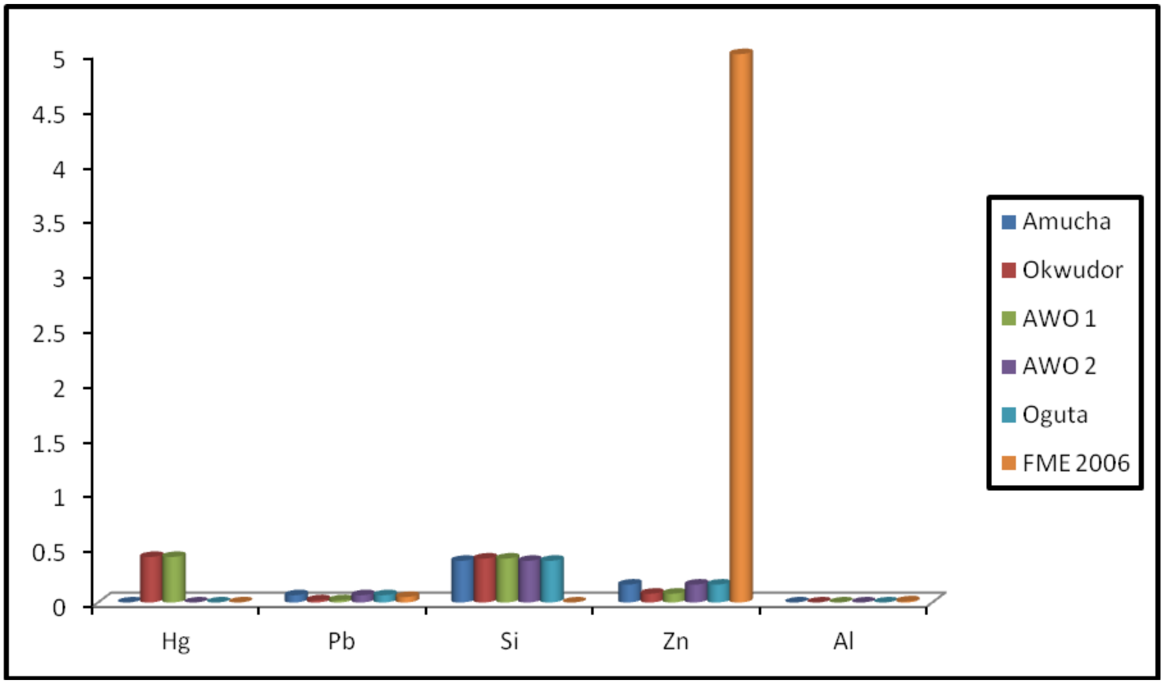

Figure 4.24: Heavy Metals of Njaba Soil

4.2.4 Microbial Assay

The Total Bacteria Count at the five stations ranges from1.3 x 10^6 to 8.7 x 10^5 cfu/ml respectively. The Total Coliform Count was1.4 x 10^5 to 2.5 x 10^5, cfu/ml respectively. The Total E. Coli Count ranges from1.2 x 10^4 to 1.4 x 10^5cfu/ml respectively. The Pseudomonas ranges were not detected at **Amucha,**

Awommamma 2, and **Oguta** stations but the values for the remaining two stations were 1.0 x 10^4 and 1.0 x 10^4 cfu/ml respectively. The Total Vibro Bacterial Count ranges from 4.0 x 10^3 and 7.0 x 10^4cfu/ml respectively while the Total Fungi Count was Not Detected at all stations. There is no standard for microbial constituents with regards to the soil but due to their high influx and presence of these microorganisms in the soil, it shows that the soil is polluted with them.

The table below shows the entire values of physicochemical and microbial characteristics of stream sediments obtained from the five stations at Njaba River. It also shows the means of comparison to a standard guideline.

