IMPACT OF ARTISANAL GOLD MINING ON THE QUALITY OF SURFACE WATER AND GROUNDWATER IN PARTS OF BOSSO LOCAL GOVERNMENT AREA, NIGER STATE, NIGERIA

BY

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MTech/SPS/2019/10415

DEPARTMENT OF GEOGRAPHY

FEDERAL UNIVERSITY OF TECHNOLOGY MINNA

JUNE, 2023

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A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL, FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA, NIGER STATE, NIGERIA IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTERS OF TECHNOLOGY (MTECH) DEGREE IN GEOGRAPHY (ENVIRONMENTAL MANAGEMENT)

JUNE, 2023

ABSTRACT

The target of artisanal gold miners in Bosso local government area of Niger state is the primary and alluvial gold deposits with little or no consideration for the environment thereby exploiting a lot of heavy metals associated with quartz as gangue and other sundry poisonous by-products into the environment and any available water source. The water quality in Bosso Local Government Area of Minna, Niger State, Nigeria was investigated in this study. Farming, artisanal mining and fishing are dominant along River Chanchaga. In analysing the physio-Chemical parameters the concentration of TDS in 8 locations (surface water) and 14 locations (groundwater) were higher than the recommended maximum permissible limit of 500.0 mg/l by the Nigerian Standard for Drinking Water Quality. The pH of the surface water is in the order of 4.52 to 7.05 with a mean value of 5.90 while the groundwater varied from 5.92 to 6.87 with an average value of 6.10 The results of the laboratory analysis of both the surface and groundwater samples indicate that the pH of the water in some locations is slightly low which makes the water acidic thereby aiding the movement of hard metals in water. The concentrations of all the analyzed major cations (sodium, calcium, magnesium and potassium) as well as major anions (sulphate, chloride, bicarbonate, carbonate and nitrate) are below World Health Organization maximum permissible limits. The concentration of copper in surface water ranged between 0.00 mg/l to 2.06 mg/l with a mean concentration value of 1.29 mg/l while copper concentration in groundwater varied from 0.10 mg/l to 2.38 mg/l with an average value of 1.46 mg/l which is above permissible limit of 1.00 mg/l. Water types in the area from Piper, Durov, Schoeller and Stiff diagrams revealed $Na+Ca/Cl+SO_4$ facies. Gibbs diagram also indicated that weathering is the major hydrogeochemical processes controlling the discharge of ions in water sources in the area. Water quality index indicates that the water in study area is of very poor quality while the heavy metals pollution index revealed lightly to moderately pollution with gold pathfinder elements. Bacteriologically, the water is also poor due to the presence of bacteria coliform, which is an indication of feacal contamination of water with human and or animal feaces. Open defecation as well as proximity of hand dug wells to soakaway/pit-latrines is responsible for the poor microbial quality. The surface water and groundwater from shallow hand dug wells should be treated before use for domestic purposes. Boiling of water before use is also advocated. Heavy metal accumulator plants such as Hydrilla Verticillata and Pistia Stratiotes should be planted in contaminated areas to aid removal of heavy metals from the polluted water without destroying other flora and fauna.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Artisanal gold mining is the use of rudimentary methods to extract and process gold. It is a subsistent type of mining which is largely driven by poverty and plays a large role in boosting the economic base of the low-income people living in rural communities. This type of gold mining operation impacts negatively on the environment as the gangue are disposed on the nearby soil and surface water without any precautionary measures. The rock hosting the gold usually contain other trace and pathfinder elements and the processing of crushing these rocks aids the liberation these metals into the environment (air, land or water) thereby posing a lot of environmental hazards. Artisanal mining has caused a lot of negative impacts on several communities in Nigeria (Amadi *et al.,* 2016). Gold mining is an economically profitable venture and a major point source of soil, surface and groundwater contamination. Recent studies around the world and Nigeria in particular have shown that gold is often associated with metals such as lead, copper, mercury, arsenic, manganese, nickel, iron and cobalt (Amadi *et al.*, 2016; Okunlola *et al.,* 2016). Sometimes mercury and cyanide are used by these artisanal miners to extract and concentrate fine gold particles from crushed rocks leading to the pollution of soil and water sources by heavy metals.

The target of the artisanal gold miners in Bosso area of Minna is the primary and alluvial gold deposits with little or no consideration for the environment thereby exploiting a lot of heavy metals associated with quartz as gangue and other sundry poisonous by-products into the environment and any available water source.

These hazards could set in during the gold exploitation process itself either from the tailings generated which has a lot of heavy metals in them or from the dangerous trenches created during mining. The process of getting gold out of the crushed rocks brings it into contact with people and water whereby the heavy metals contained in the rocks as gangue are deposited. Bosso Community hosts thousands of artisanal miners as a result of the discovery of a viable gold deposit along upstream as well as downstream of River Chanchaga. The area is strategic to the miners because of the availability of electricity and a large water body for processing the milled gold dust (Olasehinde *et al.*, 2015). According to the World Health Organization (2016) report, about 1.1 billion people globally do not have access to potable water supply while 2.4 billion people do not have access to good sanitation. Water is an essential resource for life and good health. It is so vital that it improves many health conditions such as chronic exhaustion, dehydration, toxin removal, poor blood circulation, waste removal and good kidney function. There is an increasing awareness that water will be one of the most critical natural resources in future due to the fact that about 2 million children less than 5 five years die annually in developing countries as a result of water borne diseases (WHO, 2016). According to WaterAid (2016) report, lack of potable water killed more people in Nigeria than Boko Haram.

This shocking revelation places importance on the need to regularly monitor the quality and source of our daily water supply. Water is an essential requirement of human and industrial development and the most delicate part of the environment and hence, monitoring of its quality is essential to guarantee a safe environment and healthy people. Water is a universal solvent and has the ability to dissolve and interact with organic and inorganic components of the aquifer material through which it migrates (Amadi *et al.* 2014). These materials constitute the amount of total dissolved solids present in the groundwater which enhances its conductivity. This implies that groundwater chemistry is a function of the mineral composition and the formation as it moves from recharge to discharge areas which varies spatially and temporally depending of on the chemical nature of the water, mineralogy of the geological formations and residence time of the groundwater (Okunlola *et al.*, 2014; Olasehinde *et al.*, 2015; Dan-Hassan *et al.*, 2016). There has been an increasing rise of environmental pollution globally as a result of man's activities such as mining, industrial effluent and sewage disposals into the ecosystem. Heavy metals are widespread pollutant of great environmental concern as they are non-degradable, toxic and persistent with serious ecological ramifications on local geology and ecology. In Nigeria, varying degrees of soil, water and air pollution occur in the course of mineral prospection, exploration and exploitation depending on the stage and scale of activities attained. Limestone is a sedimentary rock chiefly composed of calcium carbonate. It is formed by the compaction of corals, plants or animal remains through the action of rivers, sea, wind, and glaciers. It is formed by direct crystallization of carbonates with some impurities such as clay, sandstone, and shale. It is the most widely used non-metallic raw material in Nigeria. The largest use of limestone is in the manufacture of cement used in construction industry. Limestone deposit is also primary raw materials for some manufacturing industries such as sugar, fertilizer, and ceramics, iron, glass, chemicals and fillers.

According to Amadi *et al.* (2012) abandoned mine resulting from mine closure causes water pollution and damage to the environment such as dust, noise, leaching and subsidence. Improper management of mine waste causes increased concentration of toxic substances in soil, water and aesthetic problems. Pollution caused by quarrying and blasting in opencast mine increases not only the dust in the air but also promotes the spread of toxic chemicals and oxides. Surface mining though less dangerous than underground mining, has a greater impact on surface landscape. Opencast mining requires the removal of massive amount of top soil in order to gain access to the mineral, which can cause erosion, loss of habitat, and dust pollution leading to soil, surface and groundwater contamination. Vast agricultural lands are destroyed through opencast mining thereby affecting food production and source of income for the people (Amadi, 2011b). In terms socio-economic activities such as tourism, industry and commerce, water is an indispensable input. The suitability of groundwater for domestic, industrial and irrigational purposes depends on the composition of water. Potable and safe drinking water is a necessary requirement for the health and productive life of humans in any society. Polluted water is a major cause of epidemic and chronic diseases in human beings. Studies have revealed a correlation between cardiovascular deaths and water chemistry (El-Sayed *et al.,* 2012; Okiongbo and Douglas, 2013, Amadi *et al.,* 2016).

The present study is aimed at evaluating the pollution status of surface and groundwater due to artisanal gold mining activities in the area. The absence of organized mining techniques for gold despite the great potentials, coupled with the high rate of unemployment and poverty, led to the invasion of the Nigerian gold fields by artisanal gold miners. Though mining has a lot of economic benefits to the miners and their host communities, its environmental and health effects in terms of land degradation, air pollution and heavy metal contamination of the soil, surface and groundwater could be devastating if not properly handled (Amadi, 2011a). These unsafe mining activities are capable of contaminating the surface and groundwater system in the area, hence the need for the current study.

1.2 Statement of the Research Problem

All over the world, artisanal gold mining has resulted to water pollution. Artisanal gold mining is a means through which heavy metals are liberated from the host into the surroundings and these unregulated activities has caused huge environmental and health problems. Mercury and cyanide used by artisanal miners in the extraction and processing of gold are discharged directly into the nearby soils and surface water thereby degrading the environment. The Zamfara and Madaka (Niger State) scenario where many children died due to lead poisoning associated with artisanal gold mining has placed a demand on the need to ascertain the pollution level in surface and groundwater around Bosso gold mining sites in order to avert a repeat of these negative occurrences (Amadi *et al.,* 2016). The upsurge in gold mining activities in Bosso area especially along the Chanchaga river banks make it imperative to ascertain the quality status of the water sources in the area and this is the trust of the present research.

1.3 Aim and Objectives of the Study

The research is aimed at examining the impact of artisanal gold mining on the quality of surface water and groundwater in parts of Bosso Local Government Area, Niger State, Nigeria.

The specific objectives of the study are to:

i. analyze the physical and chemical properties of surface water and groundwater in the study area.
ii. compare the results in (i) above with the Nigerian Standard for Drinking Water Quality (NSDWQ).
iii. Apply Water Quality Index (WQI) and Metal Pollution Index (MPI) to identify the contaminants and their possible sources.
iv. Produce a concentration map showing the levels of pollution status of water samples in the study area.

1.4 Justification for the Study

The quality of life of an individual is a function of the quality of water he or she drinks. According to World Health Organization, about 55% of the disease outbreaks are attributed to consumption of polluted water. Heavy metals pollution of surface and groundwater arising from artisanal gold mining in Bosso Local Government Area of Niger State has not been adequately studied. Little work has been done on the study area and information on the mining activity in the area is very scanty, hence the need for the present study. The study when concluded will provide useful baseline information for environmentalists and other relevant stakeholders on policy formulation targeted at safeguarding the environment.

1.5 Study Area

The study area falls under Bosso Local Government Area of Niger State, North-central Nigeria. It is located between latitudes 9°30'15" to 9° 35'40"N and longitudes 6° 32'25" to 6° 36'10"E (Fig. 1). The study area is accessible through the Minna – Paiko road and other untarred roads that network movement in and out of the city. The relief of the study area is relatively flat and rocky at the river channel drained by River Chanchaga. It falls within the Guinea Savanna and consists of shrubs, grassland and trees especially along river channels. The area is also characterized by two climatic seasons: the dry and rainy seasons, each season lasting for approximately six months. The total annual rainfall of the area is between 1200 mm in the north to 1600 mm in the south. The mean maximum temperature remains high throughout the year, hovering about 32°C, particularly between March and June, while the lowest temperatures occur usually between the months of December and January during the harmattan period (Adedeji, 2011)

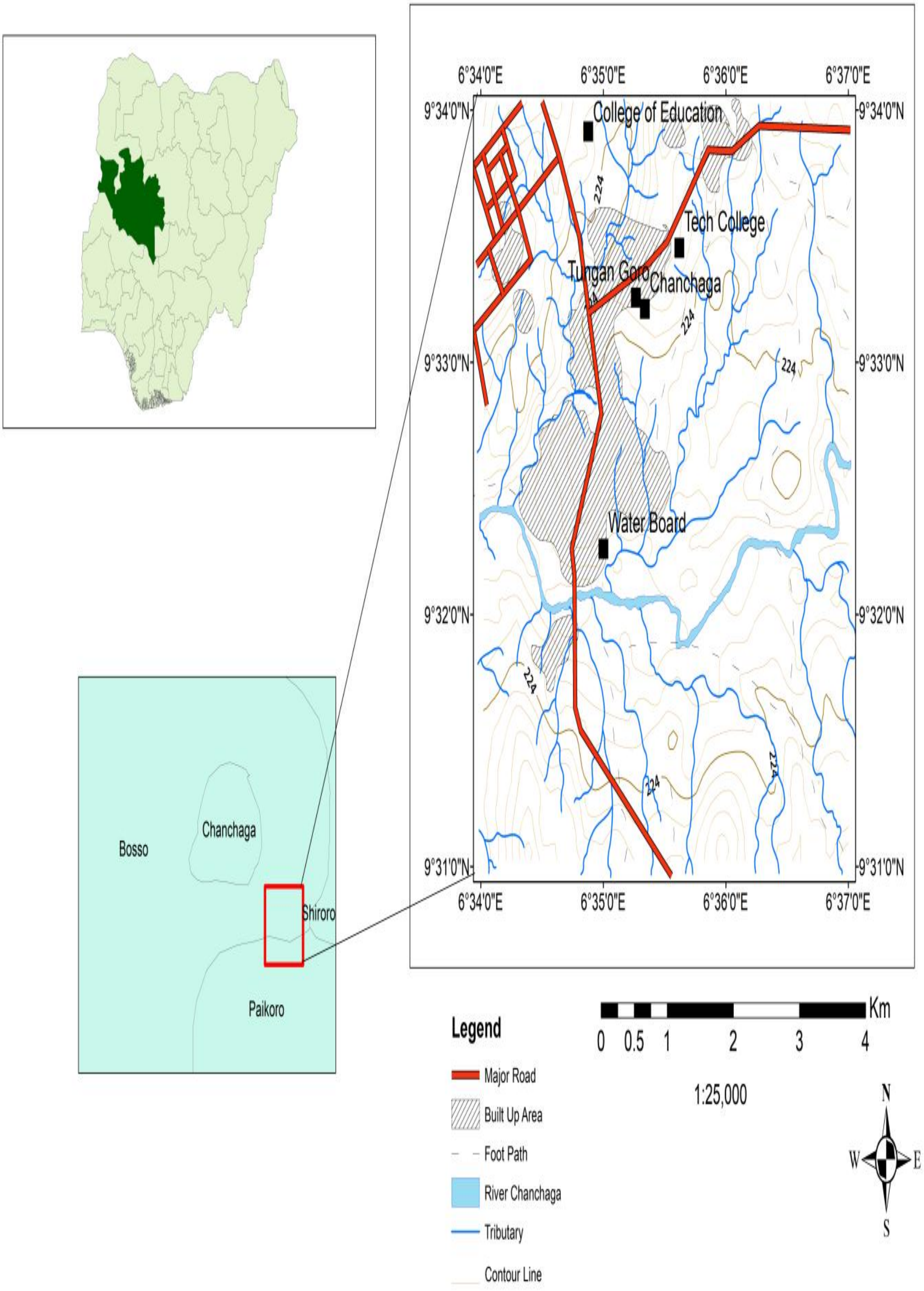

Figure 1.1: Topographical Map of the Study Area

Source: Authors work (2022)

1.6 Scope and Limitations of the Study

The present study involved sampling and analyzing both physical and chemical properties of surface water and groundwater in Bosso local government area gold mining sites, Minna, Niger State. This research covered areas with close proximity to the mining sites and specific areas along Chanchaga river banks passing across Bosso Local Government Area as shown on the field map (Fig 3.1) and concentration maps generated from the results of the laboratory analysis of samples collected from these areas.

The only limitation to this study was in the financial aspect. The project was capital intensive but I was able to push through.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Conceptual Framework

2.1.1 Water quality evaluation

Amadi *et al.* (2016) evaluated the groundwater quality in Madaka, Niger State and the study revealed the water type as calcium-magnesium-bicarbonate water. The study also confirmed that the groundwater in Paiko from shallow hand-dug aquifers is poor bacteriological due to the presence of total coliform and *E. coli*, evidence of faecal contamination. Boiling of water before drinking was recommended because bacteria cannot withstand high temperature.

In attempt to meet some of the sustainable development goals (SDGs), which includes access to safe drinking water and food security, Amadi (2007) assessed the suitability of the groundwater in Minna and environs for irrigation purposes. The parameters employed to assess the irrigation suitability are: total dissolved solids (TDS), electrical conductivity (EC), sodium absorption ratio (SAR), soluble sodium percentage (SSP), residual sodium bicarbonate (RSBC), permeability index (PI), kelly ratio (KR), magnesium adsorption ratio (MAR) and total hardness (TH). The result findings revealed that the groundwater within the study area is suitable for irrigation purposes based on the computed irrigation quality indices. Similarly, Amadi *et al.* (2016) also evaluated the suitability of groundwater in Auchi and environs for irrigation purposes. The study revealed that the groundwater in Auchi and environs is suitable for irrigation farming based on its low salinity and magnesium hazards values. These implies that farmers in Minna and Auchi can supplement rain-fed agriculture with groundwater resources thereby having an all-year-round farming, and this will go a long way in addressing the food insecurity in the country.

Mohammad (2012) assessed the quality of surface and groundwater in gold mining sites in Kaduna State, Nigeria and observed high concentration of nickel, manganese, iron, lead and arsenic in the water system in the water system in the Gussoro area. These metals are pathfinder elements that are associated with gold. In the course of gold exploration, exploitation, mining and processing, they are exposed into the surrounding soil and surface water and they get leached the water through run-off or bedrock dissolution and weathering processes. The dangers associated with illegal gold mining were highlighted in the study and use modern mining equipment that are environmentally friendly are suggested.

Amadi *et al.* (2016) evaluated the impact of artisanal gold mining in Galadima Koko in Niger State, Nigeria and it was revealed that both the surface and groundwater regimes in Galadima Koko were very poor when compared with the Nigerian Standard for Drinking Water Quality (NSDWQ, 2015) as well as World Health Organization (WHO, 2016) Standard. The concentration of mercury, iron, copper and manganese were found to be higher than the maximum permissible limits postulated by NSDWQ, (2015) and WHO, (2016). The practice of using mercury to amalgamate (concentrate) gold, washing of rocks containing gold directly in the nearby surface as well using the same mining buckets and pan to fetch water from the shallow hand-dug wells exposes the surface and groundwater system in the area to pollution. The oxidation, dissolution and weathering of pyrite bearing rocks that host gold in the area are contributing factors. The research recommended that artisanal miners should not use mercury in processing gold because of its known environmental implications.

