EFFECTS OF LEAD-ZINC MINING ON WATER SOURCES AROUND ENYIGBA SOUTH-EASTERN NIGERIA, PART OF ABAKILIKI SHEET 303 NE

BY

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MTech/SPS/2018/8096

DEPARTMENT OF GEOLOGY
FEDERAL UNIVERSITY OF TECHNOLOGY MINNA

JUNE, 2023

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA, NIGERIA IN PARTIAL FULFILMENT OF THE REQUUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTERS OF TECHNOLOGY IN GEOLOGY (ENVIRONMENTAL GEOLOGY)

JUNE, 2023

DECLARATION

I hereby declare that this thesis titled: **"Effects of Lead-Zinc Mining on Water Sources Around Enyigba South-Eastern Nigeria, Part of Abakiliki Sheet 303 NE"** is a collection of my original research work and it has not been presented for any other qualifications anywhere. Information from other sources (published and unpublished) has been duly acknowledged.

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____
Signature & Date

CERTIFICATION

This thesis titled **"Effects of Lead-Zinc Mining on Water Sources Around Enyigba South-Eastern Nigeria, Part of Abakiliki Sheet 303 NE"** by OKERE, Oluchukwu Judith REG NO: MTech/SPS/2018/8096 meets the regulations governing the award of the degree of Master of Technology in Geology (Environmental), Federal University of Technology, Minna, Nigeria and it is approved for its contribution to scientific knowledge and literary presentation.

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ABSTRACT

The work analysed and established the physicochemical composition of water and evaluation of results to established effects of mining of Lead-Zinc in water in Enyigba, South-Eastern Nigeria. The geology of the study area was carried out and the result of the geologic mapping revealed that the area is covered by shale from the Abakaliki Formation. A total of forty-four samples, that is thirteen groundwater and thirty-one surface water samples, were collected and analyzed using absorption spectroscopy and ultra violet / visible spectroscopy. The parameters used to access the contamination level of Lead-Zinc in water are PH, TDS and Temperature. The PH values range from (1.25 to 9.73), TDS (highest value 91.66 Mg/L) Temperature (highest temp. of 29^{o}C). Result shows that the area is underlain by very high levels of lead (as high as 1.68mg//l), zinc (10.62mg/l), and other associated metals such as iron (57.1mg/l) nickel (0.16mg/l) in water sources around Enyigba. Highest values were recorded from samples gotten from water resources around the mining sites and this is due to mineralization in the area. These values observed are above the WHO recommended standard for drinking water. The potential health risks associated with accumulation of toxic heavy metals in the body includes, cancer, cardiovascular diseases, arsenicosis, parkinson's disease, alzheimers amongst others. Generally, the study reveals that the water sources in the study area are unsuitable for consumption. Therefore, provision of alternative water supply and sensitization on the potential health risk is highly advocated in this community. The assessment and early curbing of the contamination level of lead-zinc in Enyigba community will greatly aid in the avoidance of another Zamfara disaster.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Mining activities has notably been responsible for heavy metal contamination of both land and water (Johnston, 2004; Foulds *et al*., 2014). Mayes *et al.,* (2013), considered flooding or water overflow in mining site as a major contaminant dispersion agent. Artisanal gold mining in Zamfara State, Nigeria resulted in a widespread acute lead poisoning of both soil and water bodies, resulting in the death of over 4000 children and more than 3500 requiring urgent, lifesaving treatment (Medecins Sans Frontieres, 2012; WHO, 2012). World Health Organization (WHO) in its Bi-Monthly Newsletter dated March to April 2012, defined this contamination outbreak as one of the worst in modern history. Azubike, (2011), Babajide, (2011), UNICEF (2010-2011) and Uriah *et al*., (2013) has also linked heavy metal contamination with mining activities.

Mining activities within the Southern Benue Trough has been intensified within the last 10 years, with a lot of artisanal miners that are unregulated and environmental assessment done to analyze the impact of these activities on soils and water bodies Mayes, *et al*., 2013. There are also lots of abandoned pits which local communities converted into water reservoirs for use during the dry season. Due to poor land reclamation practices, these communities of mostly uneducated farmers do not have the knowledge of the dangers of the water reservoirs and groundwater that's been contaminated by this poor mining practices. Poor mining activities and management also yields contamination of groundwater due to infiltration, while surface water is generally contaminated by surface runoff at and around the mine pit. This scenario has become a normwithin the active mining axis of Enyigba and Ikwo communities of Ebonyi State, which is geologically placed within the Southern Benue Trough; since these heavy metals are not degradable, they are continuously washed into the groundwater. This needs to be assessed, so as to stop, control and properly manage the levels of heavy metals in ground and surface water. Heavy metals in the environment greatly degrades soil and water quality, agricultural produce and eventually the health of organisms. The early curbing of the contamination level will greatly aid in the avoidance of another Zamfara disaster.

Ground and surface water play an important role in the livelihood of human populations. They are used as a source of domestic water supply, irrigation, fishery development, hydropower generation and flood control. According to Dudgeon (2006) and Junk (2002), freshwater ecosystems are vulnerable to human impacts hence, they are likely to be influenced by reservoir catchment activities. This is because terrestrial ecosystems have linkages with aquatic ecosystems (UNEP, 2000). Contamination of aquatic ecosystems with a wide range of pollutants has become a matter of concern over the past few decades (Dirilgen, 2001; Gosar, 2004; Vutukuru, 2005; Yousafzai and Shakoori, 2008; Vinodhini and Narayanan, 2008 and Xiao *et al*., 2017).

FAO (1992) noted that the contamination of water supplies from both natural and anthropogenic sources has impacted the health and economic status of populations. Human activities cause pollutants such as heavy metals, pesticides and herbicides to enter aquatic ecosystems. These anthropogenic activities continuously increase the number of heavy metals in the environment, especially in aquatic ecosystems. Thus, heavy metal pollution is growing at an alarming rate and has become an important worldwide problem (Malik *et al.*, 2010). Increase in population, urbanization, industrialization and agricultural practices as well as lack of environmental regulations have further aggravated the situation (Gupta *et al.*, 2009).

Heavy metals cannot be degraded but they are deposited, assimilated or incorporated in water, sediments and aquatic biota causing heavy metal pollution in water bodies (Linnik and Zubenko, 2000; Malik *et al*., 2010). Heavy metals in water can originate both from natural sources, industrial, agricultural and domestic activities in the drainage basin of a water system. As the metal levels in many aquatic ecosystems increase due to anthropogenic activities, they raise the concern on metal bioaccumulation through the food chain and related human health hazards (Wright and Welbourn, 2002; Indrajith *et al.*, 2008; Agah *et al*., 2009). The anthropogenic activities like mining and smelting, fertilizer production, battery manufacturing, electroplating, wood preservation and agricultural activities pose a high risk to the environment, ecosystem and human health (Gosar, 2004; Xiao *et al*., 2017).

1.2 Statement of the Research Problem

In 2010, widespread and acute lead poisoning in Zamfara state, northern Nigeria killed at least 400 children World Health Organization (WHO) in its Bi-Monthly Newsletter dated March to April 2012 (WHO, 2012), tied the heavy metal contamination to artisanal gold mining in Pb-rich ore within the area. Since the discovery and mining of mineral deposits in the Abakaliki area in the early 1990s, not much data exists on the geochemical attributes of mining activities in the environment. Heavy metal weathering of the mineral deposits may have adverse consequences on soil quality due to soil – water interaction. Apart from the challenges to sustainable water quality, pollutants and contaminants from mining sources constitute a major threat to human health, aquatic lives, land use and agriculture and other aspects of ecosystem imbalance. Soil/ land degradation problem is obvious within the mining axis. Mine wastes and tailings are directly discharged into farmlands and river channels. Rural dwellers in various communities commonly depend on water from the abandoned mines and drainage channels for their domestic activities. Numerous health challenges such as miscarriages, selenosis in infant, decline in fertility, physiological and mental imbalance are commonly encountered in various communities. They often attribute these health cases to evil forces and evil men and probably as penal measures for inadequate sacrifices to their gods.

It is based on this background that an assessment of the quality of the environment (especially in the area of land use safety) in the mining axis of Ebonyi State, Nigeria should be carried out. The soil shall be investigated, since the affected communities are predominantly farmers and water assessment will be carried out around polluted areas. Emphasis shall be placed on qualitative assessment of the various soils in the area and various input sources of hydrochemical significance shall be assessed. Therefore, making valuable information in this regard may likely alleviate the numerous health problems in the area and constitute a vital planning tool to healthcare providers, environmental management and regulatory authorities. There is need to investigate the movement of groundwater in the area, since the possible contaminants in the host rocks can migrate and be carried along in solution from one point to another. This will assist in the establishment of safe and unsafe areas with respect to contaminant transportation and waste management, and will also be used to determine recharge and discharge areas, which constitutes a vital tool in groundwater prospecting and management.

1.3 Justification for the Study

Mining of sulphide-bearing ore deposits exposes sulphide rocks to surface water and oxygen, which accelerate oxidation, leaching and release of metals and generation of acid – a process called Acid Mine Drainage (AMD). Any modern mining project involved with sulphide- bearing ore deposit like does within Enyigba and Abakaliki axis is faced with the greatest challenge of controlling (if not preventing) the environmental impact of mine waste and mining process, which can contain large amounts of sulphide-bearing gangue minerals. Degradation of the quality of surface and groundwater that come in contact with acid producing mine tailings piles is a major environmental problem associated with acid mine drainage and poor pit planning (associated with artesian mines). The composition of the lead- zinc ore deposit releases heavy metals such as aluminum, selenium, arsenic, cadmium, cobalt, copper, iron, manganese, nickel, lead, zinc and many others into surface and groundwater. The host communities of these mining sites depend on this water from abandoned mines and drainage channels for their domestic activities. The effect of high level of this heavy metal contamination is seen in Zamfara State, Nigeria in 2010, where more than 400 children dead off lead poison and a host of others in need of medical care (WHO, 2012).

In Enyigba and its environs, lead-zinc ore deposits within the Asu River shales have been mined for their base and precious metals for more than 75 years (Ezeh *et al.*, 2007), and due to poor site planning, little to no environmental impact assessment, there are a lot of abandoned mine pits and surface water runoff from active pits into water tributaries. The mining activities, especially in the past few years to present, have resulted in large volumes of waste rock dumps and fine-grained floatation tailings, which contain high amount of sulphide-bearing gangue minerals. Poor management of this waste has resulted oxidation of the sulphide minerals in the mines which corrode heavy metal solutions. Surface water runoff especially during the raining season results in erosion and deposition of this solutions into water channels and groundwater (infiltration), thus accelerating process of environmental pollution (Ezeh *et al.*, 2007).

1.4 Aim and Objectives of the Study

The aim of this research work is to determine the effects of mining of lead-zinc on water in Enyigba. This research lead to an understanding useful for mitigation (if not prevention) of environmental impact of mineral development such as in Zamfara State. The special objectives of the Study were to

i. Establish the geology of the area
ii. Assess and evaluate the mining techniques and processing methods in the area.

1.5 Scope and Limitations of the Study

The scope of this research work is to establish the geology of the area, to assess the mining methods and processes. To analyze the water samples and establish the physicochemical composition. Evaluate the result to establish effects of mining of Pb-Zn in water in the study area.

1.6 Significance of the Study

The research shall provide a data bank on the geochemical characteristics of both ground and surface water sources of the areas. Such data constitute the basic planning tool for economic development, especially water resources development, mineral resources development and waste management. This study will provide some surface and groundwater flow directional model and relate it with the transportation of heavy metals and its deposition within the study area.

This study will aid in the evaluation of the condition of water quality of the neighbour communities of the mining axis of Ebonyi State, using its geochemical characterization with ground water flow direction. The study will provide information on the current status of heavy metal pollution in the study area.

The study will provide information of water quality of reservoirs serving the communities. This study will define the aquifer types and groundwater conditions, hence determining the sustainability of the water for consumption.

1.7 Study Area Description

1.7.1 Location, extent and accessibility of the study area.

The study area lies between longitudes 8°07'E and 8°09'E and latitudes 6° 11' 00"N and 6°13' 00"N. It extends from Nkwagu in the north to Ameri in the south and Onuzu and Enyigba communities in the east and west respectively covering a total area of about 3.72 Km^2. The only major town within the area is Enyigba, others being rural communities such as Onuzo, Nkwegu, Amachara and Ameri where mining activities have been going on.