Table 4.8: Results of Stream Sediments Samples

PARAMETER	FME STD. 2006	AMUCHA	OKWUDOR	AWOMMAMMA 1	AWOMMAMMA 2	OGUTA LAKE
Coordinates		N 5^0 697^l E 7^0 060^l	N 5^0 714^l E 7^0 001^l	N 5^0 680^l E 7^0 938^l	N 5^0 690^l E 7^0 505^l	N 5^0 705^l E 6^0 808^l
pH	6.50	6.30	6.52	6.52	6.30	6.30
Conductivity, µS/cm	100.00	10.00	10.00	10.00	10.00	10.00
Total chloride, mg/kg Cl^-	250.00	127.96	140.96	140.96	127.96	127.96
Calci;.um, mg/kg Ca	250.00	6.73	5.89	5.89	6.73	6.73
Magnesium, mg/kg Mg	100.00	4.74	5.34	5.34	4.74	4.74
Total Nitrogen, % N	NS	0.25	0.21	0.21	0.25	0.25
Mercury, mg/kg Hg	0.002	ND	0.277	0.277	ND	ND
Carbonate, mg/kg CO^-_3	30.00	18.5	19.6	19.6	18.5	18.5
Nitrate, mg/kg NO^-_3	20.00	17.30	18.00	18.00	17.30	17.30
Phosphate, mg/kg PO^{-3}_4	>100.00	1.20	0.80	0.80	1.20	1.20
Sulphate, mg/kg SO^-_4	100.00	25.00	ND	ND	25.00	25.00
Iron, mg/kg Fe	1.00	0.10	0.08	0.08	0.10	0.10
Sodium, mg/kg Na	NS	6.15	4.90	4.90	6.15	6.15
Potassium, mg/kg K	>100.00	25.00	20.00	20.00	25.00	25.00
Lead, mg/kg Pb	0.05	0.108	0.098	0.098	0.108	0.108
Silicon, mg/kg Si	2.00	0.642	0.823	0.823	0.642	0.642
Aluminium, mg/kg Al	<0.01	ND	ND	ND	ND	ND
Zinc, mg/kg Zn	5.00	0.114	0.051	0.051	0.114	0.114
Total Bacteria Count, cfu/g	NS	9.8 x 10^5	1.6 x 10^6	1.6 x 10^6	9.8 x 10^5	9.8 x 10^5
Total Coliform Count, cfu/g	NS	2.8 x 10^5	5.0 x 10^3	5.0 x 10^3	2.8 x 10^5	2.8 x 10^5
Total E. Coli Count, cfu/g	NS	1.0 x 10^5	6.0 x 10^4	6.0 x 10^4	1.0 x 10^5	1.0 x 10^5
Pseudomonas, cfu/g	NS	NG	NG	NG	NG	NG

Total vibro bacterial count, cfu/g	NS	NG	3.0×10^3	3.0×10^3	NG	NG
Total Fungi Count, cfu/g	NS	NG	NG	NG	NG	NG

4.3 SEDIMENT SAMPLES RESULTS

4.3.1 Physical Parameters of the Njaba Sediment

The mean concentrations of pH at the five stations range from 6.30 to 6.52respectively (Table 4.8 and Figure 4.25) while the values for Electrical Conductivity were 10.00 µS/cm at all five stations respectively (Table 4.8 and Figure 4.26). The pH values indicated conformity to the FME (2006) Standard for sediment even though they were all slightly acidic at Okwudor and Awommamma 1. The Electrical Conductivity also conforms to the FME standard at the stations detected.