Okunlola *et al.* (2016) used metal pollution index (MPI) and water quality index (WQI) to evaluated water condition around gold and manganese mining sites in Lugbe mining sites in Abuja, Nigeria. The MPI and WQI values show that the water around the gold and manganese mining sites are contaminated especially with iron, manganese and lead. The need to remediate the water before use is recommended.

Amadi *et al.* (2016) worked on the groundwater quality status from hand-dug wells (shallow aquifers) in Madaka, Niger State and the study indicated that the 35 hand-dug wells samples analysed contain both *E. coli* and total coliform, as well as high concentration of iron, copper and zinc. The enrichment of these metals in the groundwater is due to rock-water interaction processes such as dissolution and weathering. The construction of pit-latrines and soakaways close to existing hand-dug wells are responsible for the presences of *E. coli* and total coliform in the hand-dug wells in the area. Boiling of water before drinking was recommended.

Amadi *et al.* (2016), investigated the impact of artisanal gold mining in Madaka and Shikira area of Rafi Local Government Area of Niger State and established the presence of lead, chromium and mercury in both the surface and groundwater resources in the area. The study revealed that rock-water interaction leading to bedrock dissolution and their subsequent migrations through various pathways were responsible for their enrichment in the water body. The study recommended that the use of mercury by miners in gold amalgamation should discontinue without any further delay due to its inherent negative consequences.

Dan Hassan (2013) studied the impact of artisanal gold mining on surface and groundwater quality in parts of Abuja, Nigeria and discovered that the gold mining in the area had led to the deterioration of both surface and groundwater systems in the area especially with high concentration of these metals in the order of manganese > copper > zinc > iron > lead. This implies that both surface and groundwater around the study area are not suitable for drinking and domestic uses. Treatment of the water before consumption is strongly advocated.

Amadi. (2011a) investigated surface and groundwater quality in Suleja and Zungeru axis of Niger State respectively. They research findings revealed that both surface and groundwater resources in these localities contain high concentration of nitrates, chloride, total coliform, bacteria coliform and *E. coli*, an indication of bacteriological contamination. The fieldwork showed that most of the hand-dug wells in these areas were close to pit-toilet, soakaways and dumpsites. Furthermore, some of the indigenes still practice open defecation. High concentration of nitrate as well as chloride is area not close to the sea like Suleja are fingerprints of urban pollution arising from poor sanitation and hygiene. The need for personal hygiene is advocated in these areas. Boiling of the water before drinking was also recommended.

Edet *et al.* (2003) investigated the groundwater quality in Calabar, Cross-River state and the study revealed poor groundwater situation within and around the housing estate with the following as pollution indicators: nitrate, iron, copper, zinc and lead. The poor quality of the groundwater from shallow aquifers in the area were attributed to urban pollution arising from unlined dumpsites, soakaways and fertilizer application by farmers within the estate. The need for the people to embrace good hygiene and sanitation was recommended.

Nwankwoala *et al.* (2017) assessed the contamination risk of heavy metal occurrence in water and sediments in Choba section of the new Calabar River and the value of the pollution load index obtained was high, signifying moderate to high pollution. The contributing elements are copper, magnesium, chromium, iron, lead and cadmium. The study suggested that the discharge from municipal storm water into the river and the corrosion from damaged and abandoned sea vessels in the river were responsible for the presence of these metals in the water. It was recommended that the necessary government agencies saddled with the responsibility of protecting our environment should remove these damaged/abandoned sea vessels without further delay as it will go a long way in reducing the pollutants coming from the abandoned sea vessels.

Amadi *et al.* (2013) studied the heavy metal pollution levels in groundwater, soils and plants in North Central, Nigeria and established that the groundwater in the area is poor with respect to high concentration of cadmium, zinc, copper, manganese, nickel, lead, cobalt, arsenic and mercury. The results were validated by computing the soil-water-plant intake and transfer factor, which also confirmed zinc, cadmium, copper, lead, nickel and manganese as the dominant metals in the soil and plants in the area while lead, cobalt, arsenic and mercury occur in trace concentration in both soil and plants in the study area. The pollution was attributed to the long-term menace of oil spill, gas flaring, dumping of sewage and non-functional equipment/machinery by oil companies in the area. The use of environmentally friendly techniques such as bioremediation and phytoremediation in the clean-up of the contaminated water and soil in the area was advocated.

Amadi (2007) assessed the groundwater quality in Eastern Niger Delta using water quality index (WQI), metal pollution index (MPI) and factor analysis (FA). The study established the groundwater system in the area were very highly polluted with nickel, highly polluted with cadmium and lead, moderately polluted with cobalt, chromium, iron, mercury and zinc as well as lightly polluted with arsenic and manganese. The study identified oil spill, gas flaring, acid-rain, agrochemical, industrial sewage and open dumpsites as the factors responsible for enrichment of the groundwater with heavy metals. The geology of the area characterized by high porosity and permeability also enhance the movement and migration of these metals into the water table. The study advocated for an end to gas flaring and indiscriminate dumping of refuse and sewage as well as proper clean-up of oil-spilled sites in the area.

Amadi *et al.* (2016) investigated the groundwater quality in Onitsha and discovered high concentration of in the order of: iron > lead > manganese > chromium > cadmium in the groundwater system. Based on water quality index (WQI), the groundwater in the area was categorized into 5, ranging from excellent water (24%), good water (27%), poor water (17%), very poor water (24%) and unsuitable for drinking (10%). The computed metal pollution index (MPI) revealed that iron, lead and manganese showed moderate pollution while chromium and cadmium fall under light pollution. The poor water quality status was attributed to poor sanitation, discriminate dumping of untreated sewage and refuse as well as industrialization.

Olasehinde and Amadi (2009) carried out preliminary assessment of water quality in Owerri, Southeastern Nigeria. Hydrochemical investigation of water samples from the town were thus, carried out. From the hydrochemical results, it was found that sodium and chloride are the most dominant ions of the total chemical budget. The pH ranges from 7.5 to 7.9, electrical conductivity range from 30 to 900s/cm. The hydrochemical characteristics of the water revealed that, the cationic concentrations are in the order of $(Na^+K) > Ca^{2+} > Mg^{2+}$ for both wells and surface waters, while the anionic concentrations are in the order of $Cl- > HCO_3- > SO_42-$. The hydrochemicalfacies of both surface and groundwater were found to be three: CaNaCl> $CaHCO_3$ >NaCl. The source of the ions in the waters was examined and classified accordingly as rock weathering dominance. Also, it was confirmed to be good for drinking and irrigation purposes.

Amadi *et al.* (2012a) carried out research on coastal plain-sand aquifer of Owerri using factor analysis for characterization of groundwater chemistry. This work was aimed at determining the hydro chemical facies of groundwater in the Benin Formation aquifer. The tendency of contaminant migrating through the porous and permeable overlying formation into the shallow water table necessitated the study. The analysis on water samples revealed five source of solutes including, factor-1 (Conductivity, Magnesium and TDS), factor-2 (pH, Salinity and TH), factor-3 (Temperature, Turbidity and Iron), factor-4 (Sulphate, Nitrate and Nitrite) and factor-5 (Fluoride and Copper) extracted from the data-set represents the signatures from dissolution of bedrock through which the groundwater passes, salt-water intrusion, leaching from the lateritic overburden, agricultural activities (fertilizer application) and effluent from industries in the area, respectively.

Rani and Babu (2008) worked on hydrochemical analysis and evaluation of groundwater quality in TamkurTaluk, Karnataka State, India. The chemistry and major ions of groundwater in TumkurTaluk was revealed using methods proposed by Piper, Back and Handshew, Wilcox, Eaton, Todd and USSL (US salinity laboratory) classification have been used to study critically the hydrochemical characteristics. Chemical analysis of the water samples reveals that the type of water that predominates in the study area is Ca-Mg-HCO_3 type during both pre- and post-monsoon seasons of the year 2006, based on hydro-chemical facies. Furthermore, suitability of water for irrigation was evaluated based on sodium adsorption ratio, residual sodium carbonate, sodium present, salinity hazard and USSL diagram.

Aremu *et al.* (2011) carried out research on geochemical characterization of aquifers and geochemical study of groundwater in the Basement Complex/Sedimentary transition zone around Kubwa, Abuja. This was to determine the relationship between groundwater chemistry and lithology through which they flow in the area. Result obtained from the analysis of water samples reveals higher values of total dissolved solids and electrical conductivity in Basement Complex than those from the sedimentary terrain. Statistical analysis of the geochemical and physical parameters of surface water samples (one from each sedimentary terrain) shows no significant difference probably due to little time of interaction with the lithology through which they flow. Apart from silica and nitrate, all other parameters are higher in concentration/values in water from the Basement Complex than those from the sedimentary terrain due to the mineral composition of the aquifer materials. The overall results show there is a strong relationship between the aquifer materials in the study area and water chemistry.

Olatunji *et al.* (2005) carried out hydrochemical evaluation of groundwater resources in shallow coastal aquifers around Ikorodu area, southwestern Nigeria. Over 120 groundwater samples from hand dug wells and boreholes were sampled and analyzed for their physicochemical properties. The general hydrochemical character of the water revealed that the cationic concentration of the water to be Na>Ca>Mg while the anionic concentration of the water is Cl>SO4>HCO3. The dominant water type in the area is Na-(K) -(Cl)-SO4 type. The water samples analysed showed that the groundwater of the area is affected more by the impact of Lagoon water.

Elueze *et al.* (2011) researched on hydrochemical assessment of surface water in part of Southeastern Nigeria. Hydrochemical parameters in the piper trilinear diagram, as well as the Gibbs plot respectively, suggest that the water is of sodium bicarbonate facies, and dissolved solids are mostly products of weathering. Application of R-mode factor analysis suggests that the main component of the water characteristics is related to hydrological, lithological and environmental controls.

Nur and Ayuni (2004) carried out research on geochemical characterization of groundwater in Taraba State, North East Nigeria, with the aim of identifying the available hydrochemical groups and their possible source. The study reveals a typical meteoric water type whose chemical composition is influenced by seawater, and ion exchange activities. Samples from the basement units are mainly Ca-(Mg)-HCO3-Cl-(SO4). The TDS values indicate salty water types in the sedimentary areas while the landlocked areas have fresh water. Also the mean CaCO3 concentration reveals a predominantly hard water types. Water in Hong, Song and Yola with high TDS and appreciable Cl- ion concentration is identified as nature waters while other areas have young or juvenile waters.

Adakole *et al.* (2010) research on quality characteristics of water in Samaru area showed that all the physical parameters considered conform to the (WHO, 2016) standards, while some of the chemical parameters like total hardness, nitrate, chloride and sulphate of the samples do not conform to the standard. Aremu *et al.* (2011) evaluated the physiochemical properties of groundwater from hand-dug wells, boreholes and stream water in Bwari and its environs. The result showed that all the parameters determined fall within the World Health Organisation (WHO, 2016) standard for drinking water quality, except for pH. The result showed that the water is slightly acidic, soft, fresh, have low to moderate chemical ions values and are classified as $Ca\text{-}Na\text{-}HCO_3$, $Ca\text{-}K\text{-}HCO_3$, $Mg\text{-}Ca\text{-}HCO_3$, and $Na\text{-}K\text{-}HCO_3$ water types.

Muhammad (2012) reported that over 90% of the water samples analysed from parts of Kaduna Metropolis are in conformity with the Nigerian Standard for Drinking Water Quality (NSDWQ, 2007) standard in term of physico-chemical quality. However, over 65% of the samples were contaminated by coliform. This confirms anthropogenic contamination of some of the groundwater in the study area. It also indicated that the borehole water is more potable than the shallow wells. Nur and Ayuni (2004) research on the water quality characteristics of groundwater in Jalingo metropolis showed that some of the water samples do not conform to WHO (2016) permissible standard in terms of pH, iron, magnesium and coliform count. It further stated that the water samples have generally low concentration of anions and cations and classified the dominant water type in the area as Na^+K - Cl- SO_4 water type.

Yusuf and Sonibore (2004) research on the characteristics and the pollution implications of the effluents from the textile industry on the water resources, human health and environment of Kaduna Metropolis indicated that the qualities of the effluent were grossly below the set limits of FEPA in majority of the textile mills. It also suggested that the air quality of the area covered by the Kaduna River basin to be likely negatively affected by both the gaseous emissions and particulates from the effluents and that meteorological condition are strong influencing factors to this situation.

In their various work on the groundwater quality and hydrogeochemical assessment of the water resources elsewhere in Nigeria and outside Nigeria, British Geological Survey (2003) regional assessment and reviews of the groundwater quality of Nigeria noted that the Nigerian shallow aquifers are potentially vulnerable to pollution from human activities like agriculture (fertilizers), domestic (waste dumps, latrines) and industrial sources, except where surface layers are of poor permeability and offered some protection of the underlying aquifers.

Adesida and Omosuyi (2005) analysed groundwater chemistry of weathered zone aquifers of an area underlain by basement complex rocks, Akure, Nigeria. The results show that there is a human activity imprint on the groundwater chemistry, which overshadows the normal expected influence of' weathering and bedrock geology. Ako *et* *al.* (2014) assessed the chemical quality of shallow groundwater from a metamorphic terrain of part of Southwest Nigeria. The study concluded that the pattern of nutrient concentration between surface and groundwater investigated show that the chemistry of the groundwater is dependent to a large extent on the host bedrock. Adekunle *et al.* (2007) evaluated the physico-chemical and biological quality of water sources in southwestern Nigeria. They attributed the contamination/ pollution of some of the water analyzed to both geogenic and anthropogenic factors.

Yenike *et al.* (2003) determined the impact of human activities on groundwater quality of shallow aquifers in Jimeta-Yola. The study revealed elevated concentration for contamination/ pollution tracers (NO_3^-, Cl^-, SO_4^{2-}) and electrical conductivity. They suggested that the contamination/pollution is due to human activities. Olobaniyi and Owoyemi (2004) determined the groundwater quality in the Deltaic plain sand aquifer of Warri area. They reported saltwater contamination in some of the samples based on high chloride content, low Ca/Mg and Na/Cl ratio. They stated that the water is suitable for domestic and industrial purposes in terms of its physico-chemical attributes. However, the presence of heterothrophic and coliform bacteria compromise this quality. Edet *et al.* (2004) assessed the contamination risk of coastal plain aquifers in Calabar by some potentially toxic elements. They concluded that the small-scale mining activities, low concentration of elements, immobility of mineral species under the prevailing Eh-pH conditions, dilution and precipitation of mineral phases make contamination risk of the coastal plain sand very low.

Dan-Hassan (2013) work on some aspect of hydrogeology of FCT, Abuja and Akujieze and Oteze (2007) determined the groundwater quality of Benin City using statistical correlation and multivariate analyses. The result showed positive correlation between lead (Pb) and other pollution indicators like magnesium (Mg^{2+}), sodium (Na^+), nitrate (NO_3^-), phosphate (PO_4^-) and chloride (Cl^-) and they concluded common sources for them. Momodu and Anyakora (2010) studied the groundwater quality of the Southwest based on their seasonal variations and proximity to pollution sources. The result revealed higher concentration of most of the parameters during the rainy season over the dry season period. They stated that the distance from pollution sources was more pronounced on faecal coliform count, which decreases with increasing distance from the waste dump.

Dan Hassan (2013) worked on the spatial and temporal distribution of nitrate pollution in groundwater of Abuja, Nigeria and Aiyegbusi *and* Akujieze (2010) determined the groundwater quality of shallow aquifer in Ilesha area. The result showed elevated concentration of some of the parameters above the WHO (2016) standard and presence of coliform in majority of the water analysed. This revealed anthropogenic imprint on groundwater quality. They classified the water asCa-Mg-HCO_3^-, Ca- Mg- Cl- SO_4^{2-} , Ca-Mg- Na- K- HCO_3^- , Ca-Mg- Na- K- Cl- SO_4^{2-}-$HCO3^-$ and Na-K-HCO_3^-. Isiaku and Ezeigbo (2010) monitored the groundwater quality of Jimeta-Yola area to determine its seasonal variation. The result revealed higher mean concentration of the chemical parameters and coliform counts during the wet season. They reported higher concentration of nitrate and coliform above the WHO (2016) limits for both seasons and linked the distribution to anthropogenic sources. Akpah and Ezeigbo (2010) investigated the hydrochemical and quality characteristics of groundwater in Itakpe and they reported that majority of the water have salty taste, high electrical conductivity and lower pH values. Aremu *et al.* (2011) evaluated the physico-chemical quality of water resources in Eggan area. They reported that the groundwater samples are moderately acidic to strongly alkaline, while the surface water is neutral to moderately alkaline in nature. They revealed that some parameters as pH, iron, TDS, potassium and chloride do not conform to the

WHO (2016) and NSDWQ (2015). They concluded that the groundwater is more potable and safer for domestic purposes than the surface water. Taiwo *et al.* (2011) determined the groundwater quality of hand dug wells in Obantoko, Abeokuta and revealed elevated concentration of some the parameters above the EPA (2003) and other regulatory Agency standards. They concluded that the groundwater quality in wells to have been compromised and unfit for healthy consumption, except when thoroughly treated.

Oyeku and Eludoyin (2010) used water quality index (WQI) method to evaluate the water qualities of surface and subsurface water of the Oluyole Industrial estate. They classified the surface water dominantly under bad quality category, while that of subsurface water is dominantly of medium quality category based on WQI scheme. Edet *et al.* (2003) studied the trace element hydrochemistry of the Calabar Coastal Plain aquifer using statistical methods. The research concluded that the sources of the trace elements in the aquifer of the area were due to geogenic processes and not anthropogenic processes. Mahanad *et al.* (2010), did a preliminary assessment of the groundwater quality of the Baghdad district, Oriss. The research noted that the high number of indicator micro-organisms counts in the groundwater in the area to be a reflection of the poor quality of water in the area. It linked the sources of the contaminations to human activities, investigated possible relationships between chemical toxicity of high concentrations of heavy metals and incidence of clinic diseases in Great Cairo city of Egypt. They associated high concentrations of Pb and Cd with renal failure, high concentrations of Cu and Mn to liver cirrhosis. They reported the presence of these metals in the urine of patients suffering chronic health effects like cancer, birth defects, organ damage, disorders of the nervous system and nervousness as well as damage to immune system.