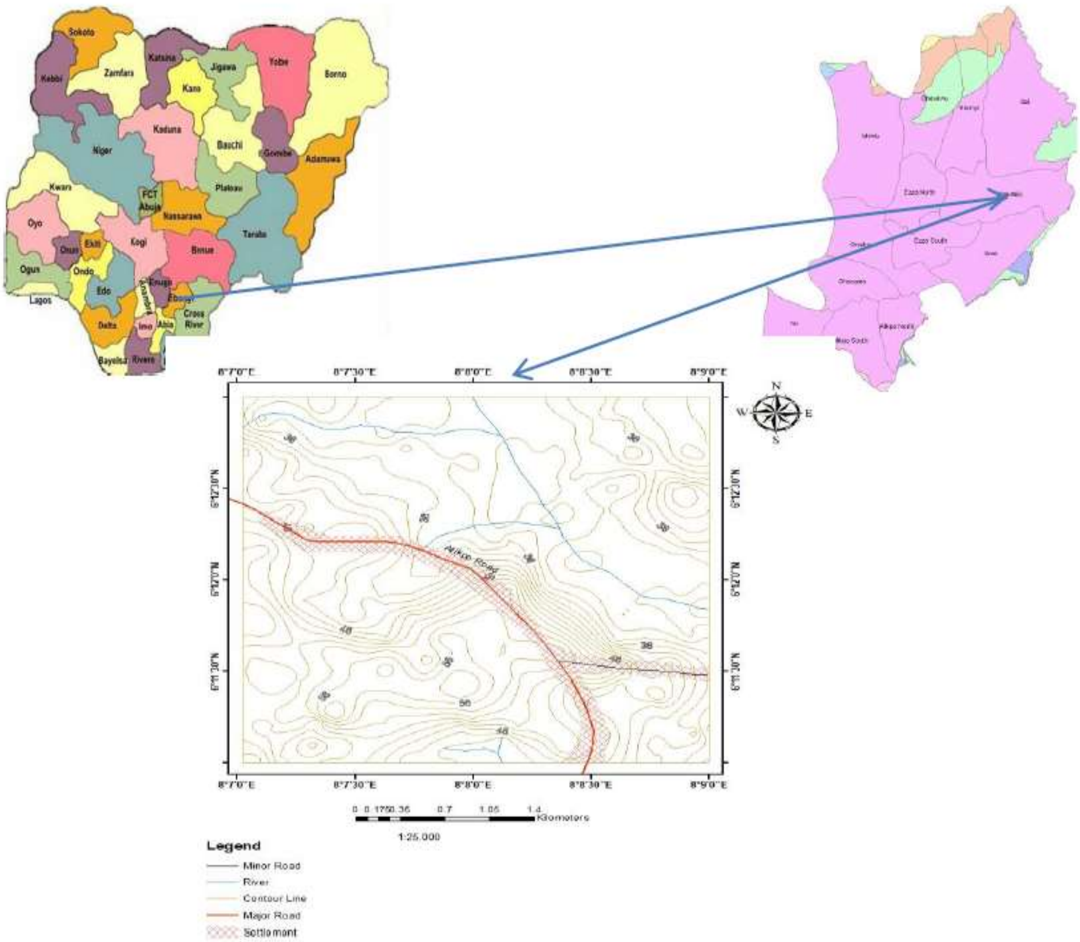

Figure 1.1: Location map of the study area

The area is accessible through a network of well-developed roads, major roads which includes the Ameka - Abakaliki road and Abakaliki - Amachara road. These roads are major express roads that lead to the area at various points. Minor roads in the area include Ameka – Ameri - Eyingba road, Amorie – Ameka road and Ameka – Amechara road. Footpaths were also available to access some villages, thereby accelerating the transverse of the area.

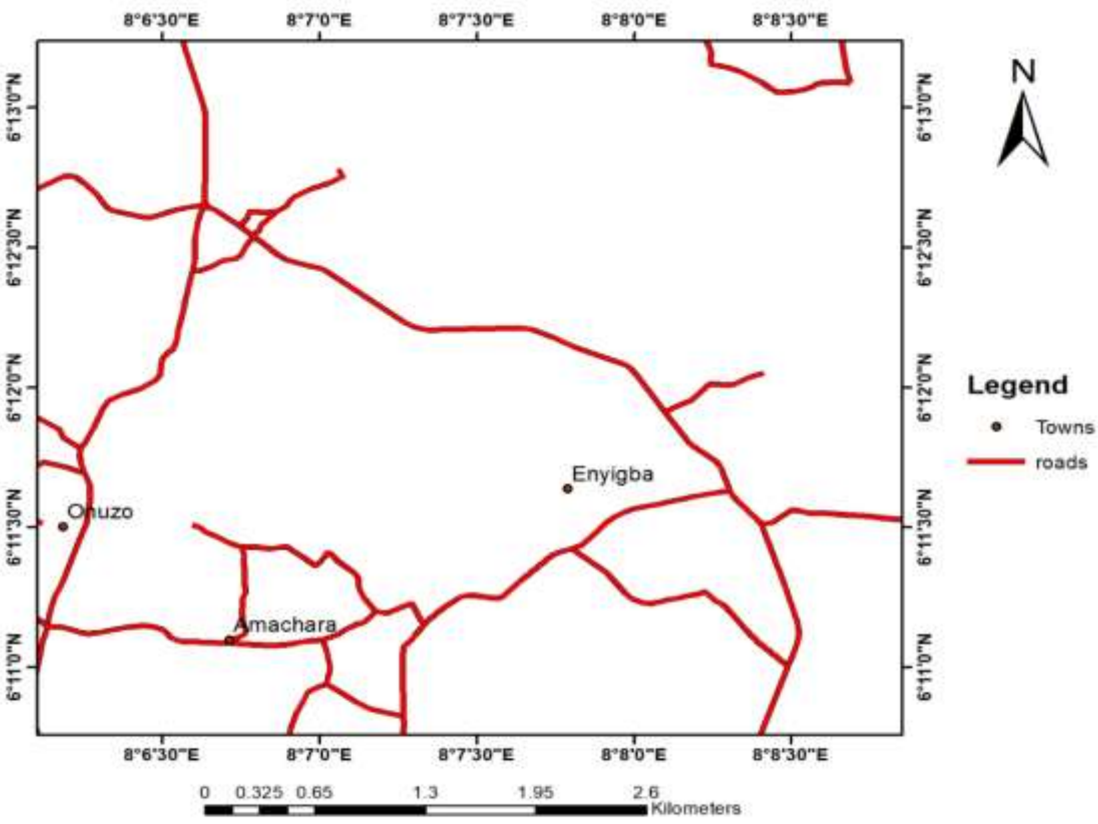

Figure 1.2: Accessibility Map of the Study Area

1.7.2 Settlement pattern and culture

The settlement within the study area is linear and nucleated. The settlement are linear long the major roads traversing the study area. Nucleated settlement is observed within villages away from the major roads. The dominate linguistic is igbo and is dominantly the Enyigba – Ameka Dialect.

1.7.3 Topography and drainage pattern

The contour interval from the topography map is 5m, contour range above sea level is 40m to 65m. Average contour is 52.5m which is the mean elevation above sea level. There are range of hills in the N/W, S/E area of the topographic map.

Surface drainage in the study area is controlled by the Ebonyi River. This river traverses the entire study area with its eminent tributaries and distributaries transporting its hydrochemical attributes from one point to another. It flows predominantly north - south. Other major rivers in the area include Rivers Abe, Iyiokwu, Ololo, Achi and Atang while some minor ones include River Akpara, Ohamini, Ewe, Ogbogbo, Awumini and Oyirigbo. These rivers and streams vary in sizes, colour, taste, flowpath and chemistry. Some are seasonal and therefore, dry up during the dry season and increase in volume during the rainy season.

The origin of most of these rivers and streams has been linked to the fractured shale and impervious contact between the shale and sandstone lenses, which characterize the lithology of the area (Okagbue and Ukpai, 2013). Due to the poor economic situation in these areas, these surface water resources have not been developed optimally. However, the Ezillo water Scheme, and more recently, the Oferekpe and Ukawu water Schemes are among the governmental efforts to extend the availability of pipe-borne water to rural areas, including this study area.

1.7.4 Climate

The study area falls within the tropical hinterland climate as proposed by Illoeje, 1981 (Figure 1.3). the annual rainfall ranges from 175 mm to 2000mm per year and it has an annual temperature of about $29^{o}C$ (Illoeje, 1981). The study area is dominated by two major climate regime which are the rainy season and dry season. The rainy season commence in March and terminates in October while the dry season commences in November and terminates in February.

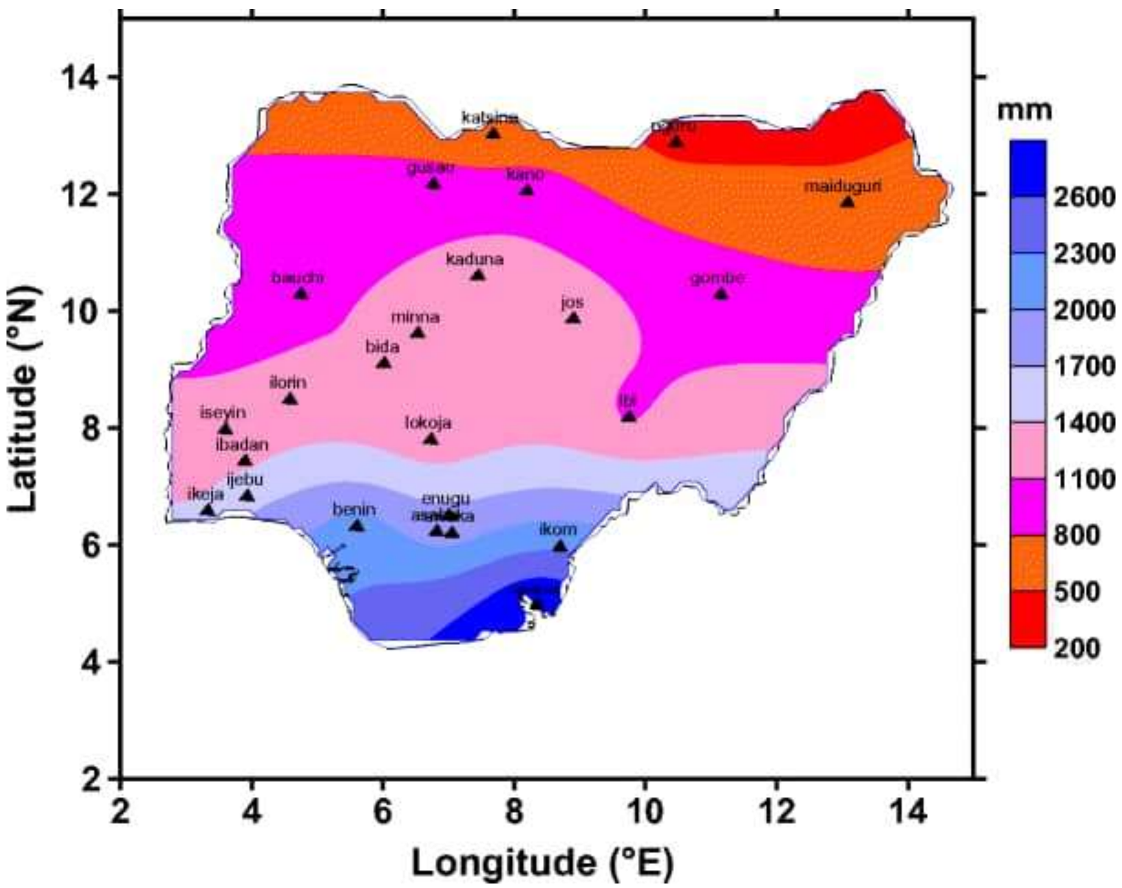

Figure 1.3: Mean annual rainfall distribution in Nigeria (Akintomide and kehinde, 2014).

1.7.5 Vegetation

The study area is part of the rain forest region of southeastern Nigeria (Figure 1.4). It has a humid climate and evergreen vegetation. The vegetation cover is composed of very dense trees and undergrowth of creepers. These trees are mostly tall, with buttress roots. However, consistent farming in the area has left some parts of the land bare, cultivated or fallowed.