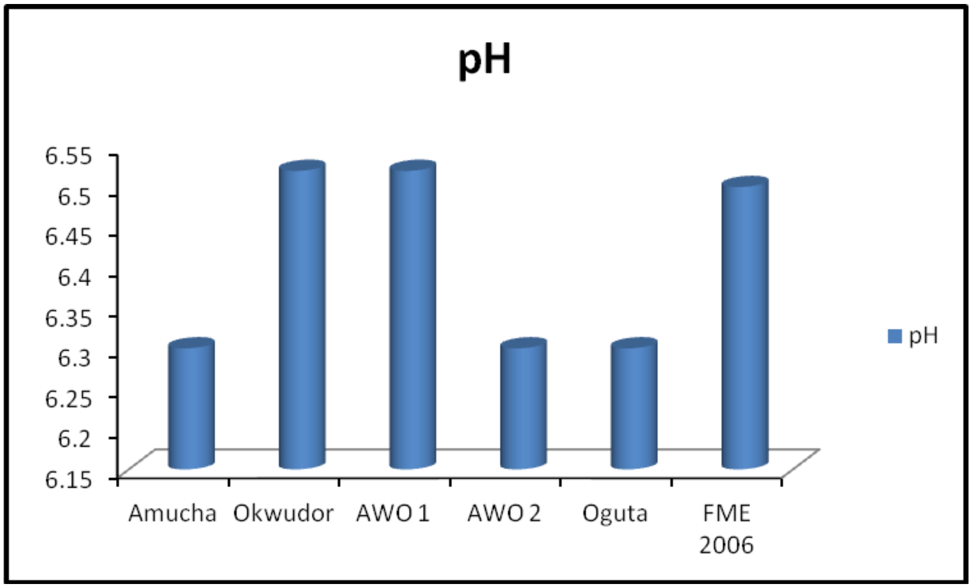

Figure 4.25: pH for Njaba Sediments

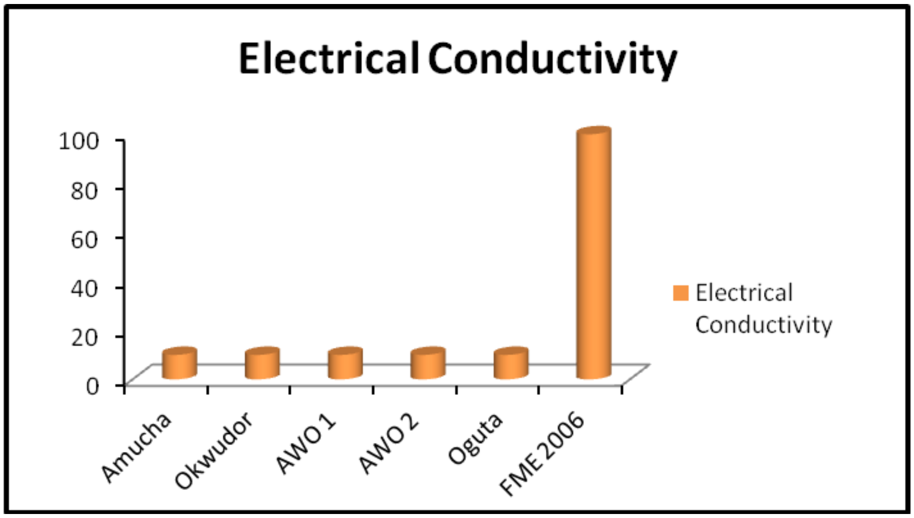

Figure 4.26: Electrical Conductivity for Sediments

4.3.2 Chemical Parameters of the Njaba Sediment

Major Cations and Anions

The mean concentrations values for Ca^{2+} range from5.89 to 6.73 mg/kg respectively. The values ofMg^{2+}ranges from 4.74 to 5.34 mg/kg respectively. The concentration values of Na^+ ranges from4.90 to 6.15 mg/kg respectively while the values for K^+ from20.00 to 25.00 mg/kg respectively. The values for the major cations such as Ca^{2+}, Mg^{2+}, Na^+, and K^+ conformed to the FME (2006) Standard for sediment.

The mean concentration values for HCO^-_3 ranges from 19.50 to 42.50 mg/l respectively. The values for NO^-_3 ranges from 17.30 to 18.00 mg/kg respectively. The values of Cl^- ranges from 127.96 to 140.96 mg/kg respectively while the values for PO^{3-}_4 range from 0.80 to 1.20 mg/kg respectively. The values for SO^-_4were not detected at **Okwudor** and **Awommamma 1** stations but the remaining three stations with values of 25.00, 25.00, and 25.00 mg/kg respectively while CO^{-}_{3} ranges from 18.5 to 19.6 mg/kg respectively. The values for other major anions such as Cl^{-},SO^{-}_{4}, $PO^{3-}_{4,}$ $NO^{-}_{3,}$ and CO^{-}_{3} did conform to the FME (2006) Standard for sediment.

4.3.3 Heavy Metals

The mean concentrations of heavy metals at the five stations for Fe range from 0.10 to 0.08 mg/kg respectively (Table 4.8 and Figure 4.27). The values for Hg were not detected at **Amucha, Awommamma 2**, and **Oguta** stations but were with 0.277 and 0.277Mg/kg respectively at the remaining two stations. The values for Pb ranges from 0.098 and 0.108 mg/kg respectively. The values for Si ranges from 0.642 to 0.823 mg/kg respectively. The values of Zn ranges from 0.114 to 0.051, mg/kg respectively while that of Aluminum at the five stations was not detected. Except for Hg and Pb, the values of the other heavy metals such as Fe, Zn, Al, and Si were within the permissible limit of the FME (2006) Standard for sediment.