Vasanthavigar *et al.* (2010) determined the quality of underground water in Nagar and nearby place of Anand district, Gujarat, India. They reported that the majority of the parameters determined were within the (WHO, 2016) standard, except for chloride, chemical oxygen demand (COD) and E-coli that exceeded the permissible limits in some samples. Sayyed and Bhosle (2011) determined the concentration of chloride, sodium and potassium in groundwater samples of Nanded City in Mahabharata, India and concluded that groundwater quality of the area is controlled by agriculture activities, geological formation and local environmental conditions. Rani and Babu (2008) reported that the major-ion chemistry of groundwater in Tamil Nada River basins, southern India is greatly influenced by mineral dissolution, anthropogenic activities and water level fluctuations in different geological formations. Mus'ab (2008) interpreted the groundwater quality data variation in Erbil city, Northern Iraq using principal components analysis technique (PCA). He identifies variation in geology, human activities, agricultural waste and storm water effects as the dominant factors that impact groundwater quality variation in the area.

Abimbola *et al.* (2002) examined groundwater quality and groundwater pollution. He pointed out that groundwater contains dissolved mineral ions which are slowly dissolved from soil particles, sediments and rocks as the water travels along mineral surfaces in the pores or fractures of the unsaturated zone and the aquifer. He grouped the dissolved ions into primary (or major), secondary and tertiary constituents in natural groundwater. He further remarked that human activities can alter the natural composition of groundwater through the disposal or dissemination of chemicals at the land surface and into soils

2.2 Sources and types of heavy metals in contaminated environments

Heavy metals occur naturally in the environment from the geological processes of weathering of parent materials at levels that are regarded as trace ($<1000\text{mg kg}^{-1}$) and rarely toxic. Due to the disturbance and acceleration of nature’s slowly occurring geochemical cycle of metals by man, most soils and water bodies of rural and urban environments may accumulate one or more of the heavy metals above defined background values high enough to cause risks to human health, plants, animals, ecosystems, or other media. The heavy metals essentially become contaminants in the environment because (i) their rates of generation via manmade cycles are more rapid relative to natural ones, (ii) they become transferred from mines to random environmental locations where higher potentials of direct exposure occur, (iii) the concentrations of the metals in discarded products are relatively high compared to those in the receiving environment, and (iv) the chemical form (species) in which a metal is found in the receiving environmental system may render it more bioavailable. A simple mass balance of the heavy metals in the environment can be expressed as follows:

$M_{total} = M_p + M_a + M_f + M_{ag} + M_{ow} + M_{ip} - (M_{cr} + M_l)$ where “M” is the heavy metal, “p” is the parent material, “a” is the atmospheric deposition, “ f ” is the fertilizer sources, “ag” are the agrochemical sources, “ow” are the organic waste sources, “ip” are other inorganic pollutants, “cr” is crop removal, and “l” is the losses by leaching, volatilization, and so forth. It is projected that the anthropogenic emission into the atmosphere, for several heavy metals, is one-to-three orders of magnitude higher than natural fluxes. Heavy metals in the environment from anthropogenic sources tend to be more mobile, hence bioavailable than lithogenic ones. Metal-bearing solids at contaminated sites can originate from a wide variety of anthropogenic sources in the form of metal mine tailings, disposal of high metal wastes in improperly protected landfills, leaded gasoline and leadbased paints, land application of fertilizer, animal manures, biosolids (sewage sludge), compost, pesticides, coal combustion residues, petrochemicals, and atmospheric deposition as discussed below;

2.2.1 Fertilizers

Historically, agriculture was the first major human influence on the soil. To grow and complete the lifecycle, plants must acquire not only macronutrients (N, P, K, S, Ca, and Mg), but also essential micronutrients. Some soils are deficient in the heavy metals (such as Co, Cu, Fe,Mn, Mo, Ni, and Zn) that are essential for healthy plant growth (Lasat, 2010), and crops may be supplied with these as an addition to the soil or as a foliar spray. Cereal crops grown on Cu deficient soils are occasionally treated with Cu as an addition to the soil, and Mn may similarly be supplied to cereal and root crops. Large quantities of fertilizers are regularly added to soils in intensive farming systems to provide adequate N, P, and K for crop growth. The compounds used to supply these elements contain trace amounts of heavy metals (e.g., Cd and Pb) as impurities, which, after continued fertilizer, application may significantly increase their content in the soil. Metals, such as Cd and Pb, have no known physiological activity. Application of certain phosphatic fertilizers inadvertently adds Cd and other potentially toxic elements to the soil, including F, Hg, and Pb.

2.2.2 Pesticides and herbicides

Several common pesticides and herbicides used fairly extensively in agriculture and horticulture in contains substantial concentrations of metals. About 10% of the chemicals approved for use as insecticides and fungicides in UK were based on compounds which contain Cu, Hg, Mn, Pb, or Zn. Examples of such are copper-containing fungicidal sprays such as Bordeaux mixture (copper sulphate) and Glyphospahte based herbicides. Lead arsenate was used in fruit orchards for many years to control some parasitic insects. Arsenic containing compounds were also used extensively to control cattle ticks and to control pests in banana in New Zealand and Australia, timbers have been preserved with formulations of Cu, Cr, and as (CCA), and there are now many derelict sites where environmental concentrations of these elements greatly exceed background concentrations. Such contamination has the potential to cause problems, particularly if sites are redeveloped for other agricultural or non-agricultural purposes. Compared with fertilizers, the use of such materials has been more localized, being restricted to particular sites or crops (McLaughlin *et al.*, 2010).

2.2.3 Biosolids and manures

The application of numerous biosolids (e.g., livestock manures, composts, and municipal sewage sludge) to land inadvertently leads to the accumulation of heavy metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Tl, Sb, and so forth, in the environment. Certain animal wastes such as poultry, cattle, and pig manures produced in agriculture are commonly applied to crops and pastures either as solids or slurries (Sumner, 2010). Although most manures are seen as valuable fertilizers, in the pig and poultry industry, the Cu and Zn added to diets as growth promoters and as contained in poultry health products may also have the potential to cause metal contamination of the soil. The manures produced from animals on such diets contain high concentrations of As, Cu, and Zn and, if repeatedly applied to restricted areas of land, can cause considerable build-up of these metals in the soil in the long run. Biosolids (sewage sludge) are primarily organic solid products, produced by wastewater treatment processes that can be beneficially recycled. Land application of biosolids materials is a common practice in many countries that allow the reuse of biosolids produced by urban populations (Weggler *et al.*, 2014). The term sewage sludge is used in many references because of its wide recognition and its regulatory definition. However, the term biosolids is becoming more common as a replacement for sewage sludge because it is thought to reflect more accurately the beneficial characteristics inherent to sewage sludge. It is estimated that in the United

States, more than half of approximately 5.6 million dry tonnes of sewage sludge used or disposed of annually is land applied, and agricultural utilization of biosolids occurs in every region of the country. In the European community, over 30% of the sewage sludge is used as fertilizer in agriculture. Most biosolids applied to agricultural land are used in arable cropping situations where they can be incorporated into the soil (McLaughlin *et al.*, 2010). There is also considerable interest in the potential for composting biosolids with other organic materials such as sawdust, straw, or garden waste. If this trend continues, there will be implications for metal contamination. The potential of biosolids for contaminating the environment with heavy metals has caused great concern about their application in agricultural practices. Heavy metals most commonly found in biosolids are Pb, Ni, Cd, Cr, Cu, and Zn, and the metal concentrations are governed by the nature and the intensity of the industrial activity, as well as the type of process employed during the biosolids treatment. Under certain conditions, metals added to soils in applications of biosolids can be leached downwards through the soil profile and can have the potential to contaminate groundwater. Recent studies on some New Zealand soils treated with biosolids have shown increased concentrations of Cd, Ni, and Zn in drainage leachates

2.2.4 Wastewater

The application of municipal and industrial wastewater and related effluents to land dates back 400 years and now is a common practice in many parts of the world. Worldwide, it is estimated that 20 million hectares of arable land are irrigated with waste water. In several Asian and African cities, studies suggest that agriculture based on wastewater irrigation accounts for 50 percent of the vegetable supply to urban areas. Farmers generally are not bothered about environmental benefits or hazards and are primarily interested in maximizing their yields and profits. Although the metal concentrations in wastewater effluents are usually relatively low, long-term irrigation of land with such can eventually result in heavy metal accumulation in the environment.

2.2.5 Mining, milling processes and industrial wastes

Mining and milling of metal ores coupled with industries have bequeathed many countries, the legacy of wide distribution of metal contaminants. During mining, tailings (heavier and larger particles settled at the bottom of the flotation cell during mining) are directly discharged into natural depressions, including onsite surface water bodies resulting in elevated concentrations (Mohammad, 2012). Extensive Pb and zinc Zn ore mining and smelting have resulted in contamination of the environment that poses risk to human and ecological health. Many reclamation methods used for these sites are lengthy and expensive and may not restore pristine levels. Heavy metal environmental risk to humans is related to bioavailability. Assimilation pathways include the ingestion of plant material grown on contaminated soil, or the direct ingestion (oral bioavailability) of contaminated water or soil.

Other materials are generated by a variety of industries such as textile, tanning, petrochemicals from accidental oil spills or utilization of petroleum-based products, pesticides, and pharmaceutical facilities and are highly variable in composition. Although some are disposed of on land, few have benefits to agriculture or forestry. In addition, many are potentially hazardous because of their contents of heavy metals (Cr, Pb, and Zn) or toxic organic compounds and are seldom, if ever, applied to land. Others are very low in plant nutrients or have no soil conditioning properties.

2.2.6 Air-Borne sources

Airborne sources of metals include stack or duct emissions of air, gas, or vapor streams, and fugitive emissions such as dust from storage areas or waste piles. Metals from airborne sources are generally released as particulates contained in the gas stream. Some metals such as As, Cd, and Pb can also volatilize during high-temperature processing. These metals will convert to oxides and condense as fine particulates unless a reducing atmosphere is maintained. Stack emissions can be distributed over a wide area by natural air currents until dry and/or wet precipitation mechanisms remove them from the gas stream. Fugitive emissions are often distributed over a much smaller area because emissions are made near the ground. In general, contaminant concentrations are lower in fugitive emissions compared to stack emissions. The type and concentration of metals emitted from both types of sources will depend on site-specific conditions. All solid particles in smoke from fires and in other emissions from factory chimneys are eventually deposited on land or sea; most forms of fossil fuels contain some heavy metals and this is, therefore, a form of contamination which has been continuing on a large scale since the industrial revolution began. For example, very high concentration of Cd, Pb, and Zn has been found in water bodies and soils adjacent to smelting works. Another major source contamination is the aerial emission of Pb from the combustion of petrol containing tetraethyl lead; this contributes substantially to the content of Pb in urban areas, especially areas adjacent to major roads. Zn and Cd are also common heavy metal contaminants in such area, the sources being tyres, and lubricant oils.

2.3 Irrigation water quality

Amadi, *et al.* (2016) interpretation of water quality for irrigation purposes is crop-specific. Crops differ in their salt tolerance and respond differently to the quality of water with which they are irrigated. The primary items of interest in your water analysis are total salts (Total Dissolved Solids), Sodium, Chloride and Sodium Adsorption Ratio (a calculation using the ratio of calcium plus magnesium to sodium). These are the main items that determine the suitability of water for irrigation.

Groundwater has become the major source of water use in the agricultural sector in many countries where river and drainage systems are not sufficient. Therefore, poor groundwater quality for irrigation purpose is a matter of worry in recent years. Under or over chemical fertilization is resulting in groundwater pollution. Groundwater quality depends on the nature of recharging water, precipitation, subsurface and surface water, hydro-geochemical processes in aquifers and land-use/land-cover change (Amadi *et al.*, 2012b)

2.4 Water Quality Index

The Water Quality Index (WQI) is a useful tool used to assess the overall water quality status of an area and is calculated using the Weighted Arithmetic Index method (Amadi *et al.*, 2012a). The quality rating scale for each parameter qi was calculated by using this expres-sion: qi = (Ci / Si) x 100. A quality rating scale (qi) for each parameter is assigned by dividing its concentration (Ci) in each water sample by its respective standard (Si) and the result multiplied by 100 Relative weight (Wi) was calculated by a value inversely proportional to the recommended standard (Si) of the corresponding parameter: Wi = 1/Si The overall Water Quality Index (WQI) was calculated by aggregating the quality rating (Qi) with unit weight (Wi) linearly. Amadi (2011a), used water quality index to characterize the water quality for surface and groundwater in the Benin Formation (coastal plain-sand) of Eastern Niger Delta, Nigeria and the findings established the overall water quality for the region is poor due to negative impact of oil exploration and exploitation in the area as well as the upsurge in the population and industrialization. The local geology of the area characterized by high porosity and permeability further enhances the leachate/contaminant movement into the water table.

2.5 Metal Pollution Index

Metal Pollution index (MPI) is a method of rating that shows the composite influence of individual parameters on the overall quality of water. The rating is a value between zero and one, reflecting the relative importance individual quality considerations. The higher the concentration of a metal compared to its maximum allowable concentration, the worse the quality of the water (Amadi *et al.*, 2016). It is also a combined physio-chemical and microbial index which makes it possible to compare the water quality of various water bodies (Nwankwoala *et al.*, 2017). It has wide application and it is used as the indicator of the quality of sea and river water as well as drinking water. Metal pollution index is an effective means of communicating water quality to stakeholders in the water sector. The MPI represents the sum of the ratio between the analysed parameters and their corresponding standard values as computed from the formula below:

$$MPI = \sum_{i=1}^{n} \left[\frac{Ci}{(MAC)i}\right] \qquad 2.1$$

where: C_i: mean concentration

MAC: maximum allowable concentration

2.6 Study Gap

Despite the growing body of research on the environmental impacts of Artisanal mining, there is lack of comprehensive studies that investigate the level of concentration of specific pollutants associated with artisanal mining in the study area. Therefore, this study aimed to address this gap by producing a concentration map of the study area using the results from the analyzed water samples.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Research Methodology

The following methodology was adopted in line with the research objectives. Thus, study was carried out in three (3) phases viz; fieldwork phase, laboratory analysis phase and data processing phase.

3.2 Fieldwork Phase

The fieldwork phase involves the collection of water samples. The geographical positioning system (GPS-GARMIN-76) device was used for geo-referencing of the locations sampled (Figure 3.1). At each location, three water samples were collected in pre-cleaned one litre plastic bottles (Plates 3.1 and 3.2) for anions analysis, for cations and trace metals analysis as well as for bacteriological analysis. Samples for the cations and trace metals analysis were acidified with few drops of concentrated tetraoxonitrate (V) acid (HNO_3) in order prevent oxidation reactions, to restrict the effects of bacterial action, and minimize the adsorption and precipitation of cations in solution. Sample for bacteriological analysis were filled two-third by volume. The space left is for aeration and for survival of the bacteria before analysis (Amadi *et al.*, 2012a).

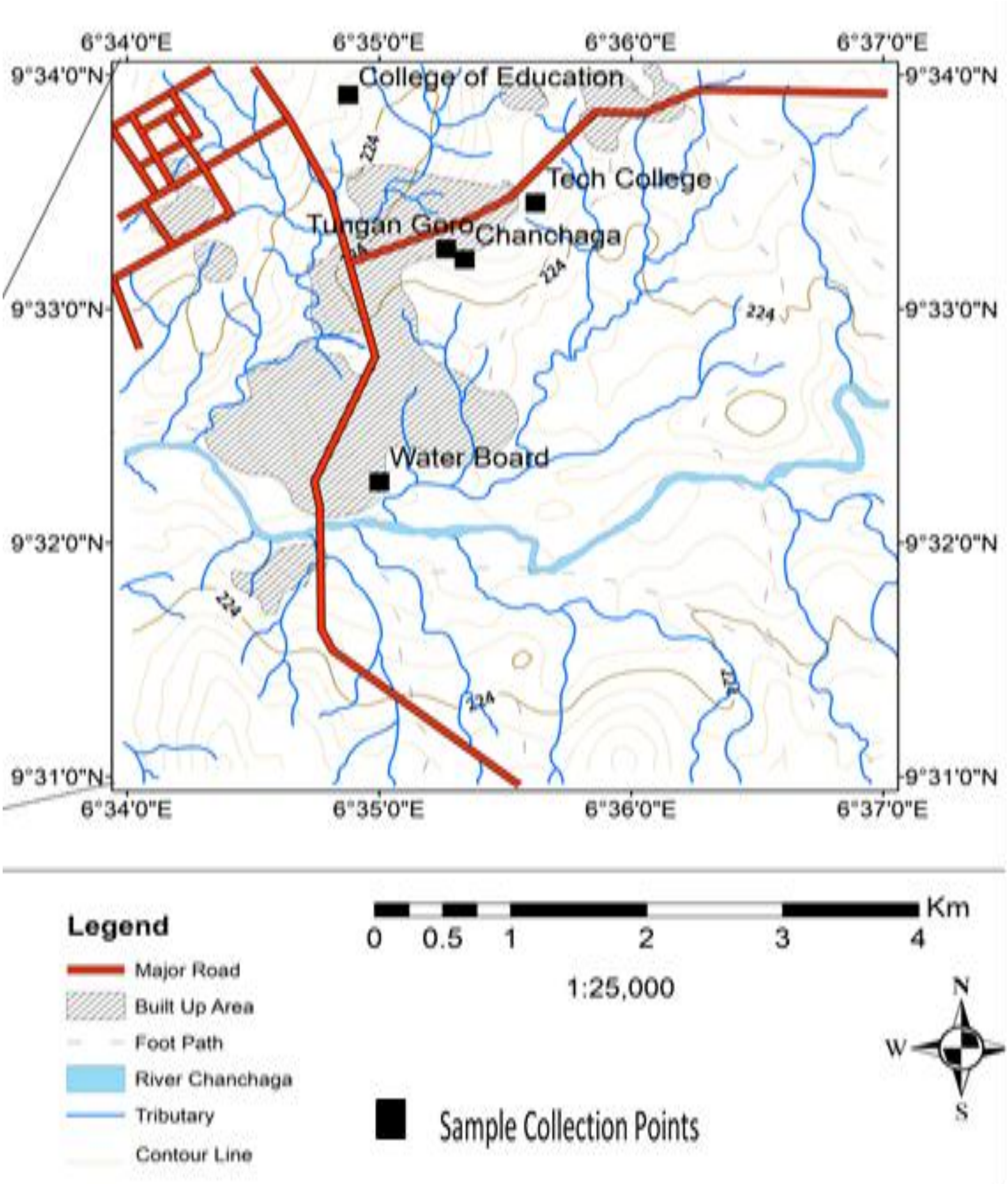

Figure 3.1: Field Map Showing Sample Collection Points

Prior to the water sampling, physical parameters (pH, temperature, electrical conductivity (EC) and total dissolved solid (TDS) were measured in-situ on the field using the HI9811-5 portable pH/EC/TDS/C multi-metre (Plate 3.4). Their determination followed standard sampling procedures prescribed by American Public Health Association (APHA, 2008) and Nigerian Standard for Drinking Water Quality (NSDWQ, 2015).