The vegetation is controlled by many factors, including the drainage, topography, lithology and rainfall. The area has been described as part of the lowland rainforest region (Nnabo *et al.*, 2011). The forest is rich in loamy and humus soils, which support the farming activities of the inhabitants of the area.

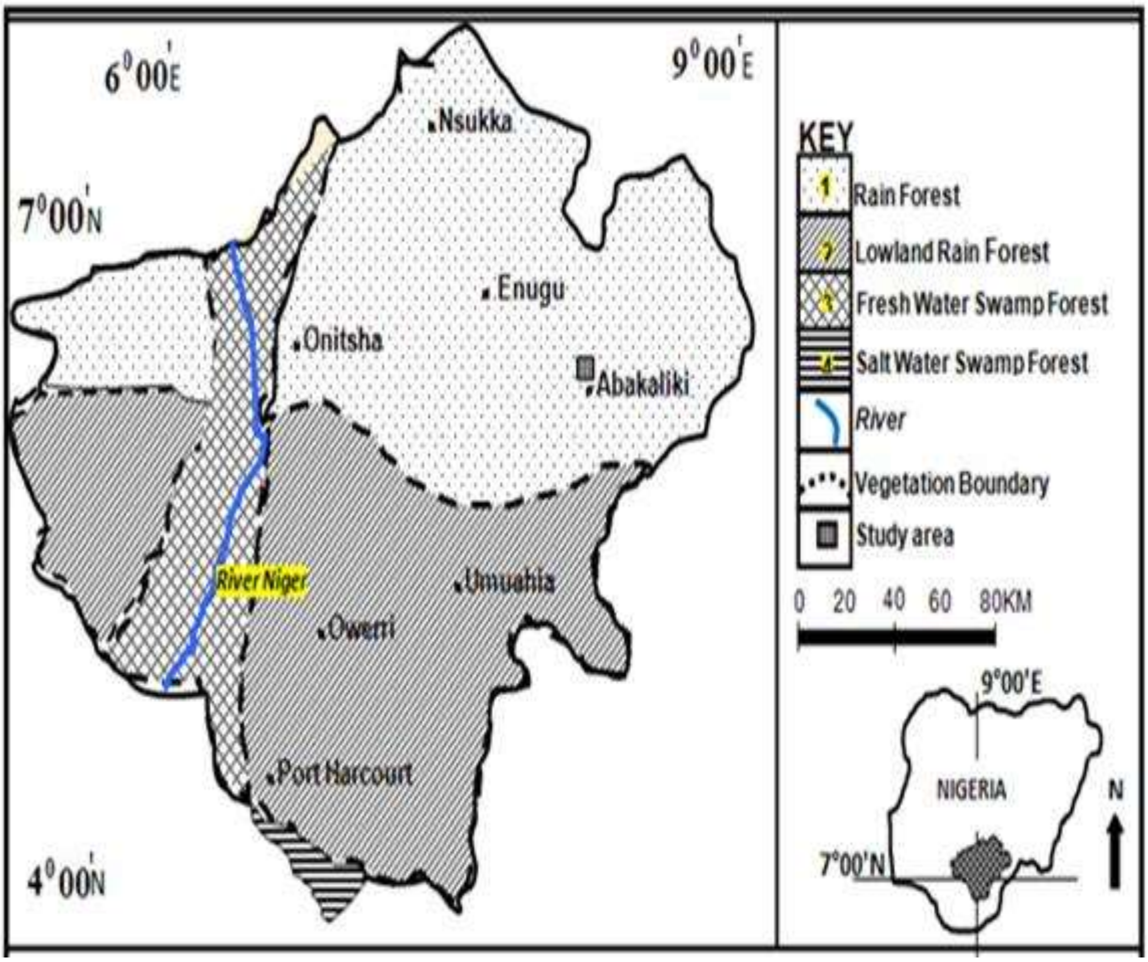

Figure 1.4: Map showing vegetative zones of Southeastern Nigeria (Modified after Murat, 1972).

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Lead Zinc Mineralization

The occurrence of lead-zinc mineralization in the Cretaceous series of the Benue Trough was firstly described about 40 years ago (Mackay, 1946). The origin of this mineralization has been variously interpreted but more generally related to magmatic intrusions (Farrington, 1952; Nwachukwu, 1975). A pure sedimentary origin was proposed (Grant, 1971; Olade, 1976; Olade and Morton, 1985) involving a circulation of connate-brines within the Cretaceous sediments. A third hypothesis (Offodile and Reyment, 1976) implies the combined effects of Juvenile and connate brines. The lead-zinc ores occur discontinuously in a 500 km long belt stretching from the Southwestern end of the Abakaliki Anticlinorium to the Upper Benue region.

The Benue Trough is a major geological feature that houses the lead/zinc mineralization in Nigeria (Mackay, 1946). Lead and zinc ores are usually found together in association with other minerals. They occur in commercial quantities in the Benue Trough, in a narrow belt over 560 km stretching from Ishiagu in the South-east to Bauchi State (Nwachukwu, 1975). Small-scale mining has been carried out in Enyigba in the Abakaliki area, where reserves of about 100,000 tonnes of lead and 80,000 tonnes of zinc have been estimated. Other major lead-zinc occurrences are at Ameka, Ameri in Ebonyi State, Arufu and Zurak in Taraba State. However, lead-zinc mining in Nigeria has been rather intermittent.

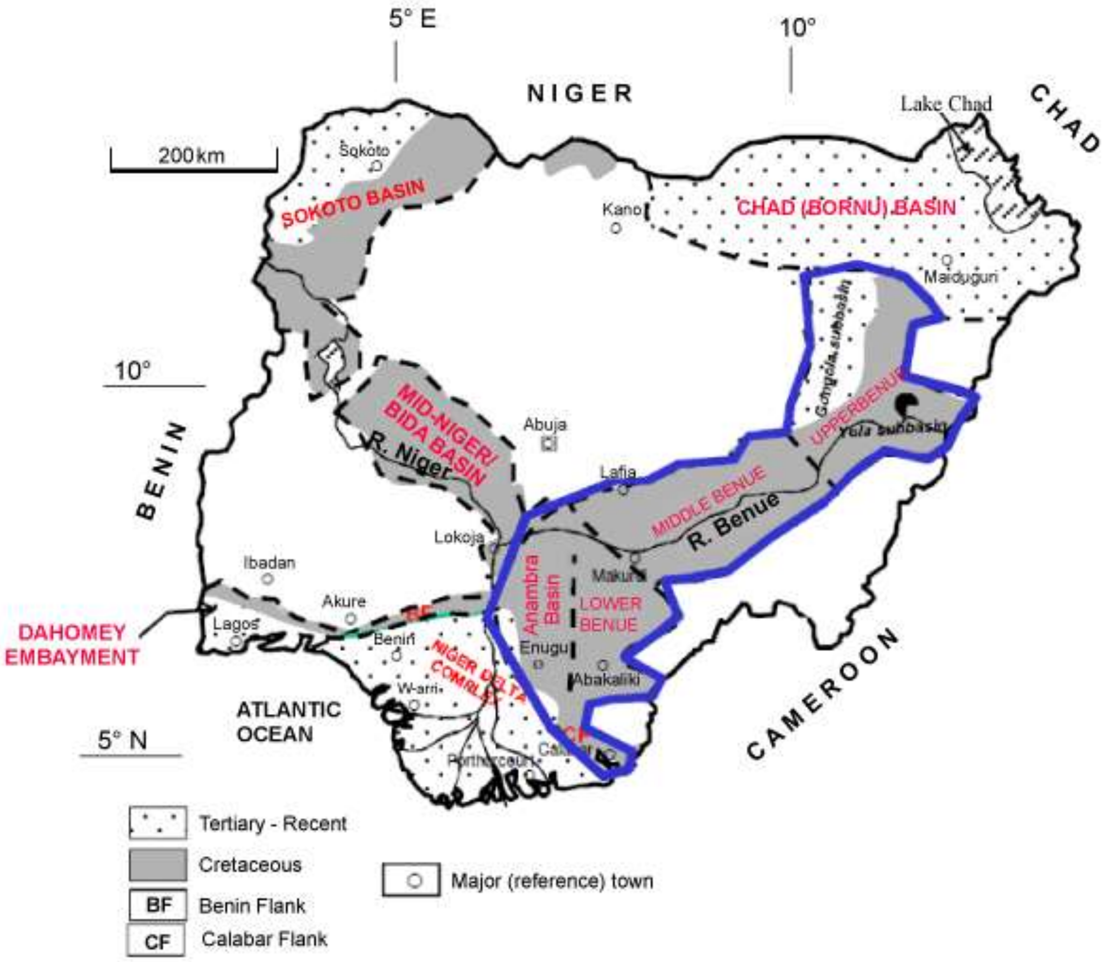

Figure 2.1. Map showing the Lower-, Middle- and Upper Benue Trough (after Abdulfatai *et al*., 2014)

The lower Benue Trough houses the Ebonyi State Pb-Zn mineralization emplaced at a low temperature of about 140°C and it is made up of primarily four lodes namely Ishiagu, Enyigba, Ameri and Ameka all in the present day Ebonyi state. The epigenetic lead-zinc deposits of the Southern-Benue Valley (Nigeria) are localized within cretaceous sediments of an intracontinental rift basin. Fluid inclusion studies of vein materials from the Abakaliki and Ishiagu ore bodies show that the sphalerite and quartz were deposited at relatively low temperatures (102-175^{o}), with ore-fluid salinity mostly in the range of 17-25 equivalent wt% NaCl. Trace element contents of sphalerite and galena are also consistent with the low temperature of formation and epigenetic origin. In other words, the mineralization is mainly sphalerite and galena with accessory minerals such as chalcopyrlte, enargite, marcassite and tetraedrite (MacKay, 1946; Farrington, 1952). The gangue Model of Pb/Zn mineralization genesis may contain calcite, fluorite and baryte in the limestone, quartz in the sandstone, manganesiferous siderite, quartz and calcite in the shales.

2.2 Mining and Processing

Open-pit mining which involves the excavation of large quantities of waste rock in order to extract the desired mineral ore, is the predominant mining method employed in the extraction of lead/zinc (Pb/Zn) mineral in Enyigba, Ebonyi State, southeastern, Nigeria. The poorly decommissioned mine afterwards, are left as part of its environmental legacy to the community, stock piles of marcasite and abandoned mine pits measuring about 15 meters in depth.

There are two fundamental operations in PbZn mineral processing in Enyigba is namely: the release of liberation of the valuable minerals from their waste gangue mineral and the separation of these values from the gangue, this latter process being known as concentration. Therefore, the liberation of the valuable minerals from the gangue is accomplished by comminution, and one of the major objectives of comminution is the liberation or release of the valuable minerals from the associated gangue mineral at the coarsest possible particle size; if such an aim is achieved, then not only is energy saved by the reduction of the amount of fines produced, but any subsequent separation stages become easier and cheaper to operate.

The mines occur in three areas: The Ishiagu-Enyigba mines, Alibaruhu Enyigba mines, and Ndinwanu Ishiagu-Enyigba–Ikwo mines (Ikwo-Ameri). The region experiences dry and rainy seasons and the streams are seasonal. The dry months are from January to

March, while the other months are characterized by precipitation and heavy rainfall. During the dry periods, vegetables are cultivated near the streams and stream beds, and irrigated using the contaminated streams and mine water. The study area is predominantly underlain by fractured shales and intermittent siltstones and limestones of Albian age.

2.3 Mobilization of Pb-Zn Into the Water Environment

The inhabitants of Enyigba which is one of the major communities where mining is heavily done in Ebonyi state are historically farmers who make use of the surrounding water bodies for irrigation and domestic purposes. Activities of small scale miners have left behind numerous artificial ponds and pits which form sources of water for drinking agricultural and other domestic purposes for the inhabitants, especially during periods of water scarcity. Open cast mining gives rise to acid rock drainage—a natural process whereby sulphuric acid is produced when sulphides in rocks are exposed to air and water. Acid mine drainage arises primarily when the mineral pyrite rocks meet oxygenated water (McCarthy 2011). The acid produced is carried off the mine site by rainwater or surface drainage and deposited into water bodies or groundwater, thereby polluting them. Acid mine drainage severely contaminates and degrades water quality causing severe damages to aquatic life and making water virtually unusable and inimical to human health (Yang *et al*., 2016). Thus, water available within the Enyigba mine vicinity might have been contaminated by potentially toxic elements from tailings emanating from mining activities through wind and water within the vicinity of the mine area.