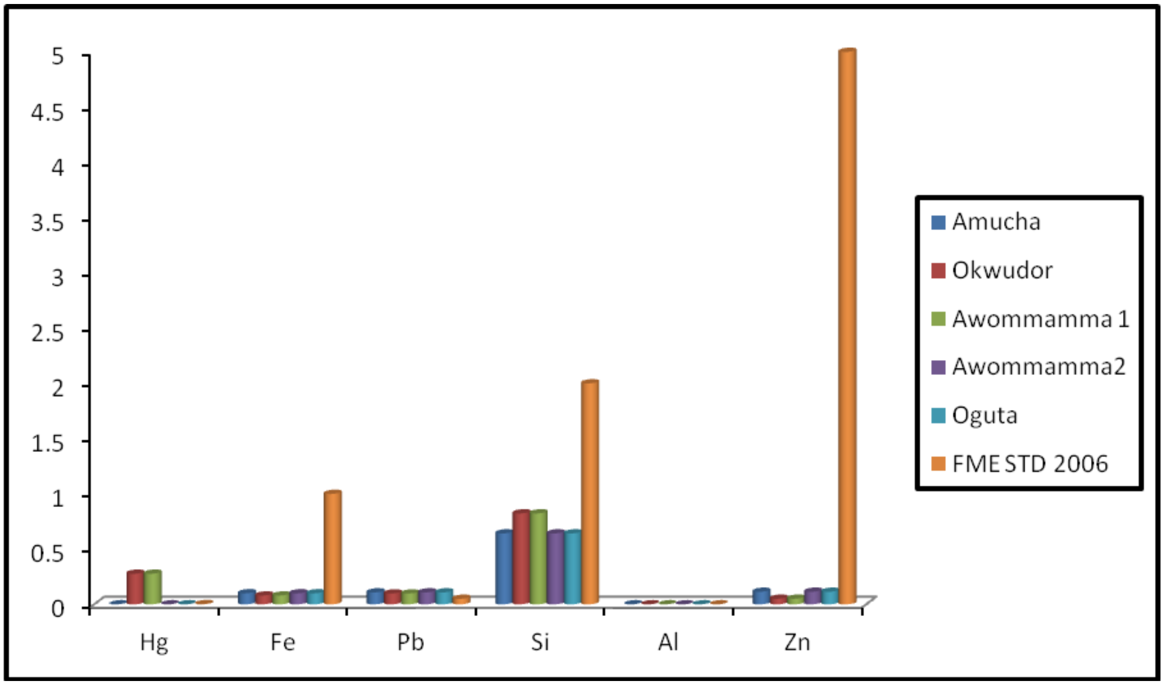

Figure 4.27: Heavy Metals for Sediments

4.3.4 Microbial Assay

The Total Bacteria Count at the five stations ranges from 1.6 x 10^6 to 9.8 x 10^5 cfu/ml respectively. The Total Coliform Count ranges from2.8 x 10^5 to 5.0 x 10^3 cfu/ml respectively. The Total E. Coli Count ranges from1.0 x 10^5 and 6.0 x 10^4 cfu/ml respectively. Pseudomonas and Total Fungi Count were Not Detected at all stations. The Total Vibro Bacterial Count was not detected at **Amucha, Awommamma 2**, and **Oguta** stations but was with3.0 x 10^3 and 3.0 x 10^3 cfu/ml respectively at the remaining two stations. There is no standard for microbial constituents with regards to sediment but due to their high influx and presence of these microorganisms in the sediment, it shows that the sediment is polluted with them.

4.4 Contamination Assessment

4.4.1 Contamination Factor

The table below depicts the values used for the calculation of heavy metal contamination factors and the pollution load index at the five stations for both water, soil, and stream sediments. The contamination factor is a method used to assess the extent of contamination of each heavy metal in soil and sediments to background concentration developed after Hakason 1980; Bonnail et al 2016.