Plate I: Water Samples from samples locations for Laboratory Analysis

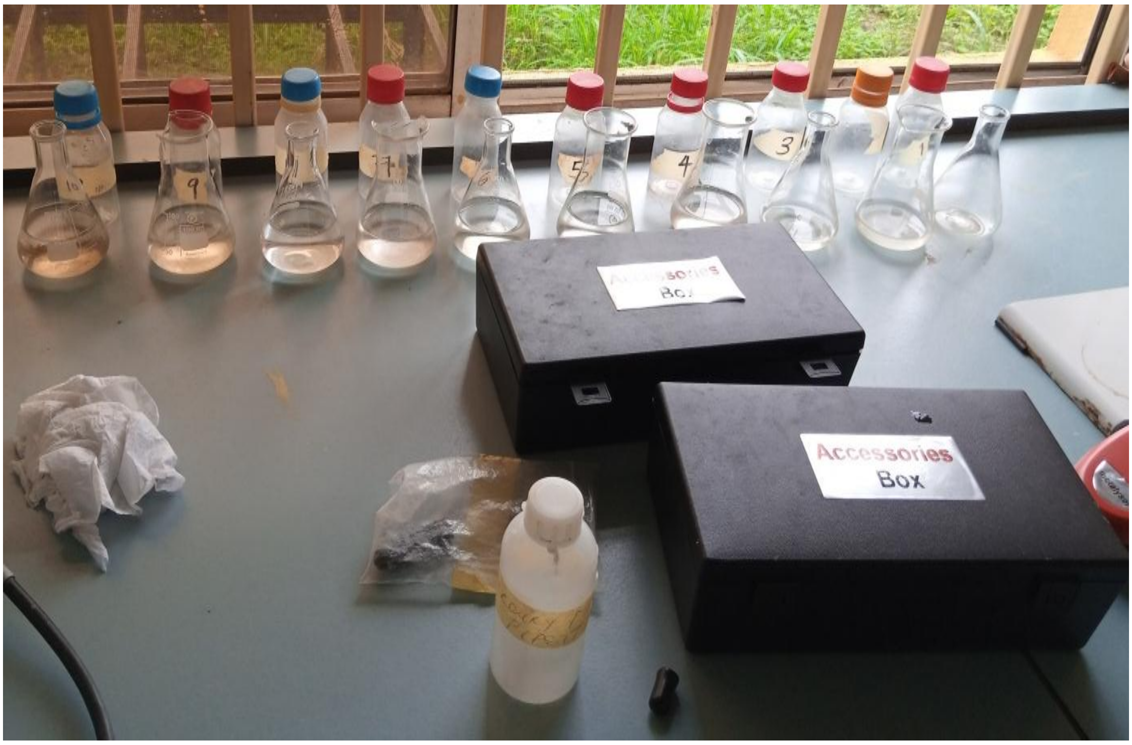

Plate II: Inside the Federal Ministry of Water Resources Regional Laboratory Minna

Plate III: Oven for maintaining the water temperature in the Lab

Plate IV: Insitu measurement of Physical Parameters using Multi-meter

3.3 Laboratory Analysis Phase

3.3.1 Analytical procedures

pH

A. Principles

pH, which is an accepted measure of acidity or alkalinity is determined by change in potential of glass – saturated calomel electrodes, as measured by the apparatus standardized against standard buffer solutions whose pH values are assigned by National Institute of Standard and Technology (NIST).

B. Apparatus and Reagent

i. pH meter

ii. Standard buffer solutions

C. Determination

Thoroughly wet electrodes and prepared in accordance with manufacturer's instructions was standardized with standard buffer solution whose pH value is near that of sample and then with 2 others to check linearity of electrode response. The samples were analyzed as soon as possible (within few hours) after collection. The sample bottles were not open before analysis. The immersed electrodes were washed 6 – 8 times with portions of sample, particularly when unbuffered solution follows buffered solution. Equilibrium as shown by absence of drift was established before readings were accepted.

3.3.2 Temperature

The temperature was always determined at the source of the sample-using thermometer in ^{0}C after having taken the sample into the sampling bottles.

3.3.3 Total dissolved solids

A. Principles

A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 108 ^{0}C. The increase in dish weight represents the total dissolved solids.

B. Apparatus

i. Glass fibre filter disk (Whatman grade 934 AH)

ii. Filtration apparatus

iii. Suction Flask

iv. Dry oven, for operation at 108 ^{0}C

v. Pipettes

C. Procedure

i. Preparation of glass-fibre filter disk

Disk with wrinkled side up was inserted into filtration apparatus. Vacuum was applied and disk was washed with three successive 20 cm^3 volumes of deionised water. The suction was continued to remove all traces of water. The washing was discarded.

ii. Preparation of evaporation dish

The clean dish was heated to 108 ^{0}C for 1 hour in an oven and stored in desiccator until needed. It was immediately weighed before use.

iii. Sample analysis

The sample was stirred with magnetic stirrer and a measured volume was pipeted into a glass fiber filter with applied vacuum. It was washed with three successive 10 cm^3 volumes of reagent grade water, allowing complete drainage between washings, and continued suction for about 3 minutes after filtration was completed. 50 cm^3 of the filtrate was transferred to a weighed evaporating dish and evaporated to dryness on a steam bath. It was then dried for at least 1 hour in an oven at 108 ^{0}C and cooled in a desiccator to balance temperature, and weighed. The cycle of drying, cooling, desiccating and weighing was repeated until a constant weight was obtained or until weight change was less than 4 % of previous weight. Duplicate determinations agree within 5 % of their mean.

D. Calculation

mg, total dissolved solids/dm^3 = (A –B) x 1000/sample volume, cm^3

Where:

A =Weight of dried residue + dish, mg and

B = Weight of dish, mg

3.3.4 Total suspended solid (TSS)

Total suspended solid was determined by differences of the total solids and total dissolved solids.

3.3.5 Conductivity

The portable conductivity meter type MC. 3 EIL was used in determining the electrical conductivity. The cell was rinsed with the sample and the sample poured into the cell unit until it was up to the top at the edge of the bore. The selector switch was set to the appropriate range X1, X10, X100 or X1000 the “ON” key depressed and the conductivity was recorded.

3.3.6 Chloride

A Principles

In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed (APHA, 2008).

B. Apparatus

i. Erlenmeyer flask, 250 cm^3

ii Burette, 50 cm^3

C. Reagents

i. Potassium chromate indicator solution: 50 g of K_2CrO_4 was dissolved in a little distilled water and $AgNO_3$ solution was added until a definite red precipitate was formed. It was allowed to stand for 12 hr, filtered and diluted to 1 litre with distilled water.

ii. Standard silver nitrate titrant, 0.0141M: 2.395 g $AgNO_3$ was dissolved in distilled water and diluted to 1000 cm^3. This was standardized against NaCl and stored in a brown bottle; 1.00 cm^3 = 500 μg Cl^-

iii. Standard sodium chloride, 0.0141 M: 824.0 mg NaCl (dried at 140^oC) was dissolved in distilled water and diluted to 1 litre; 1.00 cm^3 = 500 μg Cl^-

iv Special Reagents for removal of interference:

  a. Aluminum hydroxide suspension: 125 g of Aluminum potassium sulphate ($AlK(SO_4)_2.12H_2O$) or aluminum ammonium sulphate ($AlNH_4(SO_4)_2.12H_2O$) was dissolved in 1 litre distilled water

  b. Phenolphthalein indicator solution.

c. Sodium hydroxide, 1M.

d. Sulphuric acid, 1M

e. Hydrogen peroxide, 30 %

D. Procedure

100 cm^3 sample was transferred into a conical flask. If the sample was highly coloured, 3 cm^3 of Al $(OH)_3$ suspension was added, mixed, allowed to settle, and filtered. If sulphide, sulphite, thiosulphite were present, 1 cm^3 of H_2O_2 was added and stirred for 1 minute.

The samples were directly titrated in the pH range of 7 to 10. The sample pH was adjusted to between 7 and 10 with H_2SO_4 or NaOH when it was not in this range. 1 cm^3 of K_2CrO_4 indicator solution was added and titrated with standard $AgNO_3$ titrant to a pinkish yellow end point. End-point recognition was consistent. $AgNO_3$ titrant was standardized and reagent blank value was established by titration method outlined above. A blank of 0.2 to 0.3 cm^3 was usual

E. Calculation

$mg\ Cl^- /dm^3 = (A-B) \times M \times 35\ 450/ cm^3$ sample

Where A = cm^3 titration for sample.

B = cm^3 titration for blank

M = Molarity of $AgNO_3$

$mg\ NaCl = (mg\ Cl^-/ dm^3) \times 1.65$

3.3.7 Sulphide

A. Principle: Sulphide is determined by absorption in iodine-potassium iodide solution and subsequent titration with sodium thiosulfate.

B. Reagents

i. Hydrochloric acid, HCl, 6M: Prepared by dissolving 120.2 cm^3 of concentrated HCl (36% purity and specific gravity of 1.18) with distilled water and the solution was made up to 1dm^3 (Iodometric Method, APHA, 2008).

ii.Standard iodine solution, 0.025 M: 25 g of KI was dissolved in a little water and 3.3 g of iodine was added. After iodine had dissolved, it was diluted to 1000 cm^3 and standardized against 0.025 M $Na_2S_2O_3$, using starch solution as indicator.

iii. Standard sodium thiosulphate solution, 0.025 M: 6.205 g of $Na_2S_2O_3.5H_2O$ was dissolved in distilled water. 1.5 cm^3 of 6 M NaOH or 0.4 g solid NaOH was added and the solution diluted to 1000 cm^3. The solution was standardized with bi-iodate solution.

iv. Starch solution: 2 g laboratory – grade soluble starch was dissolved with 0.2 g salicylic acid, as a preservative in 100 cm^3 hot distilled water.

D. Procedure

i.An amount of iodine solution estimated to be an excess over the amount of sulphide present was measured and distilled water was added to bring the volume to about 20 cm^3. 2 cm^3 of 6 M HCl was added. 200 cm^3 of the sample was pipeted into flask by discharging sample under solution surface. If iodine colour disappears, more iodine was added so that colour remained. It was back titrated with $Na_2S_2O_3$ solution adding a few drops of starch solution as end point was approached, and continued until blue colour disappeared.

ii. If sulphide was precipitated with zinc and ZnS filtered out, the filter paper was returned with precipitate to original bottle and about 100 cm^3 of water added. Iodine solution and HCl were then added and titrated as in (i) above.

E. Calculation

One milliliter of 0.025 M iodine solution reacts with 0.4 mg S^{2-}:

mg $S^{2-}/dm^3 = (A \times B) – (C \times D) \times 16000/cm^3$ sample

Where: A = cm^3 of iodine solution

B =Molarity of iodine solution

C = cm^3 of $Na_2S_2O_3$ solution

D = Molarity of $Na_2S_2O_3$ solution

3.3.8 Nitrate

A. Principles

Sample is digested with H_2SO_4 to convert organic N to NH_3, which is distilled after alkalinization and determined by nesslerization or titrimetry.

Method is applicable to surface and saline waters as well as domestic and industrial waste. Some industrial waste containing materials such as amines, nitro compounds, hydrazones, oximes, semi carbazones, and some refractory tertiary amines may not be converted to NH_3.

B. Apparatus

i. Digestion apparatus

ii. Distillation apparatus or all-glass apparatus with 800 or 1000 cm^3 digestion flask and 500 cm^3 Erlenmeyer, marked at 350 and 500 cm^3, as receivers.

iii. Nessler tubes.

iv. Spectrophotometer or filter photometer for use at 425 nm

C. Reagents

i. Distilled water- NH_3 free

ii. Mercuric sulphate solution: 8 g of red HgO was dissolved in 50 cm^3 H_2SO_4 (1+5) and diluted to 100 cm^3 with water.

iii. Digestion solution: 267g K_2SO_4 was dissolved in 1300 cm^3 H_2O and 400 cm^3 H_2SO_4, and 50 cm^3 $HgSO_4$ solution added. Solution was then made up to 2 litres.

iv. Sodium hydroxide-sodium thiosulphate solution: 500 g NaOH and 25 g $Na_2S_2O_3$ $5H_2O$ was dissolved in H_2O and diluted to 1 litre.

v. Phenolphthalein indicator solution: 5g of phenolphthalein was dissolved in 500 cm^3 alcohol or isopropanol and 500 cm^3 of H_2O was added. 0.02M NaOH was added until colour turned faint pink.

vi. Sulphuric acid standard solution, 0.02M: 1.07 cm^3 of sulphuric acid was dissolved in distilled water and diluted to 1000 cm^3.

vii. Ammonia standard solution- (1) stock solution, 1.00 mg/ dm^3: 3.819g of NH_4Cl was dissolved in distilled water and diluted to 1 litre. (2) Working solution, 0.01 mg/ dm^3: 10 cm^3 of stock solution was diluted to 1 litre

viii. Boric acid indicator: 20 g of H_3BO_3 was dissolved in distilled water and diluted to 1 litre

ix Mixed indicator: 2 volumes of 0.2 % alcoholic methyl red was mixed with 1 volume of 0.2 % alcoholic methylene blue prepared freshly every 30 days.

X. Nessler reagent: 100 g HgI_2 and 70 g KI were dissolved in small amount of water. Cooled solution of 160g NaOH in 500 cm^3 of water was added slowly, with stirring and diluted to 1 litre. (The reagent is stable for 1 year if stored in Pyrex container out of direct sunlight). Reagent gave characteristic colour, and no precipitate with 0.04 mg NH_4-N in 50 cm^3 of H_2O within 10 min.

D. Digestion and distillation

The sample was placed into 800 cm^3 Kjeldhal flask and 100 cm^3 digestion solution was added. It was boiled until SO_3 fumes were evolved and solution became colourless or pale yellow. The solution was cooled and diluted with 300 cm^3 with H_2O. NaOH-$Na_2S_2O_3$ solution was added slowly down neck of tilted flask to underlay acid solution in amount sufficient to make final solution strongly alkaline as shown by phenolphthalein indicator. The flask was connected to condenser, with tip of condenser dipping into 50 cm^3 2% H_3BO_3 solution in 500 cm^3 Erlenmeyer. 200 cm^3 of the distillate (distilled NH_3 in boric acid) solution was used for titration.

E. Titrimetric determination

3 drops mixed indicator was added to the distillate and titrated with 0.02M H_2SO_4, matching end point against blank containing same volume of NH_3-free H_2O, H_3BO_3 solution, and indicator.

Total N (mg/dm^3) = (S – B) x M x 14.01 x 1000/ cm^3 sample digested

Where S = cm^3 standard H_2SO_4 for sample

B = cm^3 standard H_2SO_4 for blank

M = Molarity of standard H_2SO_4

3.3.9 Biochemical oxygen demand

A. Principle

The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 days. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO (APHA, 2008).

B Apparatus

i Incubation bottles – 250 or 300 cm^3 with glass stoppers

ii Gallenkamp Incubator - thermostatically controlled at 20 ^0C

C. Reagents

i. Phosphate buffer solution –8.50 g of KH_2PO_4, 21.75g K_2HPO_4 , 33.40 g $Na_2HPO_4.7H_2O$ and 1.70 g NH_4Cl in 500 cm^3 H_2O were mixed and diluted to 1 litre. The pH was 7.2 without further adjustment.

ii. Calcium Chloride Solution – 27. 5 g of anhydrous $CaCl_2$ was dissolved in distilled water and diluted to 1 litre

iii. Ferric Chloride Solution – 0.25 g of $FeCl_3.6H_2O$ was dissolved in distilled water and diluted to 1 litre

iv. Alkaline Iodide Solution – 125 g of NaOH was dissolved in 125 cm^3 of distilled water and 37.50 g of potassium iodide was added. The solution was kept hot until the iodide dissolved. This was called solution (a)

v. Sodium azide solution: 2.5 g NaN_3 was dissolved in 10 cm^3 distilled water. This was called solution (b)

vi. Alkaline iodide – azide solution: This was prepared by mixing solutions (a) and (b) above and making it up to 250 cm^3.

vii. Sodium thiosulphate solution-(a) 0.75 M - 46.54 g of $Na_2S_2O_3 .5H_2O$ was dissolved in 250 cm^3 of distilled water. -(b) 0.0375 M solution was prepared by diluting 50 cm^3 of solution above to 1 litre. This was standardized with potassium dichromate solution.

viii. Magnesium Sulphate Solution – 22.5 g of $MgSO_4. 7H_2O$ was dissolved in distilled water and diluted to 1 litre.

ix. Dilution Water:

The desired volume of water was placed in a suitable bottle and 1 cm^3/litre each of phosphate buffer, $MgSO_4$, $CaCl_2$ and $FeCl_3$ solutions were added. Before use, the bottles were placed in the incubator for 24 hours.

D. Procedure:

A suitable volume of sample was diluted with dilution water and mixed well avoiding entrainment of air. The mixed solution was siphoned into two BOD bottles. One was incubated at 20^{0}C for 5 days while dissolved oxygen in the other was determined immediately as follows:

2 cm^3 $MnSO_4$ was added followed by 2 cm^3 alkaline iodide – azide solution well below the surface of the sample. It was stoppered carefully and mixed by inverting it for many times. The precipitate was allowed to settle. After carefully removing the stopper, 2 cm^3 of conc. H_2SO_4 was added by running down the neck of the bottle. It was restored and mixed by gentle inversion. The contents of the bottle were decanted into a 500 cm^3 conical flask and titrated with 0.0375 M sodium thiosulphate using starch as indicator.

E. Calculation

Each cm^3 of 0.037 M $Na_2S_2O_3$ = 1 cm^3 DO when the entire bottle contents are titrated.

BOD = $(DO_1 – DO_2)/P$

Where DO_1 =initial DO before incubation

DO_2 = DO after incubation

P = % dilution used

3.3.10 Chemical oxygen demand

A. Principles

Organic substances are oxidized by $K_2Cr_2O_7$ in H_2S0_4 (1+1) at reflux temperature with Ag_2SO_4 as catalyst and $HgSO_4$ to remove chloride interference. Excess dichromate is titrated with Fe^{2+} using orthophenanthroline as indicator. Method is independent determination of organic matter in sample and has no definable relationship to biological oxygen demand (BOD). The method is applicable to surface and saline waters and industrial wastes.