2.4 Review of Previous Literature

Detailed geological work in the Abakaliki area was first carried out by the field surveyors of the British Government of the ministry of overseas (Directorate of over-seas surveys), under the special Commonwealth African Assistance Plan, published by the Federal surveys of Nigeria in 1966. Orajaka (1965), Offodile (1980) and Nwachukwu (1975) studied the origin of the Benue Trough and established that the study area lies within the Southeastern limb of an asymmetrical axis whose axis trend NE-SW.

Although several authors including Ezeh and Nnabo (2006), Ezeh *et al*., (2007), Nnabo *et al.*, (2011), Ukpai and Okagbue, (2011), Obarezi and Nwosu, (2013); Oti and Nwabue, (2013); Obasi and Akudinobi, (2015), Obasi *et al.*, (2015) Obiora *et al.*, (2015) have done some work in parts of the study area, with minimal emphasis on soil. There has not been any major assessment across the mining fields and local farmlands which, World Health Organization WHO, (2012) stated that it was the major source for heavy metals pollutant in Zamfara. Also, geohydrological studies to determine the principal water flow direction of the hydrochemical attribute has not been done.

The geo-environmental problems and water contamination levels has been evaluated by some researchers (Ezeh *et al*., 2007; Nnabo *et al*., 2011; Ukpai and Okagbue, 2011; Obarezi and Nwosu, 2013; Oti and Nwabue, 2013; Obasi and Akudinobi, 2015; Obasi *et al*., 2015) but none has developed a model relating the surface and groundwater flow direction and heavy metal contamination level as this will aid in evaluating contaminated water tributaries outside the main mining axis. The most recent research on the level of contamination in the area was done 5 years ago Nnabo *et al.*, (2011), but with the intensification of mining operations within this area due to the government increased interest and privatization of the mining sector, there has been a significate increase in mining operations especially by local artesian mines the area, hence its paramount to undergo this study so as to monitor and evaluate the current pollution status of the area. This research can lead to an understanding useful for mitigation (if not prevention) of environmental impact of mineral development such as in Zamfara State.

Mining of lead–zinc in Enyigba and adjoining areas in southeastern Nigeria has lasted for over 92 years, and small scale mining is still going on. This has led to an abundance of mine wastes and abandoned mine sites in the area. Some of these tills have been converted to farmlands; while old mine pits are used as ponds for domestic water supply. Some of the mines were located next to seasonal stream channels and tailings were deposited less than 4 m from the stream (Fig. 1.1). These streams, which are a major domestic water supply source, have been a major accumulator of potentially harmful elements (PHEs). The Enyigba community is located about 15 km south of Abakaliki, in southeastern Nigeria. The mining area is drained by three major waterways: the Nwangele-Akpara River, the Ina stream, and the Ngele-Odicha stream, which flows in a dendritic pattern to the River Akpara. Most of the mines are located in sporadic small hills that drain into these streams, which are located in the lowlands (Fig. 1.1).

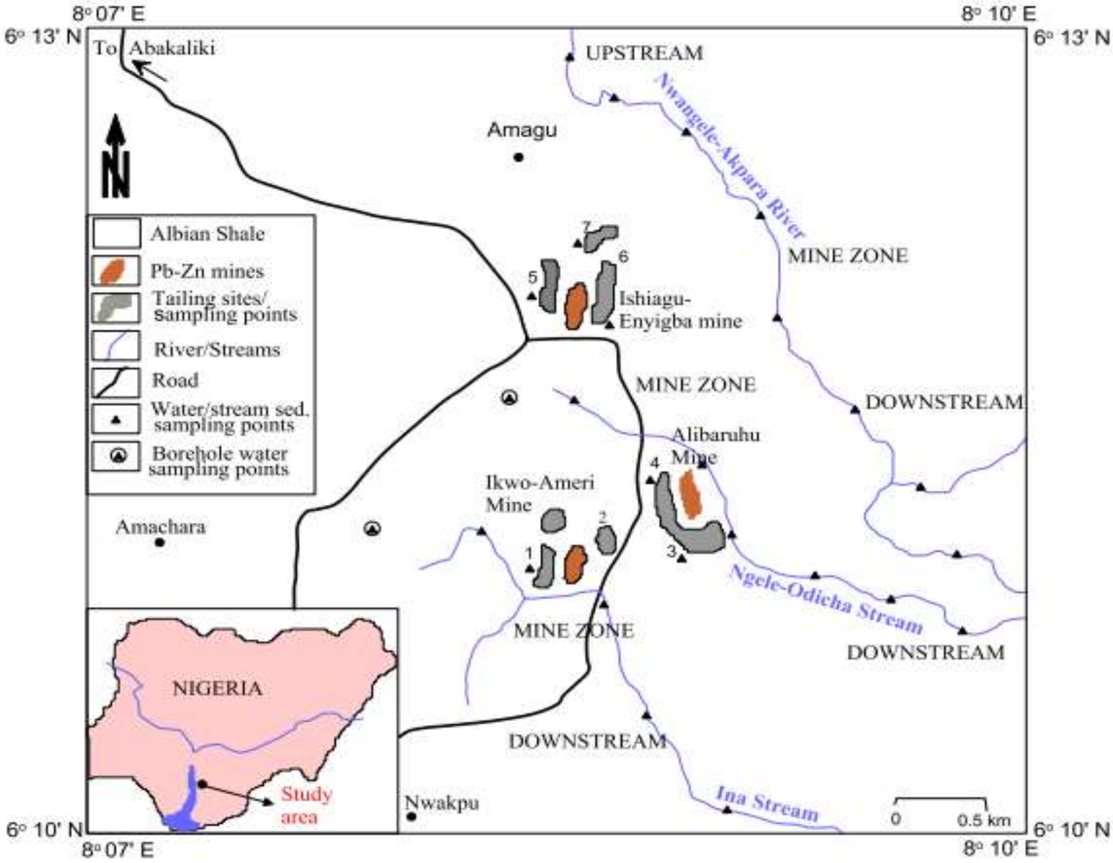

Figure 2.2: Geographical setting of study area, with local streams, Pb–Zn mines, and sample locations.

2.4.1 Result/ Recommendation from previous studies.

The data obtained from Enyigba study area carried out by Obiora *et al.*, (2016), indicates that despite the quality of Domestic and Public Water, 69% of the dwellers depend on running streams for their domestic water supply, 22% depend on well water, while 9% depend on old mine pond water. The concentrations of Potentially harmful elements (PHEs) in streams and other public water supplies are presented in Table 2.1 below. The PHEs, except for the Al from the streams used for domestic water supply (Ina, Ngele-Odicha, and Akpara streams) decrease significantly downstream and upstream of the mine influenced area (control). This shows a significant contribution from the Pb–Zn mining activities. The Chart of potentially harmful elements in water are presented in Figure 2.3. This revealed that most of the Enyigba dwellers who depend on the streams for their domestic water supply, are highly exposed to toxic levels of Pb, Al, and Fe through their intake of this contaminated water. The Ina stream water contains the highest concentration of these contaminants, including Mn. The health risk could be higher during the dry season due to an increase in PHEs concentrations brought about by evaporation.

Table 2.1: The concentrations of Potentially harmful elements (PHEs) in streams and other upstream water

Mean concentration of PHE in surface mine water μg/L										
Pb	Zn	Cd	Co	Ni	As	Cr	Cu	Mn	Fe	Al
4000	2612	750	652	332	350	300	80	31.503	13.951	6286
Mean concentration of PHE in upstream water μg/L										
Pb	Zn	Cd	Co	Ni	As	Cr	Cu	Mn	Fe	Al
23	72.5	0.165	1.59	3.7	0.6	2.85	4.75	96.62	1077	1565.5

The mean electrical conductivity of the surface mine water was over 150 times higher than the conductivity of the upstream waters, while the average pH (4.1) was strongly acidic compared to the pH of the upstream waters, which had an average pH of 7.6.

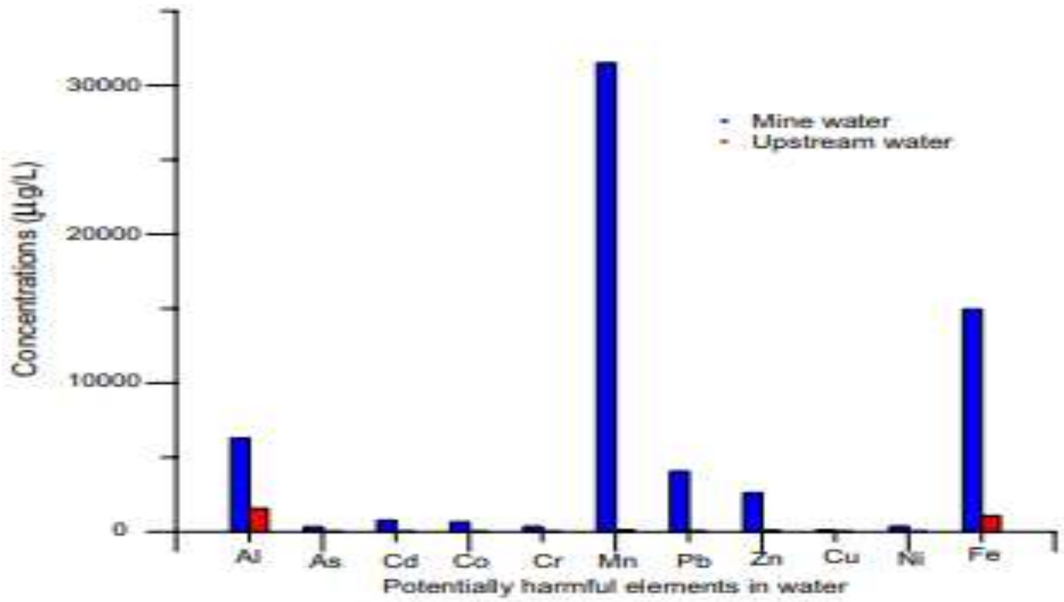

Figure 2.3: Chart potentially harmful elements in water (Obiora *et al.*, 2016).

This study revealed that most of the Enyigba dwellers who depend on the streams for their domestic water supply, are highly exposed to toxic levels of Pb, Al, and Fe through their intake of this contaminated water. The Ina stream water contains the highest concentration of these contaminants, including Mn. The health risk could be higher during the dry season due to an increase in PHEs concentrations brought about by evaporation. Among the water sources, the borehole water had the lowest PHEs contents. Treatment of mine water before it discharges into the streams, containment of tailings, adoption of erosion reduction methods, and mapping of contaminated watercourses, followed by water treatment over long periods of time could help improve the quality of domestic water supplies. Borehole water should be harnessed and residents should be encouraged to use this water to meet their domestic requirements. Reclamation of the abandoned pits with materials of tested and known elemental compositions should be adopted to avoid re-introduction of contaminated soils in the already contaminated area. Finally, further research on domestic household water contamination is recommended. Public sensitization programs should be proposed by Government and non-governmental organizations to sensitize the inhabitants on water source contamination.

2.5 Regional Stratigraphy

This is the control of the geologic history of Southern Nigeria to three major sedimentary phases during which the axis of the sedimentary basin shifted (Murat, 1972).

These three phases are;

i. The Abakaliki-Benue phase (Aptian-Santonian)

ii. The Anambra-Benin phase (Campanian-Mid Eocene)

iii. The Niger Delta phase (Late Eocene-Pliocene).

More than 3000m of rocks comprising the Asu River Group, Odukpani, the Eze-Aku and Awgu Formation were deposited during the first phase in the Abakaliki-Benue Basin, the Benue valley and the Calabar flank. The second sedimentary phase resulted from the Santonian folding and uplift of the Abakaliki region and distribution of the depocenter into the Anambra platform and Afikpo region. The resulting succession comprises the Nkporo Group, Mamu Formation, Ajali sandstone, Nsukka Formation, Imo Formation, and Ameki Group.

The third sedimentary phase is credited for the formation of the petroliferous Niger Delta which commenced in the hots Eocene as a result of a major earth movement that structurally inverted the Abakaliki region and displaced the depositional axis further to the south of Anambra Basin. These are folds which consist of series of anticlinorium and synclinorium suggesting that there was a deformational episode in the trough. These folds, coupled with the identification of the igneous rock such as Andesites in the Abakaliki area which lead to the proposing of a compressional (subduction) rather than an extensional tectonic setting for the Benue Trough (Farrington *et al*, 1952).