Table 4.9: Heavy metal contamination factors (CF) and pollution load index (PLI)

PARAMETER	AMUCHA	OKWUDOR	AWOMMAMMA	AWOMMAMMA 2	OGUTA
Soil					
CF_{Hg}	-	0.415	0.415	-	-
CF_{Pb}	7.76E-4	0.020	2.35E-4	7.76E-4	7.76E-4
CF_{Al}	-	-	-	-	-
CF_{Zn}	1.2E-3	5.71E-4	5.71E-4	1.16E-3	1.16E-3
PLI	0.21	0.05	0.02	0.03	0.03
Sediment					
CF_{Hg}	-	0.277	0.277	-	-
CF_{Fe}	2.63E-6	2.10E-6	2.10E-6	2.63E-6	2.63E-6
CF_{Pb}	1.27E-3	1.15E-3	1.15E-3	1.27E-3	1.27E-3
CF_{Al}	-	-	-	-	-
CF_{Zn}	8.14E-4	3.64E-4	3.64E-4	8.14E-4	8.14E-4
PLI	0.008	0.003	0.003	0.008	0.008
Water					
CF_{Fe}	0.93	0.1	0.5	0.5	0.92
CF_{Hg}	0.1	7.1	0.1	3.5	0.1
CF_{Pb}	16.7	6.4	6.0	23	16.7
CF_{Al}	-	-	-	-	-
CF_{Zn}	0.403	0.192	0.242	0.297	0.403
PLI	0.91	0.97	0.59	1.64	0.90

From table 4.9, the values of heavy metals (Hg, Pb, Al, Fe, and Zn) contamination factor in soil reveals low contamination factor since they were all below < 1. The values for the sediments as well indicate a low contamination factor. The values obtained for the contamination factor were categorized according to Nweke and Ukpai (2016) and Ibe *et al*. (2019).

For water, the heavy metals contamination factor Indicates Fe as a low contamination factor. The values of Hg at the five stations range from 0.1 to 7.1 respectively. Except for the values at Okwudor (7.1) indicating very high contamination factor and AWO 2 (3.5) indicating considerable contamination factor, the other three stations have low contamination factors. The concentration values of Pb at the five stations range from 6.0 to 23 respectively. These values reveal a very high contamination factor which may be a result of the high influx of wastes within and around the bank of the river. The values of Al were not indicated both in soil, sediment, and water.

The pollution load index from the five locations (Amucha, Okwudor, AWO 1, AWO 2, and Oguta) for the soil and stream sediments revealed a low pollution load index (PLI <1) showing no pollution while water indicates high contamination (PLI >1) at Awo 2.