B. Apparatus and reagents

i. Reflux apparatus: - 500 cm^3 Erlenmeyer or 300 cm^3 round bottom flask with T joint connected to 30 cm (12^0) Allihn condenser.

ii. Distilled water: - Ordinary distilled water was satisfactory: Deionized water was not used.

iii. Potassium dichromate standard solution – (a) 0.25M: 12.259g $K_2Cr_2O_7$ primary standard grade, previously dried for 2 hr at 103^{0}C was dissolved in distilled water and diluted to 1 litre. (b) 0 .025M: 100 cm^3 of 0.25M was diluted to 1 litre with distilled water.

iv. Sulphuric acid reagent: - 23.5g Ag_2SO_4 was dissolved in 1000 cm^3 concentrated H_2SO_4. (1 to 2 days was required for dissolution).

v. Ferrous ammonium sulphate standard solution –(a) 0.25M: 98 g Fe $(NH_4)_2(SO_4)_2.6H_2O$ was dissolved in distilled water, 20 cm^3 of H_2SO_4 was added and cooled, and diluted to 1 litre. This was standardized daily against 0.25M $K_2Cr_2O_7$. (b) 0 .025M: 100 cm^3 of 0.25M was diluted to 1 litre with distilled water and standardized daily against 0.025M $K_2Cr_2O_7$.

vi. Phenanthroline ferrous sulphate (ferroin) indicator solution: 1.48g of 1,10 – (ortho)-phenanthroline and 0.70 g $FeSO_4.7H_2O$ were dissolved in 100 cm^3 distilled water.

vii. Standardization of Ferrous Solutions

a. Concentrated solution: To 25 cm^3 of 0.25M $K_2Cr_2O_7$ diluted to 250 cm^3 with distilled water was added 75 cm^3 H_2SO_4 and cooled. This was titrated with 0.25M $Fe(NH_4)_2(SO_4)_2$ using 10 drops of ferroin indicator.

Molarity = (cm^3 $K_2Cr_2O_7$ x molarity)/ cm^3 $Fe(NH_4)_2(SO_4)_2$

b. Dilute solution: -15 cm^3 H_2O was added to 10 cm^3 of 0.025M $K_2Cr_2O_7$ followed by 20 cm^3 of H_2SO_4 and the solution cooled. This was titrated with 0.025M $Fe(NH_4)_2(SO_4)_2$ using 1 drop of ferroin indicator. The blue green to reddish brown colour change was sharp. The molarity was calculated as in (a).

C. Procedure

Several boiling chips and 1 g of $HgSO_4$ was placed in reflux condenser. 5 cm^3 of H_2SO_4 was added and swirled until $HgSO_4$ dissolved. This was placed in ice bath and 25 cm^3 0.25M $K_2Cr_2O_7$ and 70 cm^3 H_2SO_4-Ag_2SO_4 reagents were slowly added with swirling. While still in the bath, 50 cm^3 sample (or aliquot diluted to 50 cm^3) was added. The condenser was attached and refluxed for 2 hr.

The condenser was cooled and washed down with 25 cm^3 distilled water. About 8 to 10 drops of ferroin indicator were added and excess $K_2Cr_2O_7$ was titrated with 0.25M $Fe(NH_4)_2(SO_4)_2$ to sharp, reddish end point (S cm^3). Blank determination was performed with all reagents, including refluxing, on distilled water in place of sample and cm^3 of $Fe(NH_4)_2(SO_4)_2$ required was determined (B cm^3).

COD (mg/dm^3) = (B-S) x M x 8000/V

Where M = Molarity of $Fe(NH_4)_2(SO_4)_2$ solution

V= Volume of sample used

3.3.11 Bacteriological analysis

Coliform organisms were enumerated using the most probable number (MPN) multiple tube fermentation technique. The most probable number method using fire test tubes in each series were inoculated with 10ml/1.0ml of water sample were used.

3.3.11.1 *Presumption test*

Exactly 48.5g of Mac Conkey broth were weighed and dispended in 1 liter of de-ionized water and allowed to soak for 10minutes and swirled to mix. A sterile pipette was used to transfer 10ml of the Mac Conkey broth for double and samples strength into all the fermentation test tube of the sets. This was followed by transferring 10ml portion of the collected water sample was transferred into the second set of the fermentation tubes of single strength of Mac Conkey broth for higher dilution 0.1ml portion of the water was transferred into the third set of the fermentation test tubes of 10ml simple strength of Mac Conkey broth. All the inoculated test tube were incubated at 37 degrees centigrade and 44 degrees centigrade respectively and examined for gas production after 24 hours of incubation respectively.

3.3.11.2 *Confirmed test*

Exactly 34.5g of eosin methylene blue agar (EMBA) were weighed dispensed into 1 liter of de-ionized water, allowed to soak and then swirled to mix. It was sterilized by auto calving at 121 degrees centigrade for 15mins. Poured into places and allowed to dry in a drier. The ability of the organism to ferment lactose was shown by the production of acid with or without gas. Acid production was shown by a change in colour of the Mac Conkey broth for purple to yellow and gas production by the collection of bubbles in the inverted Durham tubes. Confirmed test was performed by streaking the cutler of positive presumptive tubes across the surface of the eosin ethylene blue agar plates by using a sterile wire loop. The inoculated plates were incubated of 37oC for 24 hours.

3.3.11.3 *E coli*

This test was performed by transferring a colony (which formed greenish metallic sheen) from the eosin ethylene blue agar (EMB) to nutrient agar and Mac Conkey agar. The plates were then incubated at 37 degree for 24 hours. Pure cultivar was maintained on nutrient agar slant.

3.3.11.4 *Total coliform*

The sets of fermentation tubes were inoculated with 10m/s 1.0m/s (APHA, 2008). The set of tubes were incubated at 44 degrees for 24 + vet result after 24 hours indicates fecal contamination of samples.

3.3.12 Atomic absorption spectrometer (AAS)

The Atomic Absorption Spectrometer (AAS) is a very common technique for detecting metals and metalloids in environmental samples. It is very reliable and simple to use. The technique is based on the fact that ground state metals absorb light at specific wavelengths. Metal ions in a solution are converted to atomic state by means of a flame. Light of the appropriate wavelength is supplied and the amount of light absorbed can be measured against a standard curve.

3.3.12.1 *Principle*

The AAS technique requires a liquid sample to be aspirated, aerosolized, and mixed with combustible gases, such as acetylene and air or acetylene and nitrous oxide. The mixture is ignited in a flame whose temperature ranges from 2100 to 2800 ^{o}C. The characteristic wavelengths are element specific and accurate to 0.01-0.1nm. To provide element specific wavelengths, a light beam from a lamp whose cathode is made of the element being determined is passed through the flame. A device such as photon-multiplier can detect the amount of reduction of the light intensity due to absorption by the analyte, and this can be directly related to the amount of the element in the sample. Flame atomic absorption hardware is divided into six fundamental groups that have two major functions: generating atomic signals and signal processing. Signal processing is a growing additional feature to be integrated or externally fitted to the instrument. Proper nebulization is required to break up an aqueous sample into a fine mist of uniform droplet size that can be readily burned in the flame. Most instruments utilize the direct aspiration.

During aspiration, the gas flow breaks down the liquid sample into droplets, and the nebulization performance depends on the physical characteristics of the liquid. Only about 10% of the sample gets into the flame. Another option for nebulization is the use of an ultrasonic wave beam, which generates high frequency waves in the liquid sample. This causes very small liquid particles to be ejected into a gas current forming a dense fog. Different flames can be achieved using different mixtures of gases, depending on the desired temperature and burning velocity. Some elements can only be converted to atoms at high temperatures. Even at high temperatures, if excess oxygen is present, some metals form oxides that do not re-dissociate into atoms. To inhibit their formation, conditions of the flame may be modified to achieve a reducing, non-oxidizing flame.

During combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths, flame atomic absorption is very convenient and widespread, and has an acceptable level of accuracy for most analytes. However, there are other devices which allow for better sensitivity and more control over the chemical environment of the analyte. Depending on the information required, total recoverable metals, dissolved metals, suspended metals, and total metals could be obtained from a certain environmental matrix. Appropriate acid digestion is employed in these methods. Hydrochloric acid digestion is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because it can cause interferences during furnace atomization.

3.4 Data Analysis Phase

3.4.1 Water quality index (WQI)

Water quality index (WQI) is one of the most effective tools to communicate information on the quality of water to the concerned stakeholders and policy makers. It has become a useful tool for the assessment and management of water resources. Water Quality Index is a scale which helps to estimate an overall quality of water based on the values of water quality parameters. It expresses the overall water quality at a certain location and time based on several water quality parameters. The word “Water Quality” is a widely used expression, which has a broad spectrum of meaning depending upon each individual interest of water for an intended use.

The objective of WQI is to turn complex water quality data into information that is understandable and useable by the public. Over the years and even today a decision regarding “quality” of water is made using a series of judgments and can be expressed using several scores of parameters obtained from water analysis in the laboratory. In response to the need for a uniform understandable yardstick of water quality, water scientists worked out to compile all the water quality parameters into what is now known as the water quality index (WQI).

3.4.1.1 *Calculation of WQI*

The Water Quality Index (WQI) was calculated using the Weighted Arithmetic Index method. The quality rating scale for each parameter q_i was calculated by using this expression:

$$q_i = (C_i / S_i) \times 100 \tag{3.1}$$

A quality rating scale (q_i) for each parameter is assigned by dividing its concentration (C_i) in each water sample by its respective standard (S_i) and the result multiplied by 100. Relative weight (W_i) was calculated by a value inversely proportional to the recommended standard (S_i) of the corresponding parameter:

$$W_i = 1/S_i \tag{3.2}$$

The overall Water Quality Index (WQI) was calculated by aggregating the quality rating (Q_i) with unit weight (W_i) linearly as shown below:

$$WQI = \left(\sum_{n=1}^{i=n} w_i q_i\right) \tag{3.3}$$

where:

q_i: the quality of the ith parameter,

w_i: the unit weight of the ith parameter and

n: the number of the parameter considered.

Generally, WQI were discussed for a specific and intended use of water. In this study the WQI for drinking purposes is considered and permissible WQI for the drinking water is taken from the overall WQI given as:

$$\text{Overall WQI} = \frac{\sum q_i w_i}{\sum w_i} \tag{3.4}$$

Water quality and its suitability for drinking purpose can be examined by determining the water quality index.

3.4.2 Metal pollution index

Metal Pollution index (MPI) is a method of rating that shows the composite influence of individual parameters on the overall quality of water. The rating is a value between zero and one, reflecting the relative importance individual quality considerations. The higher the concentration of a metal compared to its maximum allowable concentration, the worse the quality of the water (Amadi *et al.,* 2020). It is also a combined physio-chemical and microbial index which makes it possible to compare the water quality of various water bodies (Tamasi and Cini, 2004; Prasad and Kumari, 2008). It has wide application and it is used as the indicator of the quality of sea (Filatov *et al.,* 2005) and river water (Lylko, Ambalova and Vasiljeva, 2001; Mohan, Nithila and Reddy, 1996), as well as drinking water (Nikoladis, Mandalos and Vantarakis, 2008; Amadi, Yisa, Okoye and Okunlola, 2010). The MPI represents the sum of the ratio between the analyzed parameters and their corresponding national standard values as shown in Table 4.8:

$$MPI = \sum_{i=1}^{n} \left[\frac{Ci}{(MAC)i}\right] \tag{3.5}$$

where: C_i: mean concentration

MAC: maximum allowable concentration

Metal pollution index is an effective means of communicating water quality to stakeholders in the water sector.

Table 3.1: Summary of Methodology Used

S/No	Objective	Data Source	Method of Analysis
1	Analyze the physical and chemical properties of surface water and groundwater in the study area.	Sampled Locations	Laboratory Analysis
2	Compare the results of the laboratory analyses with known standards.	Nigerian Standard for Drinking Water Quality (NSDWQ,2015)	Tables
3	Apply Water Quality Index (WQI) and Metal Pollution Index (MPI) to identify the contaminants and their possible sources.		Calculations using Water Quality Index (WQI) and Metal Pollution Index (MPI) formulas
4	Produce a concentration map showing the levels in pollution status of water samples in the study area.	Laboratory results of the sampled locations in the study area	Maps generated using ARC GIS.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Results

4.1.1 Physical parameters

The statistical summary of the physico-chemical and bacteriological analyses is contained in Table 4.1. Total dissolved solid (TDS) is the amount of dissolved solute in water and its concentration in surface water ranged from 60.5 mg/l to 640.0 mg/l with a mean concentration of 180.40 mg/l while the concentration in groundwater varied from 70.0 mg/l to 830.0 mg/l with an average value of 205.20 mg/l. The concentration of TDS in 8 locations (surface water) and 14 locations (groundwater) were higher than the recommended maximum permissible limit of 500.0 mg/l by the Nigerian Standard for Drinking Water Quality. Surface run off, chemical weathering, bedrock dissolution and other rock-water interaction phenomenon are they potential ways through which solute dissolve in water.

The electrical conductivity for the surface water ranged between 91.0 µs/cm to 935.0 µs/cm with a mean value of 197.5 while the electrical conductivity of the groundwater varied between 102.0 µs/cm to 1008.0 µs/cm with an average value of 291.8 µs/cm. Except for the groundwater samples in locations 11 and 14 whose values are above the maximum permissible limit of 1000.0 µs/cm (NSDWQ, 2015), the concentration of other locations in both surface and groundwater were below the allowable limit for a safe drinking water. Both TDS and conductivity are good indicators of pollution level in water sources. The temperature is the measure of the degree of coldness or hotness of a medium and it has an essential role to play on the chemical reaction taking place in water.

The surface water temperature ranged between 27.2 °C and 29.5 °C with a mean temperature of 28.5 °C while the groundwater temperature varied between 25.3 °C and

28.1 °C with a mean temperature of 25.4 °C. The higher the water temperature, the faster solutes dissolves in water and the observed temperature values falls within the recommended ambient temperature. The pH of the surface water is in the order of 4.52 to 7.05 with a mean value of 5.90 while the groundwater varied from 5.92 to 6.87 with an average value of 6.10.

Table 4.1: Statistical Summary of Physico-chemical and Bacteriological Parameters

Parameters (mg/l)		**SW**			**GW**		**NSDWQ**
	Min.	**Max.**	**Mean**	**Min.**	**Max.**	**Mean**	**2015**
TDS	60.5	640.0	180.40	70.0	830.0	205.20	500.00
Conductivity (µS/cm)	91.0	935.0	197.5	102.0	1008.0	291.8	l000.00
Dissolved Oxygen	5.26	6.03	5.90	5.35	6.05	5.01	10.00
Temperature (^{o}C)	27.2	29.5	28.5	25.3	28.1	25.4	Ambient
Ph	4.52	7.05	5.90	5.92	6.87	6.10	6.5-8.5
Turbidity (NTU)	4.80	590.0	78.25	0.00	49.5	7.25	5.00
Chloride	9.42	48.8	15.37	11.9	93.5	22.72	250.00
Total Hardness	52.0	222.0	71.6	31.0	227.3	101.5	500.00
Fluoride	0.00	0.42	0.15	0.00	1.17	0.39	l.50
Alkalinity	13.5	68.0	41.7	18.9	82.4	51.6	l00.00
Phosphate	0.15	2.45	0.77	0.13	1.62	0.71	45.00
Carbonate	0.00	0.00	0.00	0.00	0.00	0.00	150.00
Sulphate	4.0	43.6	11.3	0.00	83.2	23.56	100.00
Copper	0.00	2.06	0.29	0.10	1.38	0.46	1.00
Bicarbonate	0.00	70.5	29.8	0.00	84.5	34.1	l00.00
Nitrite	0.00	0.17	0.045	0.01	0.19	0.048	0.20
Nitrate	0.79	65.0	9.79	2.15	67.6	13.6	50.00
Sodium	8.00	31.5	11.3	6.00	56.0	17.67	250.00
Potassium	3.00	65.0	10.2	2.00	11.0	5.00	150.00
Calcium	4.27	66.8	19.82	1.76	55.4	26.43	200.00
Magnesium	1.60	12.9	6.43	0.54	32.6	13.57	200.00
Iron	0.05	0.87	0.25	0.01	0.55	0.16	0.30
Zinc	0.05	0.68	0.11	0.00	3.97	0.69	3.00
Manganese	0.01	0.038	0.0089	0.011	0.03	0.0212	0.20
Chromium	0.01	0.05	0.017	0.02	0.07	0.0246	0.05
Arsenic	0.00	0.01	0.001	0.00	0.01	0.0017	0.01
Nickel	0.00	0.01	0.004	0.00	0.03	0.0046	0.02
B.Coliform (cfu/100m	12.0	120.0	44.3	0.00	200.0	37.11	0.00
T.Coliform (cfu/100m	64.0	529.0	279.1	0.00	420.0	92.33	10.00
Faecal Strep.(cfu/100	25.0	176.0	55.60	0.00	150.0	46.85	0.00

Key: SW-Surface Water; GW-Groundwater; TDS-Total Dissolved Solids; T.Coliform-Total Coliform
NSDWQ-Nigerian Standard for Drinking Water Quality; B.Coliform-Bacteria Coliform

The pH for both surface and groundwater are slightly lower than the acceptable limit of 6.5 – 8.5 (NSDWQ, 2015; WHO, 2016). Low pH encourages the dissolution, solubility and mobility of metals in water (Amadi *et al.* 2016)**.** Turbidity values of the surface water varied from 4.80 NTU to 590.0 NTU with a mean concentration of 78.25 NTU while the groundwater has concentration ranging from 0.0 NTU to 49.5 NTU with an average value of 7.25 NTU. From the analysis, the turbidity concentration values in all the sampled surface water are above the maximum permissible limit of 5.0 NTU (NSDWQ. 2015). The number of suspended materials in water makes it turbid, and such water are cloudy (not clear) in appearance, thereby reducing the visibility and transparency of the water. Since groundwater is covered by overlying formation and as a result turbidity values is generally low when compared to surface water which is exposed and receives all sort of materials via human activities and run off. The turbidity values in locations 11, 12, 14 and 15 of the groundwater are above the permissible limit of 5.0 NTU while the concentrations in the remaining locations falls within the acceptable value.

4.1.2 Chemical parameters

The results of the chemical analyses of surface and groundwater from the study area are contained in Table 4.1. The dissolved oxygen has concentrations for the surface water in the range of 5.26 mg/l to 6.03 mg/l with a mean value of 5.90 mg/l while the groundwater has dissolved oxygen concentration value in the range of 5.35 mg/l to 6.05 mg/l with an average of 5.01 mg/l. The dissolve oxygen measured the oxygen available for aquatic organisms and it is very essential for well-being of aquatic lives. The concentration of total hardness for the surface water ranged between 52.0 mg/l and 222.0 mg/l with a mean value of 71.6 mg/l while the concentration for groundwater is in the range of 31.0 mg/l and 227.3 mg/l with an average value of 101.5 mg/l. Groundwater is in constant interaction with the host rock through which it moves and such rock-water interaction accounts the higher values of total hardness in groundwater than in surface water. The presences of calcium and magnesium ions in water are responsible for hardness of water. Total alkalinity concentration in the surface water ranged between 13.5 mg/l and 68.0 mg/l with a mean concentration of 41.7 mg/l while its concentration in the groundwater varied between 18.9 mg/l to 82.4 mg/l with an average concentration of 51.6 mg/l. Shallow water aquifers in basement complex have high alkalinity and this serve as a pointer to the fact that the groundwater has higher alkalinity concentration than the surface water (Olasehinde *et al.*, 2015).