The Southern Benue Trough is a linear, intracratonic, graben basin, trending NE-SW. its origin is associated with the separation of the African and South American continents uplifted basement block, flanked by deep basin containing about 60 metres of sediments of various ages (Fatoye and Gideon 2013).

The southern Benue Trough is demarcated in the north by arbitrary line taken from south of Gboko to Ofukpo and Southwards along the geologic boundary between the Awgu Formation and the Nkporo Group. The southern Benue Trough has its basal part and oldest sediment as the Asu River Group with Ogoja Sandstone as its basal aspect.

The lithofacies of the southern Benue Trough is thus;

Oldest-youngest ↑

- Awgu Formation
- Ezeaku Group and
- Asu River Group.

2.5.1 The albian sediments

The oldest sediments in Southern Nigeria are around Abakaliki in Southeastern Nigeria, these sediments are unnamed and undifferentiated (Kogbe, 1989). They constitute the "Asu River Group". The type area of the group is along Asu River. The sediments consist of rather poorly bedded sandy shale known as the Abakaliki shales with sandstone and sandy limestone lenses. The limestone beds can attain a thickness of about 30m. Paleontologically, the shale is mainly characterized by specie of mortinoceras and Elobiceras. The shales are deeply weathered and contain Radiolarians, pelicipods and some gastropods (Kogbe, 1989). Sediments of the Asu River Group are folded particularly in the south of Abakaliki and the folds axes stretch NE- SW with beds associated with lead-zinc mineralization (Kogbe, 1989).

The Albian sediments are overlain by cenomanian sediments which are restricted to the Odukpani Formation of the Southeastern corner of the Nigerian Coastal Basin around Calabar, through cenomanian age has been assigned to Muri sandstone in the Central Benue Trough region (Reyment, 1965). The deposit consists of arkosic sandstone, limestone and alternating limestones and shales which become gradually more predominantly shally in its uppermost part (Nwajide, 2005). The type locality is at the village of Odukpani near Calabar and the sediments are of shallow water origin (Kogbe, 1989).

The Asu River Group of the Southern Benue Trough is packaged into the flowing formation or unit from the youngest:

1. Manfe Formation

The rocks of this unit is referred to as Manfe-Schiefer (Nwajide, 2005) established the type locality along the cross river at Manfe now in Cameron Republic. This formation, is about 800m thick and consist of arkosic sandstone, with intercalation of marls, sandy limestones and shales, there are also plant fragments and lignitic beds. The formation has been strongly folded along an East west axis with limbs dipping up to 50^{o} with presence of igneous intrusions. The age of the formation has not been clear but is considered not older than the Albian. Its fossil content is mainly fossil wood and (Nwajide, 2005) Considered the formation a sandy component of the Asu River Group and placed it within medial Albian to Cenomanian.

2. Abakaliki Formation

This unit was described by Nwajide, 2005, it consist of folded lead/zinc mineralized shales, with lenses of sandstone and limestone. The total thickness of the formation is not clear but may exceed 500 m.

3. Awe Formation

The awe formation is the basal, non-calcareous, sandy, conglomeratic unit of the Asu River Group directly overlying the Basement Complex (Oban Massif) north of calabar. It had been regarded as a part of the Odukpani Formation as defined by Reyment (1965) and discussed by Dessauvagie (1972) until Adeleye and Fayose (1978) redefined and redesignated it as a formation. The type section is at a road-cut, some 9km south of the awe village (which is actually located on the Basement Complex), along the calabar-Odukpani to Awe road.

The age is not clear but correlation with the Manfe Formation of Cameroun suggests Albian (Wilson, 1928; Fayose 1978) had suggested that the basal Awe Formation is both tectonically correlatable with the Manfe Formaion which is dated Albian. However, based on the study of foraminifora and pollens recovered from a 40m deep well drilled into the Mfansing area, Ramanathan and Kumaran (1981) extended the age of the basal paralic clastics of that part of the Benue trough to Neocomian, and also suggested a possible connection between north and south Atlantic during the Aptian-Albian time.

4. Ogoja Sandstone

This is the basal aspects of the Asu River Group directly overlying the basement Complex which have been characterized as consisting of conglomerates and arkoses sandstone in both Ikom and Ogoja areas (Reyment, 1965; Nwajide, 2005). Dating of the deposit has been uncertain environment with the pollen dating of the deposits of the Calabar Flank from a well studied by Ramanathan and Kumaran (1981). It may also be noted that the sediments as old as Barreman occur in the Yola arm of the Northern Benue Trough (Nwajide, 2005). Reijers and Petters (1987) assigned Aptan to Necomian age to the continental clastic facies sandswiched between the Basement Complex and the Albian carbonates traversed in well Ituk-2.

Correlation of these facies with the awe formation is also considered feasible, strictly on the basis of stratigraphic position;

2.5.2 The Turonian sediments

These sediments mainly belong to the Eze-Aku Formation (Simpson, 1954). The type locality is the Eze-Iyi-Aku river valley in southeastern Nigeria. The formation comprises of hard grey to black shales and siltstones with frequent facie changes, to sandstones or sandy shales. The bulk textural character of Eze-Aku sandstone comprises a coursing upward grain size gradient which ranges from fine to very coarse sandstone. Locally at Amarsiri, the Eze-Aku Formation grades laterally into the "Amasiri Sandstone" facies. The Eze-Aku Formation is structurally deformed by the santonian tectonic event (Nwachukwu, 1972).

The thickness of the main mass of the group is estimated ranging from 600m to 1200m with Ezilo formation as the basal part of the Ezeaku Group in the Abakaliki region. In the area around Nkalagu, on the Western flank of the core of the Abakaliki anticlinorium, Umeji (1984), subdivided the Ezeaku unit into several lithofacies, these includes; sandstones, siltstones, shales, and limestones. The sandstone facie of the Eze-Aku Group is best developed around Isikpuma, southeast of Nkalagu as documented in the Nkalagu area by Umeji (1984;1985;1988: Umeji *et al.,* 1993) and Amajor (1992). It occurs as a ridge directly overlying the Abakaliki shale, presumably separated by an unconformity. The sandstone is white, medium to coarse-grained and pebbly (exotic and intraformational), feldspathic, friable, planar to wavy cross-bedded (with clay drapes), some of them hummocky, and burrowed.

The limestone unit occurs as distinct horizons in the other facies, and is particularly interbedded with the black shales in which its interbeds can extend laterally for up to

2km which occurs as cross-bedded lenses in the siltstone and sandstone facies. The Eze-Aku shale represents the basal unit of the Eze-Aku Group and unconformably overlies the Asu River Group in the Afikpo Synclinorium. The type locality of the Eze-Aku Shale facie is at Eze-Uyi-Aku River at Akaeze. This facie represents the lower boundary stratotypes of Eze-Aku Group in the Afikpo synclinorium (Igwe *et al.*, 2015). The shales of this facie generally, are flaggy, dark grey to black calcareous. There is an alteration of black shales and shelly limestones shown by the stratigraphic section in the quarry at Nkalagu. The shale horizons in this section total some 24m, and grade into the Awgu shales above (Umeji, 1985).

2.5.3 The Coniacian-Santonian Sediments

These span from late Turonian through Coniacian to Early Santonian and are generally less thick than Turonian and tends to give an impression of rather quick lateral changes in facies (Kogbe, 1989). The sediments have been assigned to the Awgu Formation (Reyment, 1965). The formation is about 800 m thick and consists of marine fossiliferous bluish grey well bedded shales and sometimes intercalations of fine-grained sandstone. Sediments of santonian age have not been found in southern Nigeria as it is a regressive substate in Nigeria (Kogbe, 1989). A doubtful santonian locality, the Awgu shale in Igumale area has yielded ostracods possibly referable to this substage (Nwajide, 2005).

The Awgu Formation of the Southern Benue Trough is conformably overlying the facies of the Eze-Aku Group. The type locality of this formation is Awgu town in Enugu State, Southeastern Nigeria. Its overall thickness is estimated at 900 m from surface mapping (Simpson, 1954, and Reyment, 1965) and up to 1,100 m from well data Agugu *et al.* (1985). The succession, as logged from a borehole, commonly consists of shales, sandstones and limestones. The shales are fissile, bluish grey, pyritic, calcareous, micaceous and occasionally gypsiderous. The sandstones are pale yellow, fine to medium-grained, and Calcerous. The limestones are marly and shally, and up to several thickness. The Sekule Formation and the Numanha shale in the Northern Benue Trough are the Chrono- Correlatives or stratigraphic equivalent of the Awgu Formation, all deposited during the third transgressive cycle in the upper Turonian-Lower Santonian. It's deltaic (sandy) aspects are almost exclusively subsurface and have mainly been encountered by wells penetrating the Anambra platform, such as Bopo-1, Okpaya-1, Adoka-1, Aiddo-1, IOkem-1, and Amansiodo-1.

2.5.4 The Campanian-Maastrichtian

These sediments in Southeastern Nigeria begins with dark grey, often fissile shale with occasional thin beds of limestone and sandstone which belong to the Nkporo Formation. The Owelli sandstone, Enugu Shale and Asata shales are lateral equivalents of the Nkporo Formation. These inner-basin sediments are all of shallow water origin and these are frequent sharp facies changes (Kogbe, 1989).

2.5.5 The Coal Measure of the Southern Benue Trough

The basal part of the coal measure sequence previously known as the "Lower Coal Measures" but now known as the Mamu Formation, contains shales (Nwajide, 2005). The coal bearing part of the sequence consist of predominatly fresh water and low salinity sandstone, shale, mudstones and sandy shales, coal seams occur at several levels (Simposon, 1954). Mamu Formation is well exposed along the Enugu-Onitsha road at the Milliken Hill just on the outskirt of Enugu. The Mamu Formation is overlain by the Ajali near Enugu. This formation consists of thick friable poorly sorted sandstone typically white in colour but sometimes iron stained (Kogbe, 1989). The Ajali Formation is exposed along the road cut between 9th miles (from Enugu) to the foot of the Milliken

Hill. Ajali sandstone is subsequently overlain by Nsukka Formation (Upper Coal Measures). This formation is marked by the deposition of carbonaceous shales, sandstones and some thin coal seams. The upper-most unit has been recorded as containing Paleocene fauna in Southern Nigeria (Chiaghanam *et al.*,2012). Outcrops of this formation can be observed in the valley of the Nadu River and on road cuts along Enugu-Ontisha road.

Table 2.2: Regional stratigraphic sequence of south eastern Nigeria (adapted from Murat 1972; Hoque, 1977 and Reyment 1965).

Period	Age	Formation	Sedimentary basin
Quaternary	Pelistocene/Pliocene Miocene/Oligocene	Benin Formation Ogwashi Asaba	3rd sedimentary cycle Niger Delta Developed in the upper Eocene
Tertiary	Eocene Paleocene	Ameki Group Imo Shale	
Upper cretaceous	Maastrichtian	Nsukka Formation	2nd sedimentary cycle Anambra/Afikpo basin
Upper cretaceous	Campanian	Nkporo shale	1st sedimentary cycle Abakaliki basin
	Santonian	Unconformity	
	Coniacian	Awgu shale	
	Turonian	Ezeaku Group	
	Cenomanian	Odukpani	
	Albian	Asu River Group	

(Adapted from Murat 1972; Hoque, 1977 and Reyment 1965).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Preliminary Studies

The present work commenced with desk study. This involves reviewing all literature pertaining to the subject matter and the area of study. This was done through the use of both published and unpublished works, journals, periodicals, bulletins, online sources, libraries, information repositories in ministries, departments and agencies and acquisition of satellite imageries.

Compilation of maps and materials needed for field work. At this point maps and topographic maps were produced, acquisition of materials needed for field works, seeking of permits to access restricted areas and letters of introduction from the university.

Reconnaissance survey of the area was done to note the accessibility and general geology of the area to enable efficient working plan. Simple field equipment's including compass, Global Positioning System (GPS), the geologic hammer, measuring tapes, water sample bottles, pencil, field notebooks and camera were used.

3.2 Field Work

The field work is tied to objectives 1, 2 and parts of 3 of the work and was conducted as follows.

Establishing of the geology: this was done using the traverse method, employing the use of compass/clinometers, geological hammer and topographic base map. The topo map was on the scale of 1:25,000 and extracted from Abakaliki Sheet 303 NE.