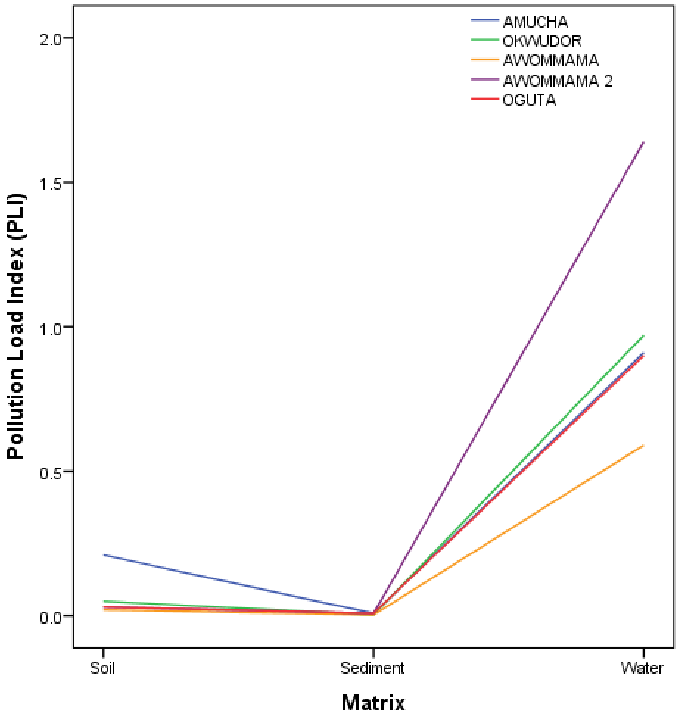

Figure 4.28:Pollution load index for heavy metals in the different matrix

4.4.2: Geo-accumulation Index (I-geo) for heavy metals

Table 4.10: Geo-accumulation Index (I-geo) for heavy metals in the five stations

PARAMETER	AMUCHA	OKWUDOR	AWOMMAMMA	AWOMMAMMA 2	OGUTA
Soil					
Hg	-	0.28	0.28	-	-
Pb	5.20E-4	0.01	1.57E-4	5.20E-4	5.20E-4
Al	-	-	-	-	-
Zn	8.04E-4	3.83E-4	3.83E-4	7.77E-4	7.77E-4
Sediment					
Hg	-	0.277	0.277	-	-
Fe	2.63E-6	2.10E-6	2.10E-6	2.63E-6	2.63E-6
Pb	1.27E-3	1.15E-3	1.15E-3	1.27E-3	1.27E-3
Al	-	-	-	-	-
Zn	8.14E-4	3.64E-4	3.64E-4	8.14E-4	8.14E-4
PLI	0.008	0.003	0.003	0.008	0.008

The geo-accumulation Index (I_{geo}) was introduced by Muller (1969). This approach involves comparing the current concentration of heavy metal in a system to pre-industrial concentrations. The values of the Geoaccumulation Index for the soil and sediments indicate uncontaminated to moderately polluted since values were within 0-1 Igeo value.

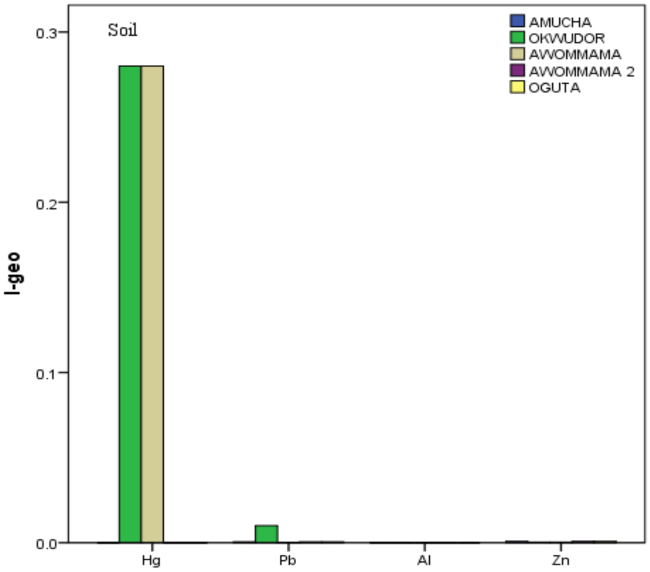

Figure 4.29: Geoaccumulation of heavy metals in soil

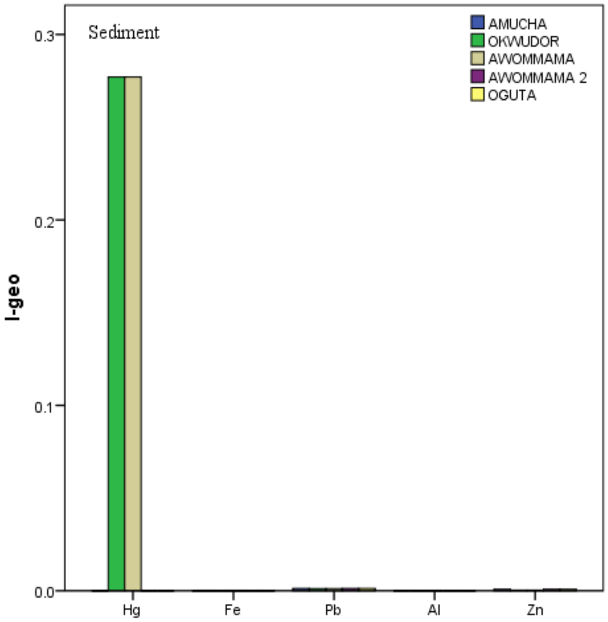

Figure 4.30: Geoaccumulation of heavy metals in sediment

4.4.3 Enrichment Factor

The tables below depict the enrichment factor for both soil and sediment samples from four-station within the study area. The Enrichment factor is a method of estimating the anthropogenic impact on soil and sediments b calculating the difference between the metals originating from human activities and those from a natural source.