Sodium concentration level in the surface water ranged from 8.0 mg/l to 31.5 mg/l with an average value of 11.3 mg/l and the groundwater has concentration value in the order of of 6.0 mg/l to 56.0 mg/l with a mean value of 17.67 mg/l. The sodium content in surface and groundwater are below the maximum permissible value of 250 mg/l (NSDWQ, 2015). High concentration of sodium in drinking water can cause hypertension in humans (Nwankwoala *et al.*, 2015). Potassium concentration in the surface water ranges between 3.0 mg/l to 65.0 mg/l with a mean concentration of 10.2 mg/l while the groundwater concentration varies from 2.0 mg/l to 11.0 mg/l with an average value of 5.00 mg/l. The concentration of calcium in surface water range between 4.27 mg/l and 66.80 mg/l with an average concentration of 19.82 mg/l while the concentration in groundwater varied from 1.76 mg/l and 55.4 mg/l with a mean value of 26.43 mg/l. The concentration of calcium in surface and the groundwater falls within the maximum permissible limit of 200.0 mg/l (NSDWQ, 2015) for potable water. Calcium is an essential element for the development of teeth and bones in the animals (Tukur and Amadi, 2014; Okiongbo and Douglas, 2013; El-Sayed *et al.*, 2012; Okunlola *et al.*, 2014).

Magnesium concentration in surface water is in the range of 1.6 mg/l to 12.9 mg/l with a mean value of 6.43 mg/l while the concentration in groundwater varied from 0.54 mg/l to

32.6 mg/l and an average value of 13.57 mg/l. These values far below the maximum permissible limit of 200.0 mg/l (NSDWQ, 2015). Magnesium is easily absorbed in water than magnesium in diet. Studies have revealed that intake of magnesium from water sufficient quantity prevents nervous disturbance and arterial hypertension (Vasanthavigar *et al.*, 2010; Nur and Ayuni, 2004). The concentration of sulphate in surface water ranged from 4.0 mg/l to 43.6 mg/l with a mean value of 11.3 mg/l while the concentration in the groundwater varied from 0.00 mg/l to 83.2 mg/l with an average value of 23.56 mg/l. The sulphate concentration in both surface and groundwater are within the maximum permissible limit of 100.0 mg/l (NSDWQ, 2015). High sulphate concentration may result from chemical weathering and dissolution of bedrocks and may also be due to anthropogenic influences resulting from urban pollution such as mining activities and fertilizer application in farming system (Dan Hassan 2013; Aboud and Nandini, 2009).

The concentration of nitrate in surface water ranged from 0.79 mg/l to 65.0 mg/l with a mean value of 9.79 mg/l while the concentration in groundwater varied from 2.15 mg/l to 67.6 mg/l with an average value of 13.6 mg/l. Four locations in the surface water and two locations in groundwater have values higher than the recommended maximum permissible limit of 50.0 mg/l (WHO, 2016; NSDWQ, 2015). High nitrate concentration in water for drinking purposes may cause methemoglobinemia in infants (blue-baby syndrome), metabolic disorder and poisoning of livestock. Nitrate concentration in groundwater can be attributed to man activities like leachate from waste dumpsite, application of fertilizer in farming and poor sanitation (Olatunji *et al.*, 2005; Elueze *et al.*, 2011). The nitrite concentration in surface water ranged from 0.00 mg/l to 0.17 mg/l with a mean value of 0.045 mg/l while the concentration of nitrite in groundwater varied from 0.01 mg/l to 0.19 mg/l with an average value of 0.048 mg/l. These values fall within the permissible limit 0.2 mg/l (NSDWQ, 2015). The phosphate concentration in surface water ranged from 0.15 mg/l to 2.45 mg/l and with a mean concentration of 0.77 mg/l while the concentration of phosphate in the groundwater varied from 0.13 mg/l to 1.62 mg/l and with a mean of 0.71 mg/l. High concentration of sulphate, nitrate, nitrite and phosphate in water are indicators of anthropogenic pollution (Dan Hassan, 2013).

The concentration of fluoride ranged from 0.00 mg/l to 0.42 mg/l with a mean concentration of 0.15 mg/l while fluoride concentration in groundwater varied from 0.00 mg/l and 1.17 mg/l with an average value of 0.39 mg/l. These values are below the recommended maximum permissible limit of 1.50 mg/l (NSDWQ, 2015). Fluoride content in water is both beneficial and detrimental to the body depending on the concentration. Fluoride content below 1.50 mg/l helps in the formation of strong bones and tooth while concentrations exceeding 1.50 mg/l cause fluorosis and skeletal paralysis (Nwankwoala *et al.*, 2017). High fluoride content in groundwater can be attributed to either natural means via chemical weathering and rock dissolution processes or anthropogenic interference through the application of fluoride rich fertilizer (Okunlola *et al.*, 2016; Nwankwoala *et al.*, 2016). This study revealed that the highest concentration of fluoride in groundwater in the area occurs in the portion underlain by granite while fluoride concentration within the schist lithology was found to be averagely low. The fluoride-bearing minerals in granitic and metamorphic rocks are apatite, selecite, topaz, fluorite, flouroapatite and cryolite (Abimbola *et al.*, 2002; Amadi *et al.*, 2016). The high fluoride content in water in the area may be due natural release of fluoride rich mineral in the granite dominated portion via chemical weathering and bedrock dissolution processes.

Chloride concentration in surface water ranged from 9.42 mg/l to 48.8 mg/l with a mean concentration of 15.37 mg/l while in groundwater, the concentration ranged between 11.9 mg/l and 93.5 mg/l with an average value of 22.72 mg/l as against the maximum permissible limit of 250 mg/l (NSDWQ, 2015 and WHO, 2016). High chloride content in water causes hypertension in humans, corrosion in metallic pipes and is harmful to plants that are non-halophytic. Bicarbonate concentration in surface water ranged from 0.00 mg/l to 70.5 mg/l with a mean value of 29.8 mg/l while the concentration of bicarbonate in groundwater varied from 0.00 mg/l to 84.5 mg/l with a mean concentration value of 34.1 mg/l. High concentration of bicarbonate in water does not pose any health challenge. Carbonate was not detected in surface and groundwater. The paucity of carbonate in the area may be a function of the geology of the area.

4.1.3 Heavy metals

The results of the laboratory analyses of the heavy metals in surface and groundwater are shown in Table 4.1. These are chemical elements that are naturally metallic and they relatively have high density and are very toxic at considerably low concentration. They are unique because of their characteristic distinguishing properties that include density, solubility, valency and redox potential. The concentration of iron in surface water ranged between 0.05 mg/l to 0.87 mg/l with a mean concentration of 0.25 mg/l while iron concentration in groundwater varied from 0.01 mg/l to 0.55 mg/l with an average value of 0.16 mg/l. The mean concentration of both surface and groundwater are below the maximum permissible limit of 0.30 mg/l (NSDWQ, 2015). However, surface water samples in locations 2 and 8 and groundwater samples from locations 11, 14, 20 and 26 have values higher than the permissible limit. The concentration of iron in water has some merit and demerit. Lack of iron in water (< 0.3 mg/l) causes goiter while in higher concentration it makes the water turbid, colored, tasty and causes hemochromatosis. The concentration of zinc in surface water ranged from 0.05 mg/l to 0.68 mg/l with a mean concentration value of 0.11 mg/l while zinc concentration in groundwater varied from 0.00 mg/l to 3.97 mg/l with an average value of 0.69 mg/l. The concentration of zinc in both surface and groundwater water are within the permissible limit. Only location 14 of the groundwater samples has a slightly elevated value of 3.47 mg/l as against the acceptable value of 3.0 mg/l (NSDWQ, 2015). In aquatic system, high zinc concentration could pose adverse effect to the aquatic ecosystem as it causes toxicity in fisheries and livestock.

The concentration of copper in surface water ranged between 0.00 mg/l to 2.06 mg/l with a mean concentration value of 0.29 mg/l while copper concentration in groundwater varied from 0.10 mg/l to 1.38 mg/l with an average value of 0.46 mg/l. The concentration of copper in surface water at locations 2, 5 and 7 as well as groundwater in locations 14 and 16 were above the permissible limit of 1.00 mg/l (NSDWQ, 2015). Copper is an important element to human life, but when its concentration is high, it may result to some diseases like anemia, kidney and liver damages, irritation in the intestine and stomach.

The concentration of manganese in surface water ranged between 0.01 mg/l to 0.018 mg/l with a mean value of 0.0089 mg/l while the manganese concentration in groundwater varied from 0.011 mg/l to 0.03 mg/l with an average value of 0.0212 mg/l. All the samples from surface water are below the maximum permissible limit of 0.20 mg/l (WHO, 2016; NSDWQ, 2015). However, the concentration is different for the groundwater samples, as locations 2, 5 6, 9 19 and 23 were higher that the acceptable limit of 0.02 mg/l. High concentration of manganese in water causes neurological disorder in animals.

The concentration of chromium in the surface water ranged from 0.01 mg/l to 0.05 mg/l with a mean value of 0.017 mg/l while the chromium concentration in groundwater ranged from 0.02 mg/l to 0.07 mg/l with an average value of 0.0246 mg/l. The concentrations of chromium in surface water are within the permissible limit of 0.05 mg/l while the locations 5, 7 and 8 have concentrations slightly above the maximum acceptable limit. High chromium content in water causes cancer humans (NSDWQ, 2015).

The concentration of arsenic in surface water ranged from 0.00 mg/l to 0.01 mg/l with a mean value of 0.001 mg/l while the concentration in groundwater varied from 0.00 mg/l to 0.01 mg/l with an average value of 0.0017 mg/l. Arsenic is a pathfinder element to gold. Gold mining releases it to the environment and is the major cause of acute poisoning and cancer in human organs. When it enters the environment bedrock dissolution processes, it remains until it is absorbed in soil and infiltrate into groundwater or surface water through runoff. The concentration of nickel in surface water ranged from 0.00 mg/l to 0.01 mg/l with a mean concentration value of 0.004 mg/l while the concentration in groundwater varied from 0.00 mg/l to 0.03 mg/l with an average value of 0.0046 mg/l. The concentration value is within the acceptable limit of 0.02 mg/l (WHO, 2016; NSDWQ, 2015) except the groundwater samples in location 10 at 0.03 mg/l that is slightly above the permissible limit. High concentration of nickel results to allergic reactions and possible carcinogen.

4.1.4 Bacteriological parameters

The results of the bacteriological parameters are contained in Table 4.1 for both the surface and groundwater. The concentration total coliform for the surface water ranged from 64.0 cfu/100ml to 529 cfu/100ml with a mean value of 279.1 cfu/100ml while the concentration total coliform in groundwater varied from 0.00 cfu/100ml to 420 cfu/100ml with an average value of 92.33 cfu/100ml. These values are higher than maximum recommended value of 10.00 cfu/100ml (NSDWQ, 2015). The presence of total coliform in water is an indication that the water in the area is polluted with human faeces. The concentration of bacteria coliform for the surface water ranged between 12.0 cfu/100ml and 120 cfu/100ml with a mean concentration of 44.3 cfu/100ml while the concentration of bacteria coliform for the groundwater varied between 0.00 cfu/100ml and 200 cfu/100ml with a mean concentration of 37.11 cfu/100ml. The mean concentration of bacteria coliform in surface and groundwater falls above the recommended value of 0.00 cfu/100ml (NSDWQ, 2015 and WHO, 2016). This is also an indication of faecal contamination of the surface and groundwater system in the area (Amadi *et al.*, 2016). The concentration of faecal streptococci concentration for the surface water ranged from 25.0 cfu/100ml to 176 cfu/100ml with a mean concentration of 55.6 cfu/100ml while the concentration value for the groundwater ranges between 0.00 cfu/100ml to 150 cfu/100ml as against the acceptable value of 0.0 cfu/100ml. The presence of total coliform, bacterian coliform and faecal streptococci in water is an indication of faecal contamination. This is responsible for water borne diseases such cholera, diarrhea, yellow fever, acute renal failure and haemolytic anaemia.

4.2 Hydrochemical Facies

4.2.1 Piper diagram

This method was devised by Piper in 1944 to outline certain fundamental principles in a graphic procedure which appears to be an effective tool in separating analytical data for critical study with respect to sources of the dissolved constituents in water. Piper diagram consists of three parts: two trilinear diagrams along the bottom and one diamond-shaped diagram in the middle. The trilinear diagram illustrates the relative concentration of cations (left diagram) and anions (right diagram) in each sample. The concentration of 8 major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, CO_3^{2-}, HCO^-_3 and SO_4^{2-}) are represented on a trilinear diagram by grouping the K^+ with Na^+ and the CO_3^{2-} with HCO^-_3, thus reducing the number of parameters for plotting to 6. On the Piper diagram, the relative concentration of the cations and anions are plotted in the lower triangles, and the resulting two points are extended into the central field to represent the total ion concentrations. The degree of mixing between freshwater and saltwater can also be shown on the Piper diagram. The Piper diagram (Figure 4.1) can also be used to classify the hydrochemical facies of the groundwater samples according to their dominant ions. The water in the area is calcium-bicarbonate facies, typical of groundwater from shallow aquifers in a basement terrain.

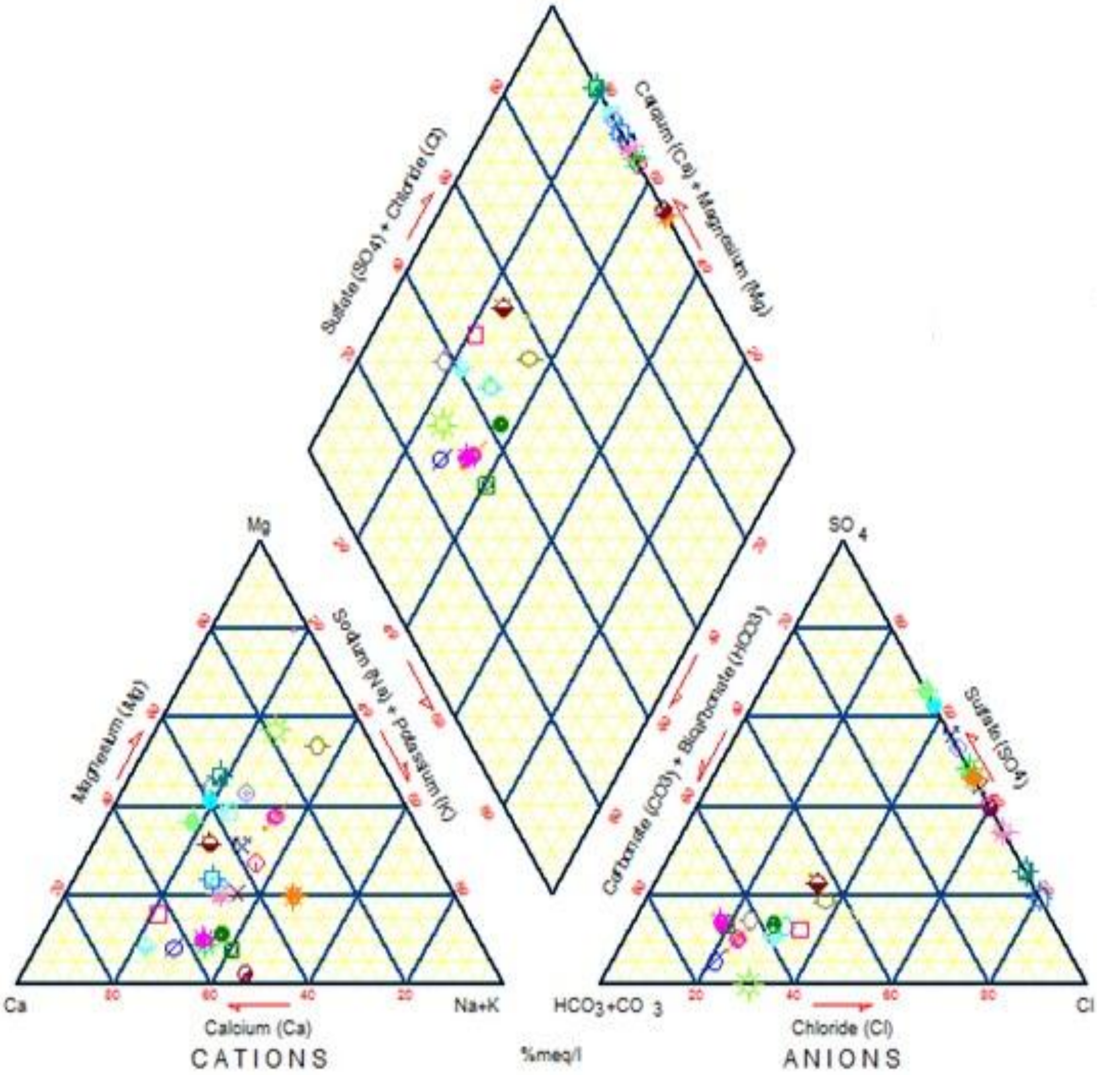

Figure 4.1: Piper Diagram for the Study Area

4.2.2 Durov diagrams

Durov diagram is another mean of categorizing the hydrochemical facies of both surface and groundwater. The Durov diagram plots the major ions as percentages of milli-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 which lies perpendicular to the third axis in each triangle. This plot reveals useful properties and relationships for large sample groups. The Durov diagram (Figure 4.2) shows clustering of data points and this indicate samples that have similar compositions. The Durov diagram also confirms the presence of calcium-bicarbonate water type for the area.