Colour changes on the surface that may be a reflection of the changes in geology were noted, ditches or eroded areas were observed with the aim of unraveling the geology of the area.

Taking inventories of wells and boreholes in the area which involved the determination of well depths, water level etc. of the area.

3.2.1 Water Sample collection/preservation

Water sampling was carried out according to the American Public Health Association Standard (APHA, 2008). Water samples were collected from groundwater and surface water sources for hydro-geochemical analysis. Surface water sources considered include active and abandoned mine pits, rivers, streams and lakes, while groundwater sources include shallow wells/boreholes (hand dug wells and hand pump wells). A total of forty-four water samples were collected systematically from different locations comprising of eight groundwater sources and fifteen surface sources.

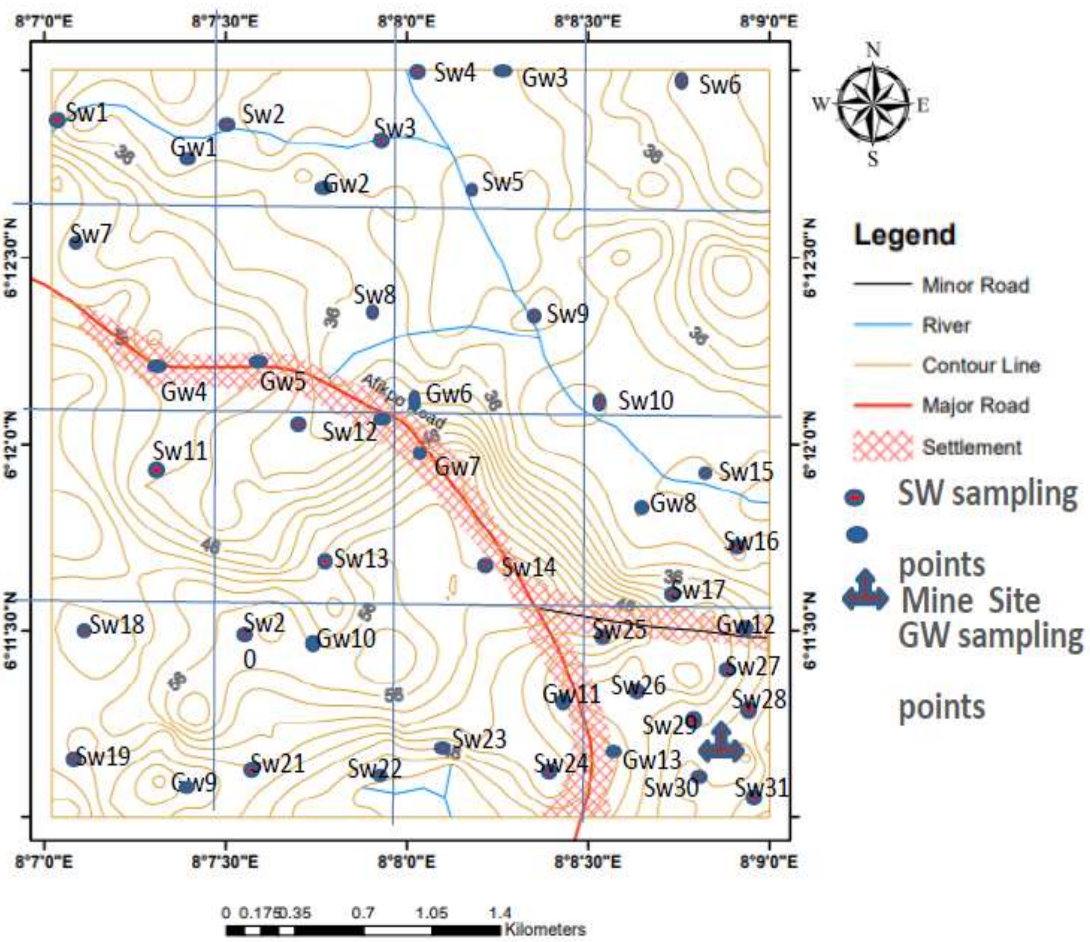

Figure 3.1: Geologic map showing sample collection points.

Table 3.1: Locations of mines in the study area

S N	Sample ID	Location	Latitude	Longitude
1	SW1	Active mine in Enyigba	06^{o} 11' 14"	008^{o} 09' 02"
2	SW1	Active mine in Ameri	06^{o} 10' 00"	008^{o} 007' 01"
3	SW3	Salt Lake Ameri	06^{o} 08' 53"	008^{o} 06' 01"
4	SW4	Abandoned Pit Ameri	06^{o} 10' 43"	008^{o} 007' 58"
5	SW5	Active mine Amanchara	06^{o} 32' 02"	008^{o} 006' 01"
6	SW6	Active mine pond Enyigba	06^{o} 12' 03"	008^{o} 007' 29"
7	SW7	Abandoned mine pond Enyigba	06^{o} 09' 59"	008^{o} 06' 08"
8	SW8	Active Pit Onuzu	06^{o} 10' 58"	008^{o} 006' 00"
9	SW9	Alibaruhu mine site waterway	06^{o} 10' 05'	008^{o} 005' 34"
10	SW10	Akpara River in Enyigba	06^{o} 11' 34"	008^{o} 007' 56"
11	SW11	Oyirigbo River in Amanchara	06^{o} 30' 18"	008^{o} 006' 12"
12	GW 1	Hand dug well 1, Agu's compound Enyigba	06^{o} 12" 17"	008^{o} 06' 41'
13	GW 5	Enyigba 2 borehole	06^{o} 11' 57"	008^{o} 008' 30"
14	GW 7	Hand dug well Ebulu's compound Enyigba	06^{o} 11' 31"	008^{o} 08" 27"
15	GW13	Ameri Royal salt borehole	06^{o} 09' 58"	008^{o} 06' 52"

At each location, observations on the physical component of water quality such as colour, taste, odour and pH were done. one sample were collected at each location and were stored in ethylene – free plastic bottles with fitted lids, and preserved in an ice – packed coolers below 4^{o}c prior to laboratory analysis. Plate 4.1 and 4.2 are locations for sample SW7 and SW5 respectively.

3.3 Laboratory Analysis of Water Sample

The analysis was carried out within forty-eight (48) hours of collection. The samples were analyzed at Springboard Analytical Laboratory, Awka, Anambra State. Temperature and pH were measured in-situ at the points of collection, mercury- in-glass thermometer and pH meter (Hanna model H1991300) were used respectively. Laboratory analysis for the concentration S0 $^{2-}$was done using Ultra Violet/ Visible (UV /VIS) Spectroscopy (PV 300 Opel). Trace constituents including Zn^{2+} and Pb^{2+} were analyzed using Fast Sequential (FS) (Varian 240 AA) Atomic Absorbtion Spectrophotometer. The results were discussed and compared with the World Health Organization (WHO) standards for water quality.

CHAPTER FOUR

4.0 RESULT AND DISCUSSION

The Study Area

4.1 Geology of the Study Area

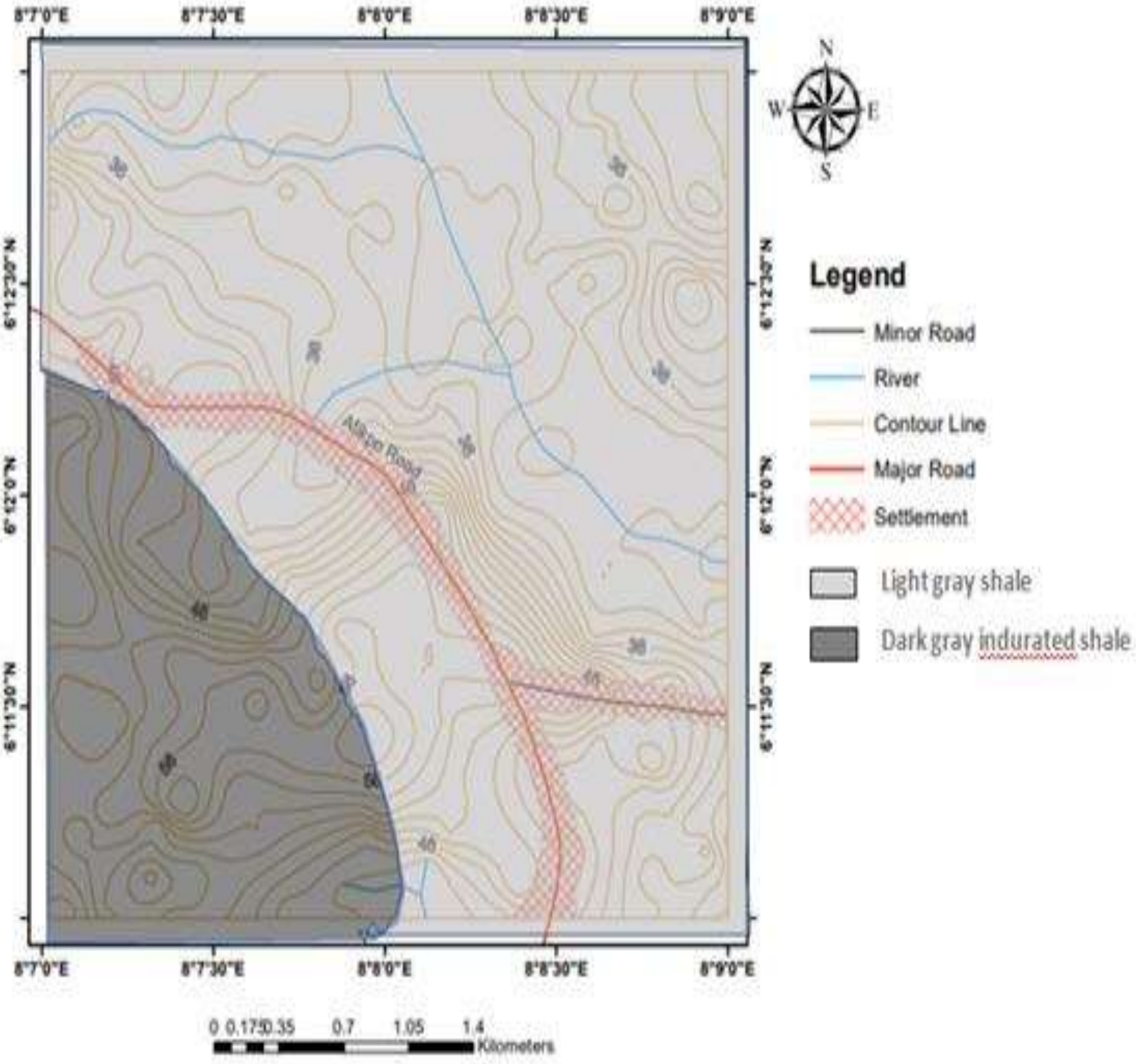

Figure 4.1: Geology map of the study area.

Shale rocks overlie the study area (Enyigba and its environs). This shale unit is divided into two lithofacies: dark grey shale lithofacies and light grey fissile shale (Table 4.1). The division is based on the lithological characteristics observed in the field. The information obtained from geologic mapping was used to produce the geologic map of the study area (figure 4.1).

Table 4.1: Local Stratigraphy of the study area

Age	Group	Formation	Lithostratigraphic unit	Lithofacies
Middle Albian	Asu River Group	Abakaliki Shale	Light Grey Fissile Shale	Grey shales and sandstone
			Dark Grey Shale	Indurated massive shale and mudstone

4.1.1 Dark grey shale unit

This shale unit is dark grey in colour and is indurated in nature (Plate 4.1). Induration in geoscience is the baking/hardening of rocks by the action of temperature. The outcrop of the unit is observed within the mining pits within Enyigba. The rocks unit has a northeast-southwest strike and a southeast dip direction at an angle ranging from 10^{o} to 45^{o}. The shale unit is massive and highly consolidated beds (Plate 4.2) in some pits and is characterised by macro and micro faults; these faults are healed by quartz as observed in a mining pit in Enyigba (Plate 4.3). The faults have a major N-S, and NW-SE trend, with minor NE-SW orientation and this trend, also controls the direction of lead-zinc veins within the study area. Carbonaceous (dark) patches appear mostly superficial within the unit. The hardness and lack of fissility in the shale are interpreted as temperature increase from hydrothermal fluids during the Santonian age. Miners use the indurated nature of the shale and the fracture system as a critical mapper for targeting lead-zinc deposits. The shales unit was observed at mining pits in Enyigba and the riverbank of River Ozaza within the Enyigba community.