Table 4.11: EF for heavy metal in soil

PARAMETER	OKWUDOR	AWOMMAMMA 1	AWOMMAMMA 2	OGUTA
Mercury, mg/kg Hg	0	0	0	0
Lead, mg/kg Pb	0.303	0.303	1.000	1.000
Silicon, mg/kg Si	1.053	1.053	1.000	1.000
Aluminium, mg/kg Al	0	0	0	0
Zinc, mg/kg Zn	0.491	0.491	1.000	1.000

Table 4.12:EF for heavy metal in Sediment

PARAMETER	OKWUDOR	AWOMMAMMA 1	AWOMMAMMA 2	OGUTA
Mercury, mg/kg Hg	0	0	0	0
Iron, mg/kg Fe	0.800	0.800	1.000	1.000
Lead, mg/kg Pb	0.907	0.907	1.000	1.000
Silicon, mg/kg Si	1.282	1.282	1.000	1.000
Aluminium, mg/kg Al	ND	ND	ND	ND
Zinc, mg/kg Zn	0.051	0.051	0.114	0.114

From the table, the values for the enrichment factor for soil at the five stations range from 0-303 to 1.00 while for sediment range from 0.800 to 1.282. Zhang & Liu (2002) reported that EF values within 0.5-1.5 indicate that the heavy metals are entirely from lithogenic or natural sources, while EF values higher than 1.5 suggest that the source is likely from human activities. This implies that from the computed EF values the concentration of heavy metals in the soils and sediments of the Njaba River are of lithogenic or natural sources. These values also indicate a deficiency in terms of enrichment since they were less than 2 (<2). Thus, the rate of addition of heavy metal within the study area is low or minimal enrichment.

CHAPTER FIVE

SUMMARY, CONCLUSION, AND RECOMMENDATIONS

5.1 Conclusion

The physical and biochemical properties of the Njaba River water samples at the five gauge stations indicated some environmental problems such as pH which was slightly acidic to alkaline in nature. This trend was also found in the soil and sediments samples. The Odour of the water was unobjectionable while the appearance was slightly brownish respectively. The presence of heavy metals such as Hg, Fe, Pb, Al, Si, and Zn was assessed. In the water, Hg and Pb were high at some stations for water, soil, and stream sediment. The microbial assay of water, soil, and sediments indicates the presence of organisms such as Ecoli bacteria, pseudomonas, fecal coliform, and fungi. These organisms reveal contamination and a poor assay of the river due to their presence.

The pollution index indicated the values of Amucha and Awommamma 2 stations are at a critical value which indicates a high rate of degradation of the river resource due to the high influx of incessant waste disposal along the channel of the river. However, there is a need to monitor the PI value of Awommamma 1 and Oguta stations since they are already tending to the critical value of 1. The constituent budget at Okwudor and Oguta over the periods of eight (8) and seven (7) years respectively indicates an increasing rate of loading of constituents within the rivers with a decline of Bicarbonate at Okwudor and Nitrate at Oguta lake.

The Njaba River is suitable for agricultural purposes based on SAR and consists of Na+K-Cl water type. Most of the Njaba River is Oligotrophic.

In terms of contamination assessment, the heavy metals (Hg, Pb, Al, Fe, and Zn) contamination factor in soil reveals low contamination factor since they were all below < 1. The values for the sediments as well indicate a low contamination factor. For water, the heavy metals contamination factor Indicates Fe as a low contamination factor. Except for the values of Hg at Okwudor indicating very high contamination factor and at AWO 2 indicating considerable contamination factor, the other three stations have low contamination factors. The concentration values of Pb at the five stations reveal a very high contamination factor which may be as a result of the high influx of wastes within and around the bank of the river. The values of Al were not indicated both in soil, sediment, and water. The pollution load index for all samples (soil, sediment, and water) at the five locations (Amucha, Okwudor, AWO 1, AWO 2, and Oguta) revealed a low pollution load index (PLI <1) showing no pollution.

The values of the Geoaccumulation Index for the soil and sediments indicate uncontaminated to moderately polluted since values were within 0-1 Igeo value.