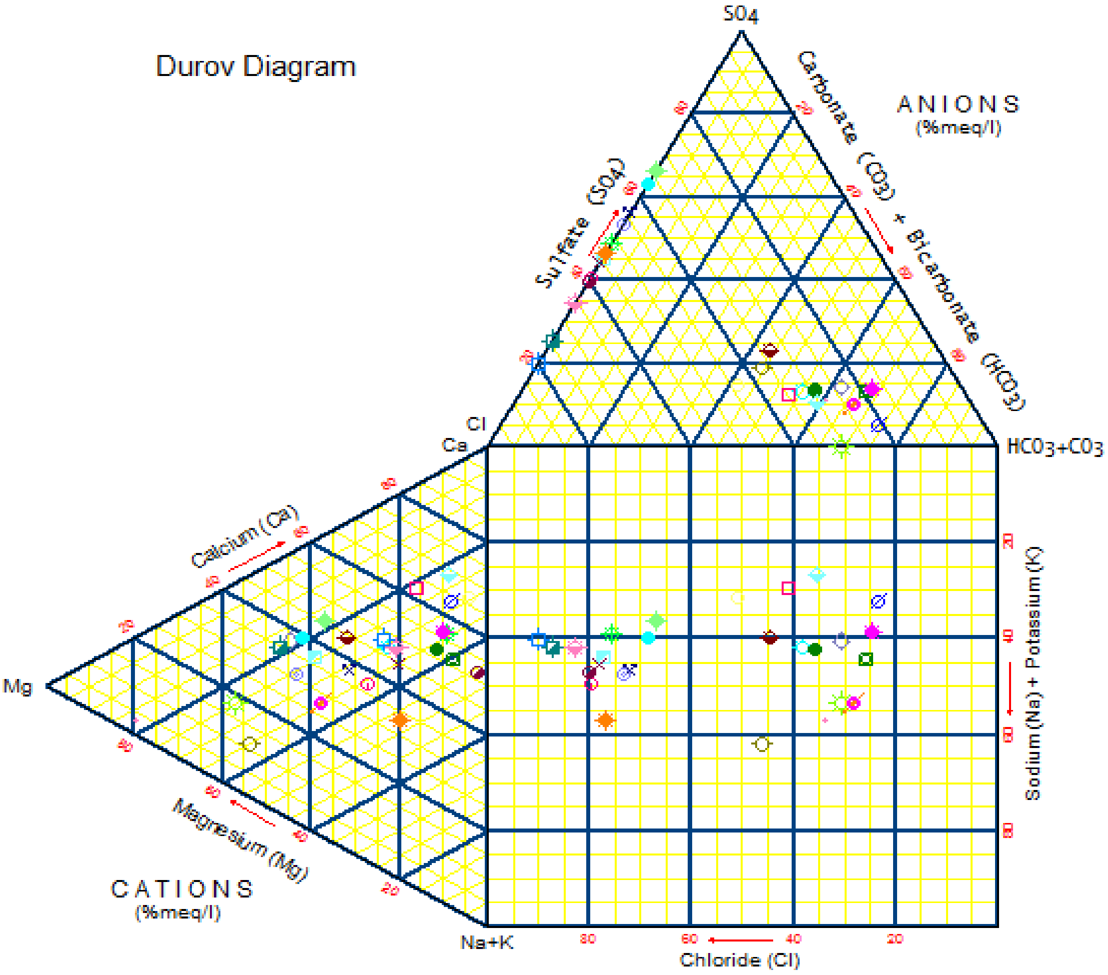

Figure 4.2: Durov Diagram of the Study Area

4.2.3 Stiff plot

The Stiff plot is quite similar to the Piper and Durov diagrams as sodium and potassium as well as carbonate and bicarbonate are also combined in the plotting. However, in Stiff plot (Fig. 4.3), individual locations are plotted different, unlike in Piper and Durov diagrams where several locations can be plotted on a single Piper or Durov diagram. In Stiff plots, similar shapes imply similar water type and possibly similar source. Plots with same or similar shape are grouped and interpreted as the same facies type.

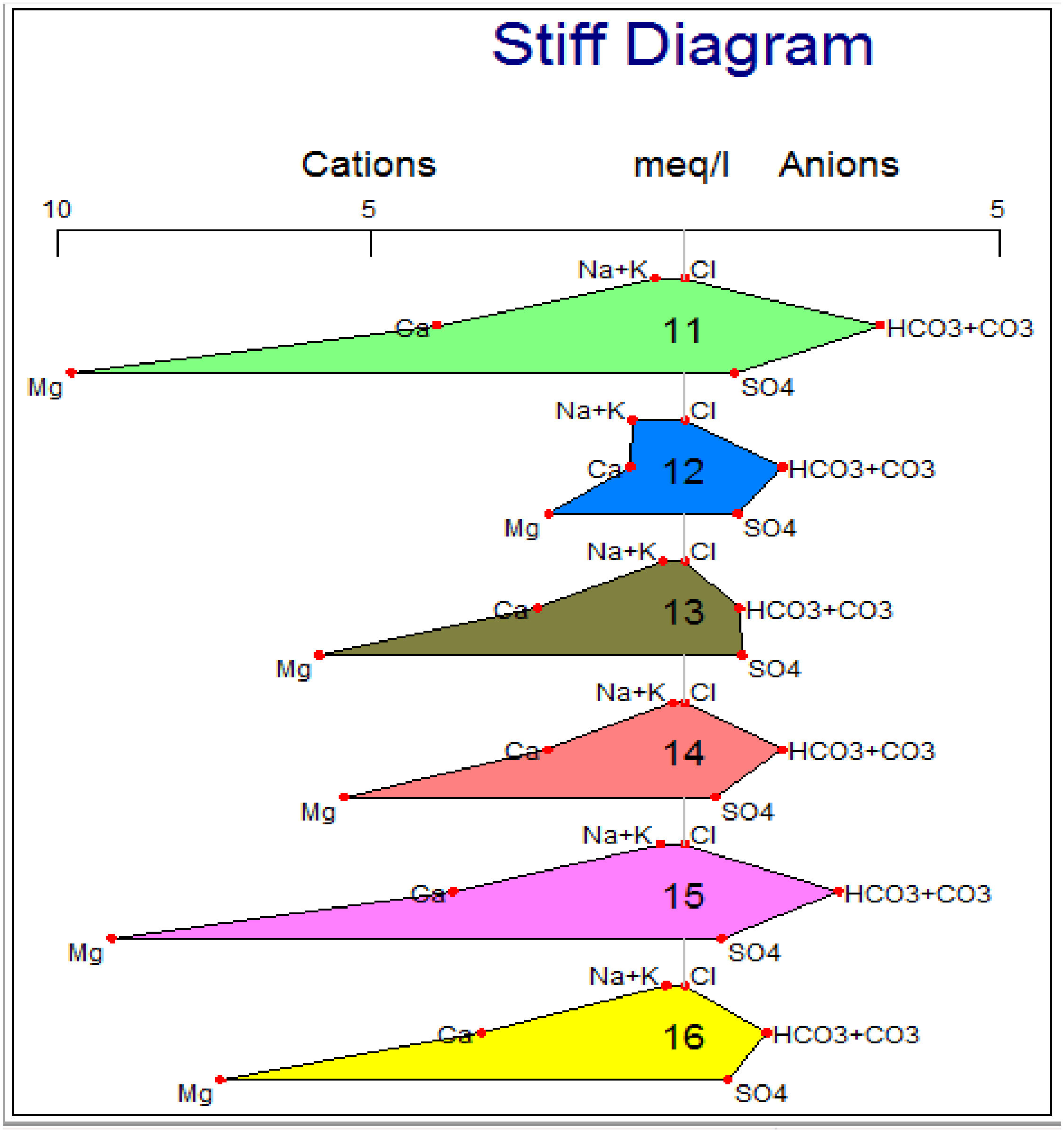

Figure 4.3: Stiff plot of the Study Area

4.2.4 Schoeller plot

These semi-logarithmic diagrams were developed to represent major ion analyses in meq/l and to demonstrate different hydrochemical water types on the same diagram (Fig. 4.9). This type of graphical representation has the advantage of revealing the individual concentrations of the elements unlike the Piper and Durov where elements are combined (Na +K) and (HCO_3 +CO_3) before plotting is done. This leads to shielding (hiding) effect of one element by another.

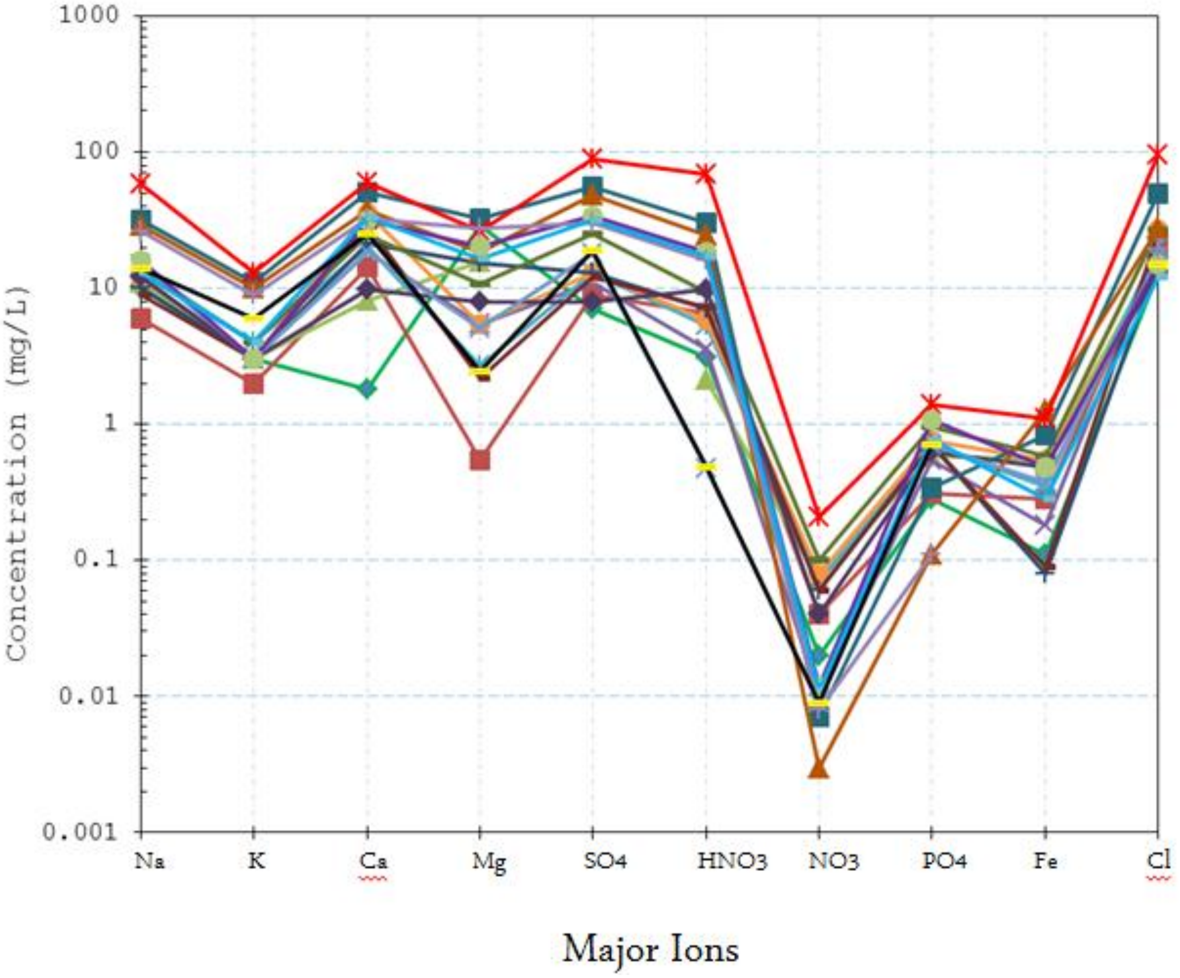

Figure 4.4: Schoeller plot for the Study Area

4.2.5 Gibbs plots

Gibbs (1970) suggested that a simple plot of TDS versus the weight ratio of $(Na^+ + K^+)/(Na^+ + K^+ + Ca^{2+})$ and TDS versus the weight ratio of $Cl^-/(Cl^- + HCO^-_3)$ could provide information on the relative importance of the major natural mechanisms controlling surface and groundwater chemistry such as precipitation, rock weathering and evaporation. The Gibbs scatter diagram plotted using surface and groundwater data from the area. In the diagram, samples falling in the centre of the curve are characterized by chemistry influencing rock-water interaction (Fig. 4.5). This suggests that chemical weathering of rock-forming minerals is the main causative factor in the evolution of the chemical composition of both surface and groundwater in the study area.

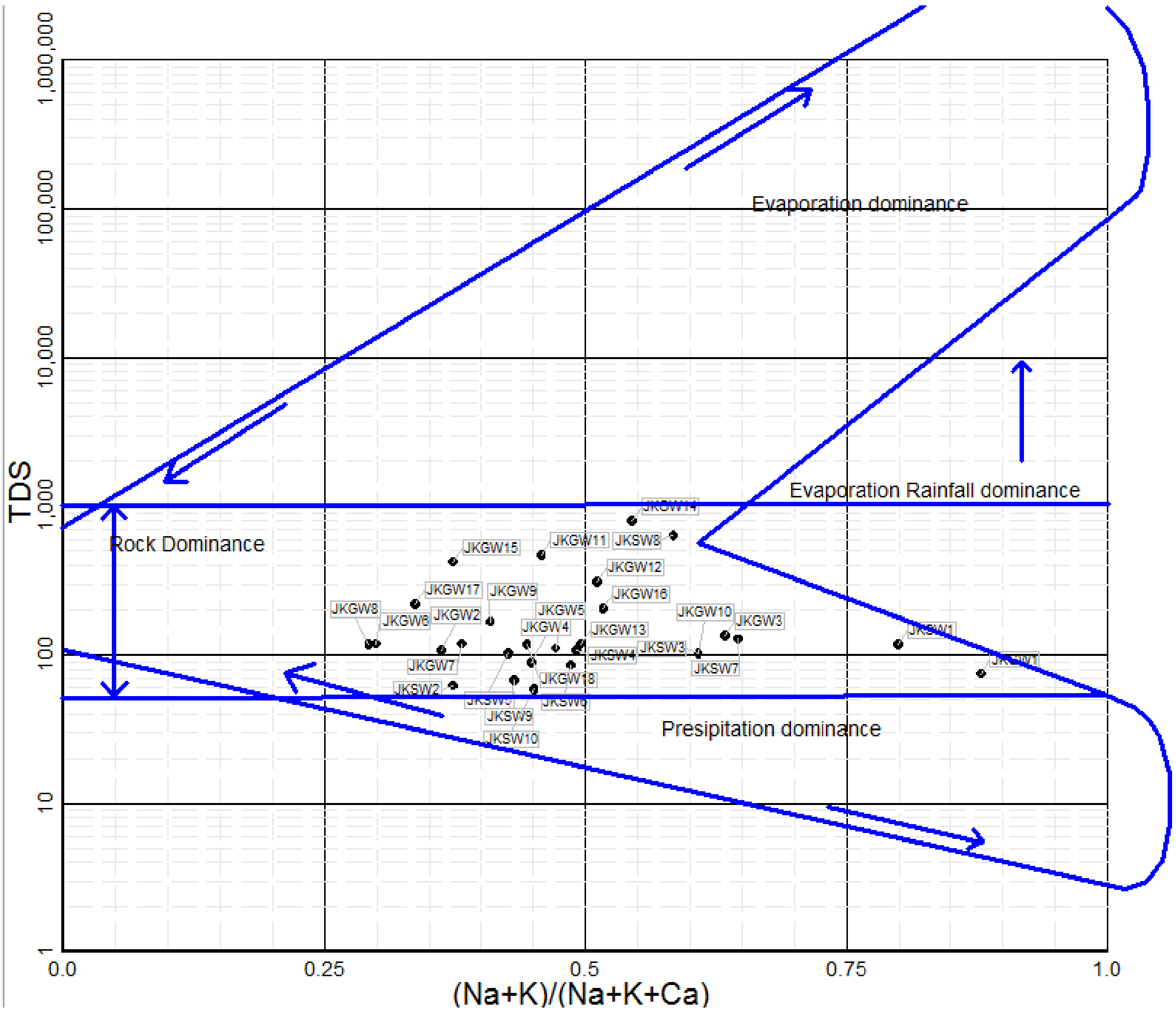

Figure 4.5: Gibbs Plot for the Study Area

4.3 Water Quality Index

Water quality index (WQI) of the studied groundwater samples was performed in order to get an overall impression about the samples in a multidimensional space defined by the analyzed parameters. The water quality index (WQI) was calculated from the point view of suitability of the water for human consumption by using the weighted arithmetic index method. The quality rating scale for each parameter q_i was calculated by using this expression:

$$q_i = (C_i / S_i) \times 100 \qquad (4.1)$$

A quality rating scale (q_i) for each parameter is assigned by dividing its concentration (C_i) in each water sample by its respective Nigerian Standard for Drinking Water Quality (S_i) and the result multiplied by 100. The Relative weight (w_i) was obtained by a value inversely proportional to the recommended standard (S_i) of the corresponding parameter:

$$w_i = 1/S_i \qquad (4.2)$$

The overall Water Quality Index (WQI) was calculated by aggregating the quality rating (q_i) with unit weight (w_i) linearly.

$$WQI = (\sum_{n=1}^{i=n} q_i w_i) \qquad (4.3)$$

Where:

q_i: the quality of the ith parameter,

w_i: the unit weight of the ith parameter and

n: the number of the parameter considered.

The overall water quality of an area is therefore obtained using the formular:

$$\text{Overall } WQI = \frac{\sum q_i w_i}{\sum w_i} \qquad (4.4)$$

The physico-chemical and bacteriological parameters analyzed were used to calculate the WQI in accordance with the procedures explained above and contained in Table 4.12. The computed overall WQI value was 285.20 and this means that the groundwater in the area falls within the ‘very poor quality’ as illustrated in Table 4.13.

$$\text{Overall WQI} = \frac{\sum q_i w_i}{\sum w_i} = \frac{10357.18}{74.72} \qquad (4.5)$$

Table 4.2: Computation of water quality index

Parameters	Ci	Si	qi	wi	$qiwi$
T.Hardness	107.5	150	71.67	0.0067	0.48
Cl^-	10.4	250	4.16	0.004	0.02
Ca^{2+}	43.8	75	58.4	0.013	0.76
Mg^{2+}	39.6	200	19.8	0.005	0.10
Conductivity	169.4	1000	16.9	0.001	0.02
TDS	113.5	500	22.7	0.002	0.05
Turbidity	3.8	5	76	0.2	15.2
Ph	7.6	8.5	89.4	0.118	10.52
Fe^{3+}	0.2	0.3	66.67	3.33	222.23
Cu^{2+}	1.02	2	51	0.5	25.5
Zn^{2+}	0.05	3	1.67	0.33	0.56
NO_3^-	33.2	50	66.4	0.02	1.33
$SO4^{2-}$	26.1	100	26.1	0.01	0.261
Cr^{2+}	0.0001	0.05	0.2	20	4
Sus. Solid	45.375	1000	4.54	0.001	0.005
Colour	80.375	15	535.83	0.067	35.72
Mn^{2+}	0.04	0.02	200	50	10000
K^+	0.06925	150	0.046	0.00067	0.00031
Na^{2+}	8.96775	200	4.484	0.005	0.022
T.Coli	40.4	10	404	0.1	40.4
Summation				74.72	10357.18

Table 4.3: Water Quality Classification Based on WQI Value

WQI value	Water quality	Water samples (%)
<50	Excellent	02
50-100	Good water	04
100-200	Poor water	06
200-300	Very poor water	08
>300	Unsuitable for drinking	05

The high value of WQI obtained may be attributed to artisanal mining activities going on in the area.