Plate I: Dark grey shale at a mining site in Enyigba

Plate II: Highly Indurated bedded shale at a mining Pit in Amanchara, Enyigba

4.1.2 Light Grey Shale unit

The shales are generally light greyish in colour, fissile, laminated and jointed. Sedimentary structures observed within these unit includes fissility, lamination and beds (Plate 4.3, 4.4 and 4.5). Fissility is the splitting of rocks along their plane of weakness, forming thin sheets. At the same time, lamination or laminae is a small-scale sequence of fine layers that occurs in sedimentary rocks. This shale unit has a northeast-southwest trend with a dip direction ranging from 4^{o} to 10^{o}. The light grey shale overlies the dark grey shale unit, and it looks to have been affected by a mild temperature increase. The shale unit is majorly observed around road cuts and shallow lying exposures at Onuzu.

Plate III: Shale outcrop at a road cut in Onuzu.

Plate IV: Shale outcrop at a River in Onuzu

Plate V: Near horizontal shale beds north of Onuzu (dip: 4^{o})

4.1.3 Correlation with a named Formation

The shale lithofacies show similarity in characteristics with the Abakaliki Formation of the Asu River Group (Reyment, 1965). The joints of the Abakaliki Formation runs NW-SE majorly as those measured in this unit of the study area. Ojoh (1988) stated that outcrops of the Albian age are well developed in the Southern Benue Trough, where they generally outcropped in the core of the marine anticline structures (Abakaliki Anticlinorium), which was also seen in this unit of the study area (Enyigba and its environs). Therefore, the shale unit is correlatable to the Abakaliki Formation of the Asu River Group, which is Albian in age.

4.1.4 Groundwater resources / aquifer characteristics

The water resources of the study area consist of both surface and groundwater systems. The hydrogeology and hydrology of the study area are controlled by its geology, faults/fractures, and topography of the rocks that underlain the area (Todd, 1980). The geology of the area is mainly composed of shales and mudstone, the fractured shales from the primary aquifer system in the study area. These fractures formed during the Santonian Orogeny, which uplifted, folded and faulted the sediments of the Benue Trough, thus creating secondary porosity structures (in the shales) which houses groundwater. Within the study area and its environs, fracture system analysis/mapping during geologic mapping shows a significant trend of NW - SE with few in the NE - SW direction. These fractures within the study area do not transmit a sufficient amount of groundwater, which is interpreted as a result of the high dip amount (38^{o} – 52^{o}) of the beds. This is accountable for the high number of aborted and very low-yield wells observed around the Ameka, Ameri, Enyigba, and Amachara areas.

4.2 Mining Technique / Processes

The method of exploitation of the mineral ore is the open cast method. Since the general depth to ore ranges from 10m to 30m, mining companies employ the open cast method for mining the deposits. During the processing of the exploited mineral, the ore is exposed to the surface (Plate 4.6) by blasting and moving boulders with excavators and trucks; local miners separate the gange minerals from the target ore for bagging and selling. Big mining companies like Royal Salt mining company built a processing plant in Ameri (Plate 4.7); the lead-zinc ore is usually crushed then separated from the gange by amalgamating the mineral. The processed ore is then bagged from sale/shipping.

The mining method open cast is very challenging to manage during the rainy season; water is also challenging to manage during the mining process. Water is also used to wash the ore after mining. During the rainy season, the pits are usually filled with water. Small scale and local miners abandon their pits during this period. This generally leads to ponds forming a water reservoir that serves the communities during the dry season (Plate 4.8). During the rainy season, big mining companies employ a submission pump to extract the water from the pits; this usually leads to the formation of surface runoff of water that flows into surface water bodies (rivers).

Plate VI: Exposed lead-zinc ore at a mining pit in Enyigba

Plate VII: Royal Salt Mining Company Processing Plant in Ameri

Plate VIII: Seasonal Mining Pit in Enyigba

4.3 Result of the Geochemical Analysis

The analysis was carried out within forty-eight (48) hours of collection. Temperature and pH were measured in-situ at the collection points, mercury-in-glass thermometer and pH meter (Hanna model H1991300) were used, respectively. Laboratory analysis for the concentration SO_4^{2-} was done using Ultra Violet/ Visible (UV /VIS) Spectroscopy (PV 300 Opel).

Trace constituents including Zn^{2+} and Pb^{2+} were analysed using a Fast Sequential (FS) (Varian 240 AA) Atomic Absorption Spectrophotometer. The results were discussed and compared with the World Health Organization (WHO) standards for water quality. The results are presented in Tables 4.2 to 4.5.

Table 4.2: Result for the physical properties of groundwater

S/N	Sample No	Location	pH	TDS (mg/l)	Temperature (ºC)
1	GW 1	Ameri 1 Royal Salt (borehole)	6.68	34.2	26
2	GW 2	Ameri 2 (borehole)	6.47	53	25
3	GW 3	Enyigba 1 Mining Site	6.25	71.58	28
4	GW 4	Enyigba 2 Madukas Compound (Borehole)	6.47	53	25
5	GW 5	Enyigba 3 Chief Eze (borehole)	6.03	59	27
6	GW 6	Amachara Chief Peter	6.61	28.4	26
7	GW 7	Onuzo - Ekezie Chuma	6.68	34.2	26
8	GW 8	Amagu	7.17	0.8	26
9	GW 9	Amachara pri. Sch.(Borehole)	6.02	51	26
10	GW 10	ST. Peter and Paul Catholic Parish	4.68	16.9	26
11	GW 11	Close to Enyigba (Borehole)	6.83	17.1	27
12	GW 12	Close to Salt Lake Enyigba	6.77	4.7	28
13	GW 13	(Borehole) Holy Rosary Catholic Church, Enyigba (borehole)	7.53	2.1	28

Table 4.3: Result for the physical properties of surface water

Location	Sample ID	pH	TDS (mg/l)	Temperature (°C)
Active mine in Enyigba 1	SW1	6.14	70.3	29
Active mine in Ameri 1	SW2	5.06	71.2	27
Salt Lake Ameri	SW3	6.21	68.23	26
Abandoned Pit Ameri 1	SW4	5.14	91.66	27
Active mine Amanchara	SW5	5.3	123	26
Active mine pond Enyigba	SW6	4.59	195	28
Abandoned mine pond Enyigba	SW7	5.11	89.31	27
Active Pit Onuzu	SW8	4.13	77.39	26
Alibaruhu mine site water way	SW9	6.37	2.26	25
Akpara River in Enyigba	SW10	4.73	3.81	27
Oyirigbo River in Amanchara	SW11	7.61	3.65	26
River Akpara in Enyigba 2	SW12	6.53	12.8	27
River in Enyigba 3	SW13	7.32	4.21	27
Salt Lake in Enyigbe	SW14	4.01	70.3	27
Ameri Pond	SW15	5.28	88.2	26
Active mine in Enyigba 2	SW16	3.27	79.1	28
Active mine Amanchara 2	SW17	7.62	50.3	27
Oyirigbo River in Amanchara	SW18	1.26	78.43	27
Active mine Amanchara 2	SW19	1.25	65.5	28
Active Pit Onuzu 2	SW20	2.72	69.4	27
Ngele River Enyigba 1 (close to mine)	SW21	1.68	69	28
Active Pit Onuzu 3	SW22	1.63	70.5	26
Active Alibaruhu mine site Enyigba	SW23	3.42	70.8	26
Akpara River in Enyigba 3	SW24	6.24	13.8	25
River Oyirigbo in Amanchara	SW25	9.73	6.22	29
Akpara River in Enyigba 2	SW26	5.64	52.7	28
Enyigbe Salt Lake 2	SW27	2.76	53.2	28
Royal Salt Mining Pit	SW28	6.25	9.6	26
Abandoned Pit Enyigba	SW29	9.66	8.9	28
River Oyirigbo in Amanchara 2	SW30	5.68	50	28
Ngele River Enyigba 1 (close to mine)	SW31	2.97	51.6	28

Table 4.4: Result for the study of Lead, zinc and sulfate in ground water

S/N	Sample	Location	Pb(mg/l)	Zn (mg/l)	SO_4^{2-} (mg/l)
1	GW 1	Ameri 1 Royal Salt	0.04	0	47
2	GW 2	Ameri 2 (borehole)	0	0	61
3	GW 3	Enyigba 1 Mining Site (Borehole)	12	0	421.1
4	GW 4	Enyigba 2 Madukas Compound (Borehole)	0	0.157	223.8
5	GW 5	Enyigba 3 Chief Eze (borehole)	3.2	1.72	342.1
6	GW 6	Amachara Chief Iduma	2	0.086	127.2
7	GW 7	Onuzo - Ekezie Chuma	2.77	0.036	72
8	GW 8	Amagu	2.31	0.02	25
9	GW 9	Amachara pri. Sch.(Borehole)	2.43	0	421.6
10	GW 10	ST. Peter and Paul Catholic Parish (Borehole)	2.76	0	276.1
11	GW 11	Close to Enyigba (Borehole)	1.76	0.13	358.7
12	GW 12	Close to enyigba salt lake(Borehole)	0.95	0.02	864.2
13	GW 13	Holy Rosary Catholic Church, Enyigba (Borehole)	38	0.06	258

Table 4.5: Result for the study of Lead, zinc and sulfate in surface water

Sample Location	Sample ID	Pb (mg/l)	Zn (mg/l)	$SO4^{-2}$ mg/l
Active mine in Enyigba 1	SW1	0.08	0.05	77
Active mine in Ameri 1	SW2	0.1	0.11	71
Salt Lake Ameri	SW3	0.72	6.21	86
Abandoned Pit Ameri 1	SW4	1.59	8.921	81
Active mine Amanchara	SW5	1.81	1.24	73
Active mine pond Enyigba	SW6	0.47	2.29	62
Abandoned mine pond Enyigba	SW7	3.12	0.96	59
Active Pit Onuzu	SW8	0.23	0.41	40
Alibaruhu mine site water way	SW9	6.11	1.37	63
Akpara River in Enyigba	SW10	0.69	0.29	40
Oyirigbo River in Amanchara	SW11	0.13	0.83	72
River Akpara in Enyigba 2	SW12	0.61	0.17	107
River in Enyigba 3	SW13	0.63	0.19	54
Salt Lake in Enyigbe	SW14	2.88	0.31	142
Ameri Pond	SW15	2.17	1.31	191
Active mine in Enyigba 2	SW16	0.1	0.3	78
Active mine Amanchara 2	SW17	5.28	10.62	51
Oyirigbo River in Amanchara	SW18	0.17	0.04	27
Active mine Amanchara 2	SW19	1.34	1.19	88
Active Pit Onuzu 2	SW20	0.9	2.53	42
Ngele River Enyigba 1	SW21	1.41	0.18	53
Active Pit Onuzu 3	SW22	0.26	0.94	46
Active Alibaruhu mine site Enyigba	SW23	5.06	1.4804	54
Akpara River in Enyigba 3	SW24	0.42	0.98	58
River Oyirigbo in Amanchara	SW25	0.04	1.173	60
Akpara River in Enyigba 2	SW26	0.01	0.04	189.4
Enyigbe Salt Lake 2	SW27	3.72	0.38	200.5
Royal Salt Mining Pit	SW28	10.21	0.05	300.6
Abandoned Pit Enyigba	SW29	1.47	9.45	85
River Oyirigbo in Amanchara 2	SW30	1.93	1.42	79
Ngele River Enyigba 1 (close to mine)	SW31	5.89	9.4	29

Data analysis was also carried out on the dataset by employing bar charts, contour plots and histogram. The aim is to determine the contamination levels of heavy metals within the soils in the study area. The bar charts, contour plots, histogram and statistical analysis results are presented below.