The computed Enrichment Factor (EF) values for the concentration of heavy metals in the soils and sediments of the Njaba River are of lithogenic or natural sources.

5.2 Recommendations

In the light of these, there is a need for necessary treatment procedures which should be applied to raise the quality of the river water to the FME standards for safe drinking water. For example, the pH can be corrected (raised) using sodium bicarbonate (soda ash). Heavy metals can be treated using ascorbic acid or ion exchange methods. While the microbial assay can be improved upon subjection to treatment using chlorine.

The observed contamination and pollution trends in the Njaba River watershed are in dire need of appropriate monitoring procedures for pollution control and mitigation for sustainable development of the resource.

5.3 Contribution to Knowledge

The contribution to knowledge is as follows:

i. The present study has delineated the hydrogeochemical facies of the Njaba River.
ii. The pollution and ecological risk assessment of the Njaba river and environs have been carried out using pollution risk models.
iii. The present study has also evaluated the constituent budget of the Njaba River.

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APPENDIX

Appendix 1: Federal Ministry of Environment (1999) Standard for drinking water with permissible limit

S/NO	Parameters	Permissible limit
1	pH	6.50 -8.50
2	Odour	Unobjectionable
3	Appearance	Clear
4	Total Dissolved Solid, mg/l TDS	500.00
5	Conductivity, µS/cm	1000.00
6	Turbidity, NTU	10.00
7	Total chloride, mg/l Cl^-	250.00
8	Total hardness, mg/l $CaCO_3$	200.00
9	Calcium Hardness, mg/l $CaCO_3$	150.00
10	Magnesium Hardness, mg/l $MgCO_3$	150.00
11	Iron, mg/l Fe	1.00
12	Calcium, mg/l Ca	250.00
13	Magnesium, mg/l Mg	100.00
14	Carbonate mg/l CO^-_3	150.00
15	Mercury, mg/l Hg	0.001
16	Bi-carbonate, mg/l HCO^-_3	30.00
17	Nitrate, mg/l NO^-_3	50.00
18	Phosphate, mg/l PO^{-3}_4	<5.00
19	Sulphate, mg/l SO^-_4	200.00-400.00
20	Sodium, mg/l Na	200.00
21	Potassium, mg/l K	10.00
22	Lead, mg/l Pb	0.01
23	Aluminium, mg/l Al	1.00
24	Silicon, mg/l Si	NS
25	Zinc, mg/l Zn	3.00
26	Total Bacteria count, cfu/ml	0-30
27	Total Coliform Count, cfu/ml	0-10
28	Total E. Coli Count, cfu/ml	0
29	Pseudomonas, cfu/ml	0
30	Total vibro bacterial count, cfu/ml	0
31	Total Fungi Count, cfu/ml	0

Appendix 2: Federal Ministry of Environment (1999) Standard for Soil with permissible limit

S/NO	**Parameter**	**Permissible limit**
1	pH	6.50
2	Conductivity, µS/cm	100.00
3	Total chloride, mg/kg Cl^-	250.00
4	Calcium, mg/kg Ca	200.00
5	Magnesium, mg/kg Mg	100.00
6	Carbonate, mg/kg CO^-_3	150.00
7	Total Nitrogen, % N	NS
8	Mercury, mg/kg Hg	0.001
9	Nitrate, mg/kg NO^-_3	20.00
10	Phosphate, mg/kg PO^{-3}_4	>100.00
11	Sulphate, mg/kg SO^-_4	100.00
12	Sodium, mg/kg Na	NS
13	Potassium, mg/kg K	>100.00
14	Lead, mg/kg Pb	0.05
15	Silicon, mg/kg Si	NS
16	Aluminium, mg/kg Al	<0.01
17	Zinc, mg/kg Zn	5.00
18	Total Bacteria count, cfu/g	NS
19	Total Coliform Count, cfu/g	NS
20	Total E. Coli Count, cfu/g	NS
21	Pseudomonas,cfu/g	NS
22	Total vibro bacterial count, cfu/g	NS
23	Total Fungi, cfu/g	NS

Plate 1: Collection of water samples in the study area

Plate 2: Collection of sediment samples in the study area

Plate 3: Collection of Soil samples in the study area using Hand Auger