4.4 Metal Pollution Index

Heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. They cannot be degraded or destroyed and can enter our bodies through food, drinking water and air. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation is an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment.

Metal pollution index (MPI) is a method of rating that shows the composite influence of individual parameters on the overall quality of water. The rating is a value between zero and one, reflecting the relative importance individual quality considerations. The higher the concentration of a metal compared to its maximum allowable concentration, the worse the quality of the water (Amadi, 2011a). It is also a combined physio-chemical and microbial index which makes it possible to compare the water quality of various water bodies. It has wide application and it is used as the indicator of the quality of sea and river water (Amadi *et al.*, 2012a; Lylko *et al.*, 2001), as well as drinking water (Amadi *et al.*, 2012a). The MPI represents the sum of the ratio between the analyzed parameters and their corresponding national standard values as shown in Table 4.14 below:

$$MPI = \sum_{i=1}^{n} \left[\frac{Ci}{(MAC)i} \right] \tag{4.6}$$

where: C_i: mean concentration

MAC: maximum allowable concentration

Water quality and its suitability for drinking purpose can be examined by determining the metal pollution index.

Table 4.4: Calculated Metal Pollution Index for the Groundwater in the Area

Parameters (mg/l)	***Cᵢ***	***MACᵢ***	**MPI Value**	**Rating**
Arsenic	0.007	0.01	0.70	Lightly polluted
Cadmium	0.11	0.02	4.50	Moderately polluted
Cobalt	0.02	0.01	2.00	Moderately polluted
Chromium	0.07	0.05	1.40	Moderately polluted
Copper	0.8	1.00	1.90	Moderately polluted
Iron	0.62	0.30	2.10	Moderately polluted
Lead	0.04	0.01	4.00	Moderately polluted
Manganese	0.19	0.20	0.95	Lightly polluted
Mercury	0.003	0.001	3.00	Moderately polluted
Nickel	0.02	0.01	2.00	Moderately polluted
Zinc	0.17	3.00	1.57	Moderately polluted

Key: < 0.01= Very lightly polluted; 0.01-1.0= Lightly polluted; 1.0-5.0= Moderately polluted; 5.0-10.0= Highly polluted; > 10.0= Very highly polluted

4.5 Concentration Maps of the Study Area

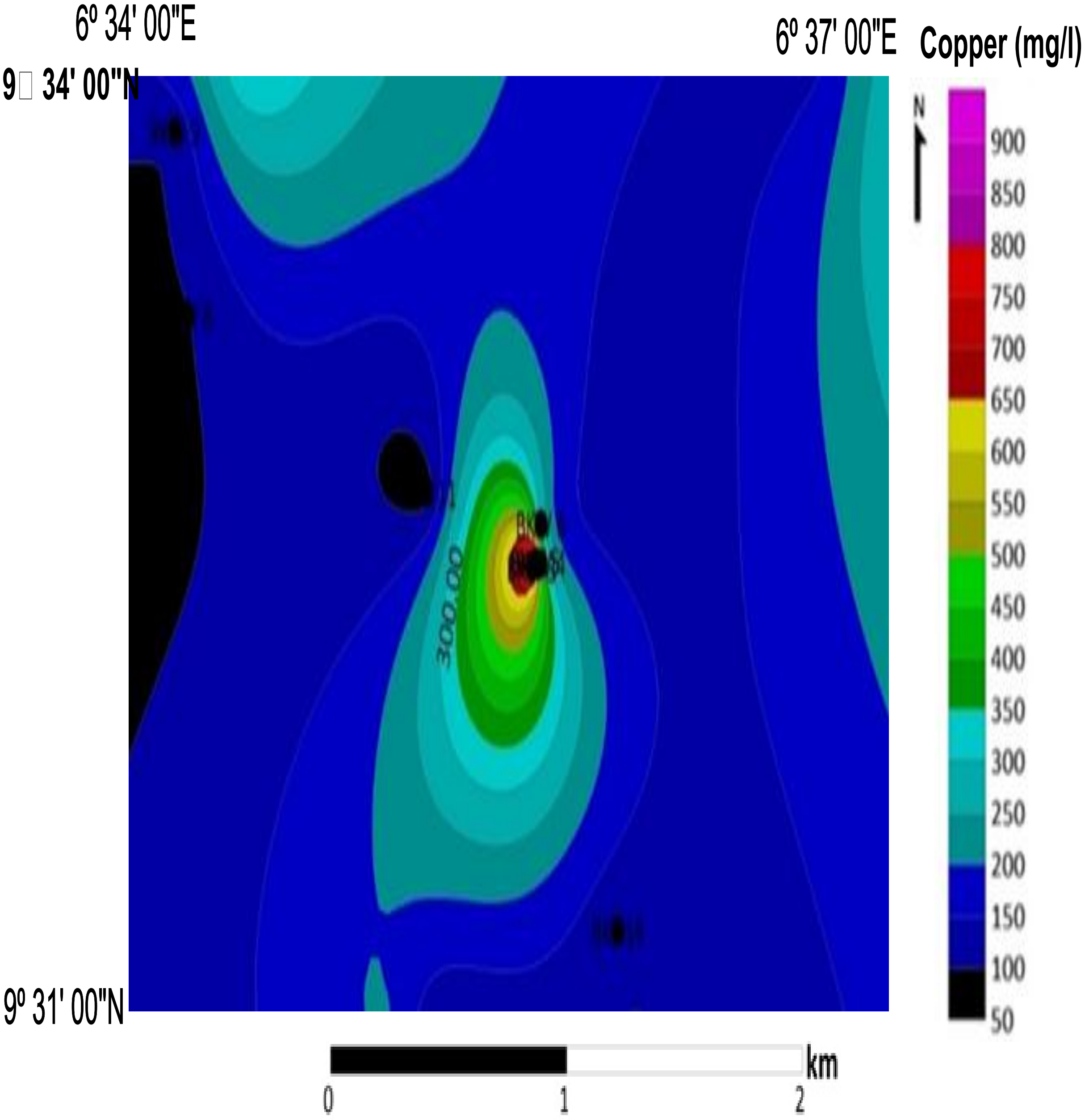

Figure 4.6: Copper Concentrated Map

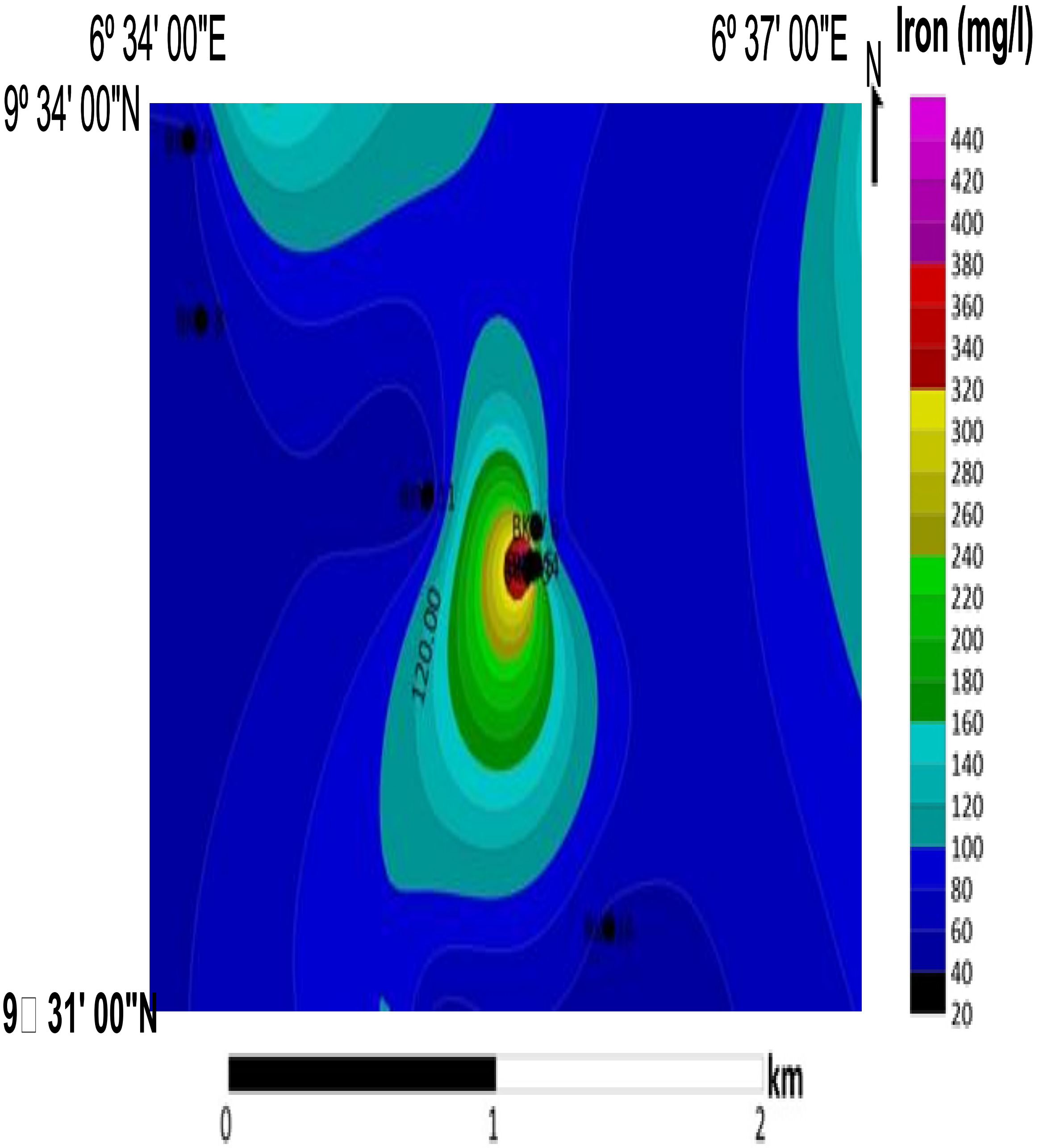

Figure 4.7: Iron Concentrated Map

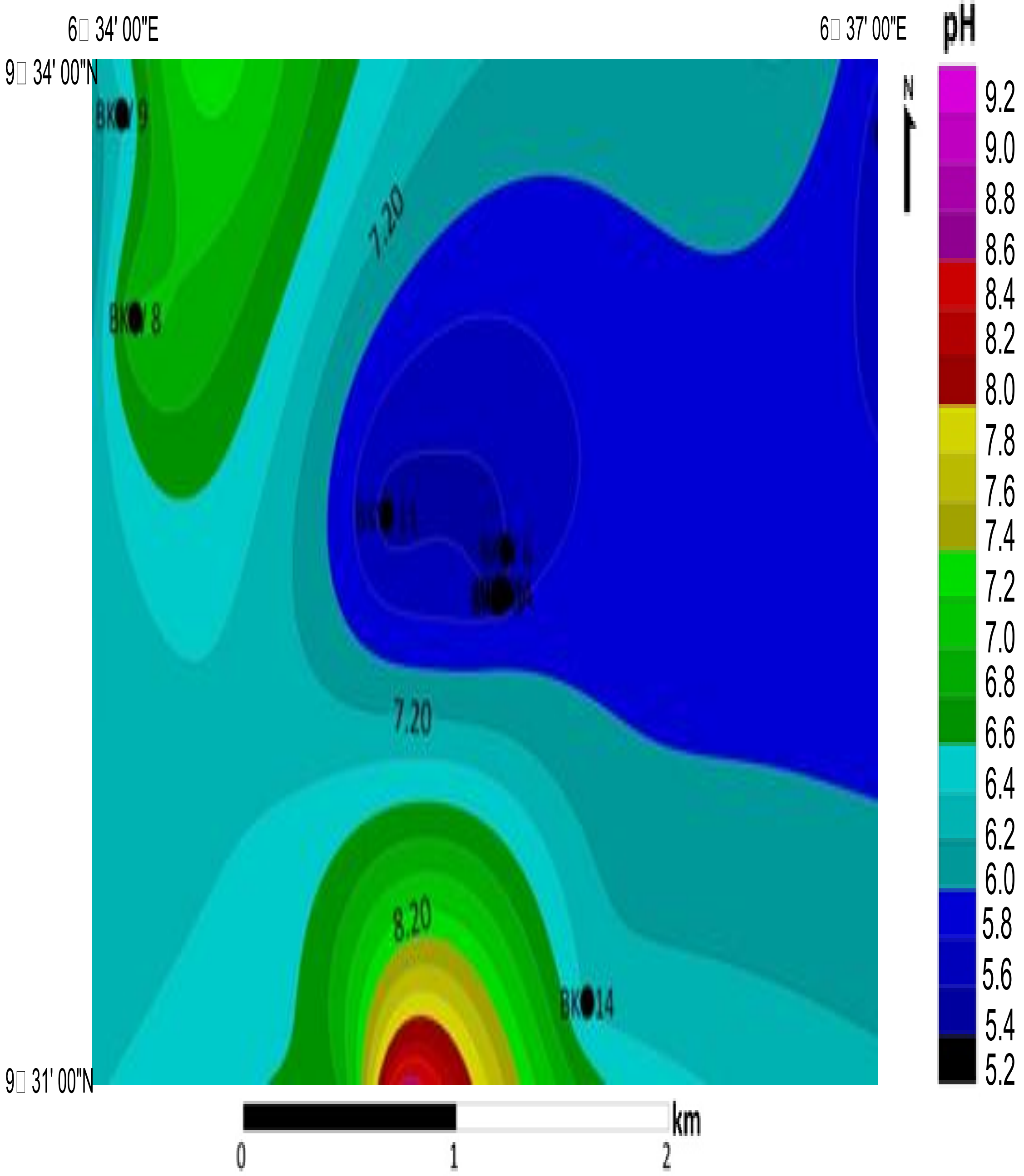

Figure 4.8: Ph Concentrated Map

The mining site is located at the center of the study and that explains why the concentration of copper and iron is high near the mining sites and decreases away from the mining site. Heavy metal concentrations in water are of great concern because of their toxicity, persistence and bio-accumulative nature as this has serious effects on both plants and animal health through food chain (Amadi *et al.*, 2012b). Iron is among the earth's most abundant elements. Rainwater dissolves it mainly because it infiltrates the soil perfectly to the underlying geological formations. Although iron is not hazardous to health, it is considered a secondary or aesthetic contaminant. It is essential for good health as it helps transport oxygen in the blood. Iron causes taste and odour problem in water and may result in water colouration when it exceeds the maximum permissible limit of 0.3mg/l (WHO, 2016; NSDWQ, 2015). The concentration of iron in all the water samples analyzed is generally high while anomalous values are found in the active mining pits areas of Chanchaga area. The explanation for the anomalous concentration of iron in all the water samples could be attributed to the geology of the underlying rocks in the study area which are mostly granite and schist in nature, highly weathered and rich in iron bearing minerals (Amadi *et al.*, 2016). The concentration map of iron in the area is shown in Figure 4.7

Similarly, copper is an essential substance to human life, but in high concentrations it can cause anemia, liver and kidney diseases in addition to stomach and intestinal disorders. The concentration of copper is high around the mining sites (centre) as it exceeds the permissible limit of 1.0 mg/l (NSDWQ, 2015). A map showing the distribution of copper in the study area is illustrated in Figure 4.6.

Furthermore, the ore hosting the gold that is mined occur in association with these metals and are dumped into the nearby soil and stream channel as gangue. During weathering processes, these metals (copper and iron) are liberated from the gangue material and mobilized into the environment (soil and water) thereby contaminating them.

The pH of water is an indicator of the water quality and extent of pollution. The gold mining activity going on in the area may be responsible for the low pH of less than 6.5 especially around the gold mining locations, an indication of that the water is slightly acidity. Metals are mobilized and demobilized faster under acidic condition, which is characterized by pH lower than 6.5. The permissible limit of pH is between 6.5-8.6 (WHO, 2016; NSDWQ, 2015). The pH concentration map indicated that the pH is lowest at the mining area and increasing away from the mining area and this attributed to the high concentrations of copper and iron were high near the mining sites.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The hydrogeochemical investigation of surface water and groundwater quality around Bosso Local Government area, Minna, Niger State, Nigeria was studied in the present research work. The study was aimed at evaluating the quality status of surface water and groundwater in the vicinity of a gold mining site around River Chanchaga area. The physical parameters were determined insitu while the chemical and bacteriological parameters were determined in the laboratory. Results of the water analysis were interpreted and compared with the Nigeria Standards for Drinking Water Quality (NSDWQ, 2015) and World Health Organization (WHO, 2016). The cations and anions analyzed for both surface and groundwater samples were within the WHO permissible limits and their source in the water is traced to natural geological process of rock weathering, bedrock dissolution and surface run-off. The concentration level of some of the analysed heavy metals in surface and groundwater slightly exceeds the NSDWQ, (2015) and WHO, (2016) permissible limits in few locations and these include Cu, Fe, Mn and Ni. The slight contamination may be attributed to anthropogenic via mining activities and geogenic through weathering and rock-water interaction. Bacteriologically, both surface and groundwater were heavily contaminated with total coliform, bacteria coliform and faecal streptococci which are an indication of faecal contamination. It is a confirmation that the water systems in the area is in contact with animal faeces.

5.2 Recommendations

The following recommendations are suggested:

1. Plants like Hydrilla Verticillata and Pistia Stratiotes are already proven to be heavy metal accumulators, they should be utilized and planted in contaminated areas to enable removal of heavy metals from the polluted water bodies and soil without endangering the lives of other flora and fauna.
2. Microbial contamination can be treated by the water as bacteria do not survive high temperature.
3. The miners should be grouped into associations and equipped with modern mining tools.
4. Treatment of mining waste before disposal into nearby surface water or farmlands is recommended.
5. Proper sensitization should be carried out in the area of the dangers of crude mining methods, but safer mining techniques should be encouraged.

5.3 Contribution to Knowledge

The study contribute to knowledge by establishing the physical and chemical properties of surface water and groundwater in which the pH value ranges from 6.5 – 8.5, while the dissolved oxygen has concentrations for the surface water ranges from 5.26 mg/l to 6.03 mg/l with a mean value of 5.90 mg/l. The study also establishes a concentration map showing the levels of pollution status of water samples in the study area in which the concentration of copper is high around the mining sites (centre) as it exceeds the permissible limit of 1.0 mg/l

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APPENDICES

SITE PICTURES