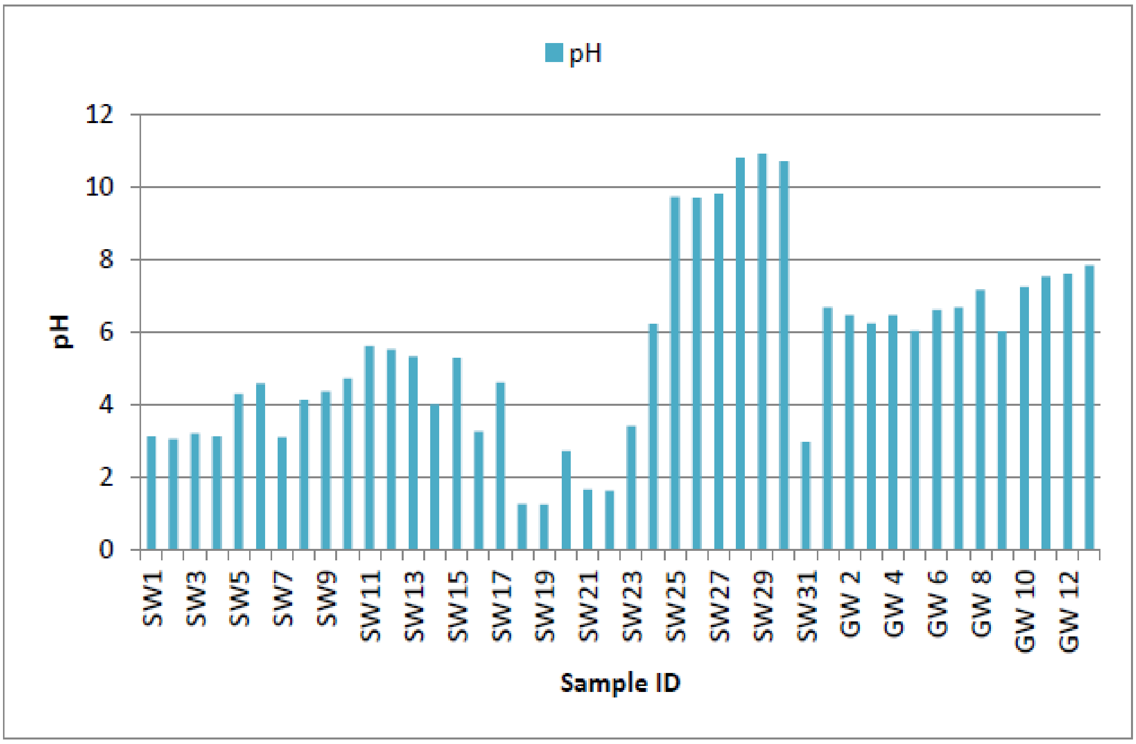

Figure 4.2: Chart showing pH of surface and ground water

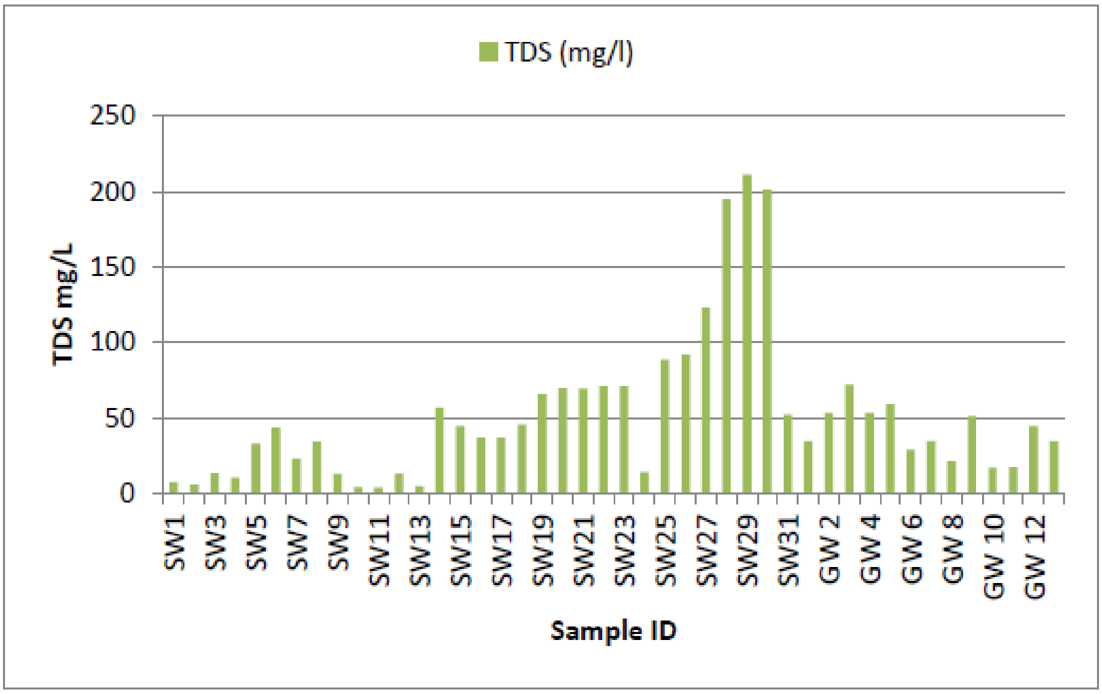

Figure 4.3: Chart showing TDS of surface and ground water

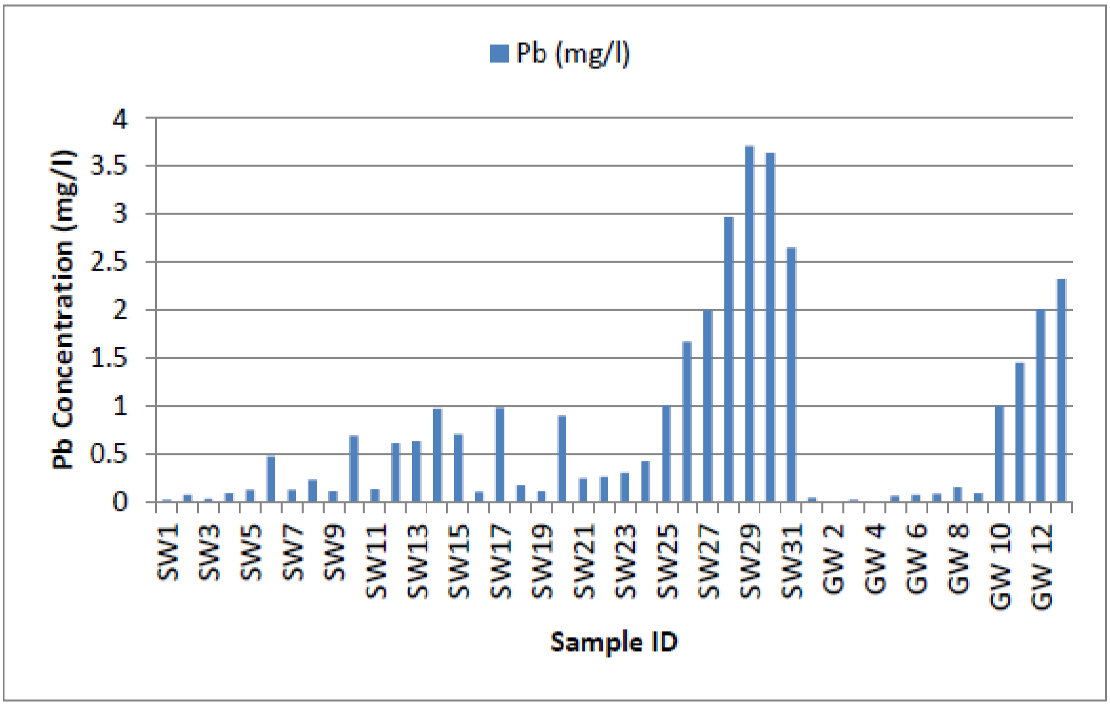

Figure 4.4: Chart showing Pb of surface and ground water

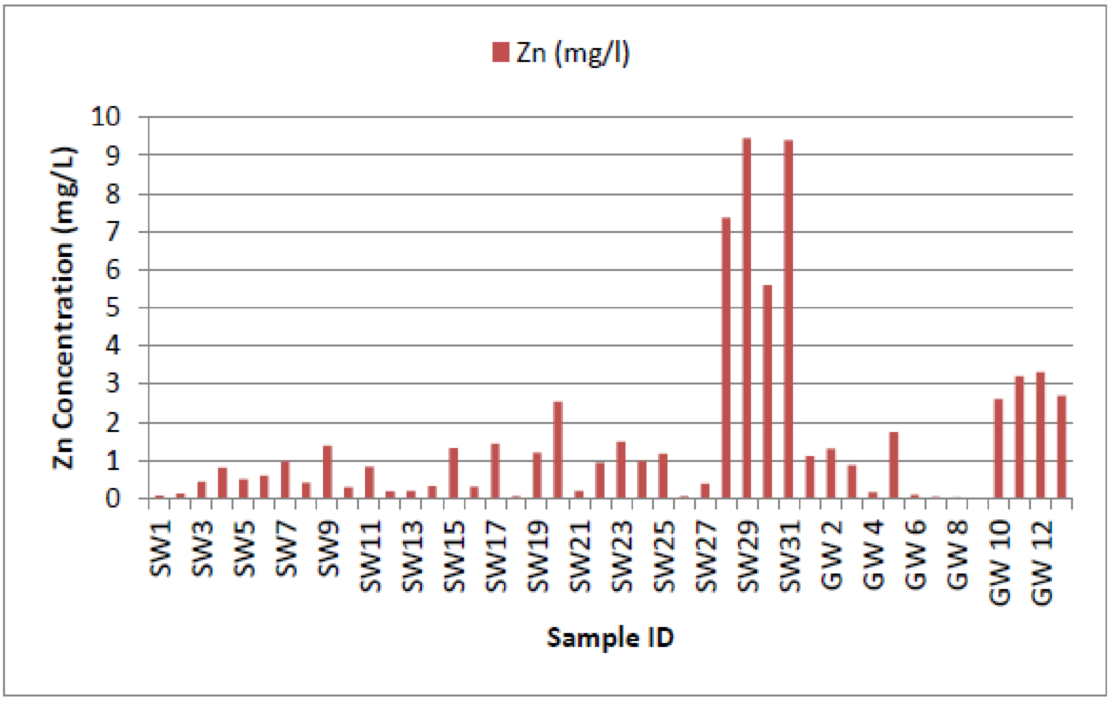

Figure 4.5: Chart showing Zn concentration in surface and ground water

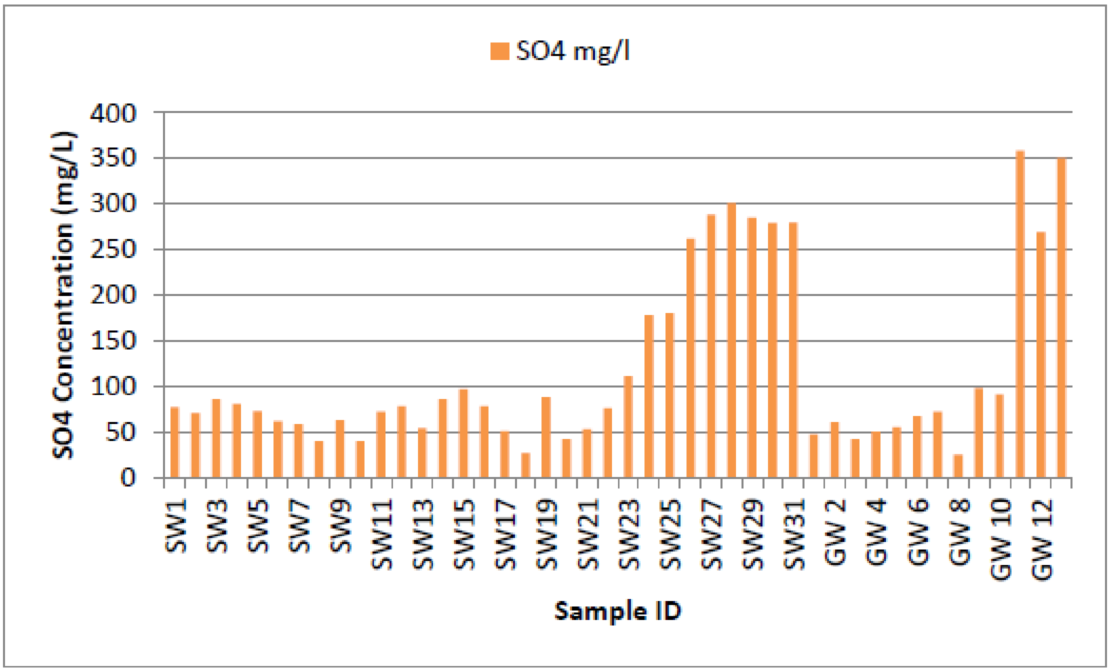

Figure 4.6: Chart showing SO_4 concentration in surface and ground water

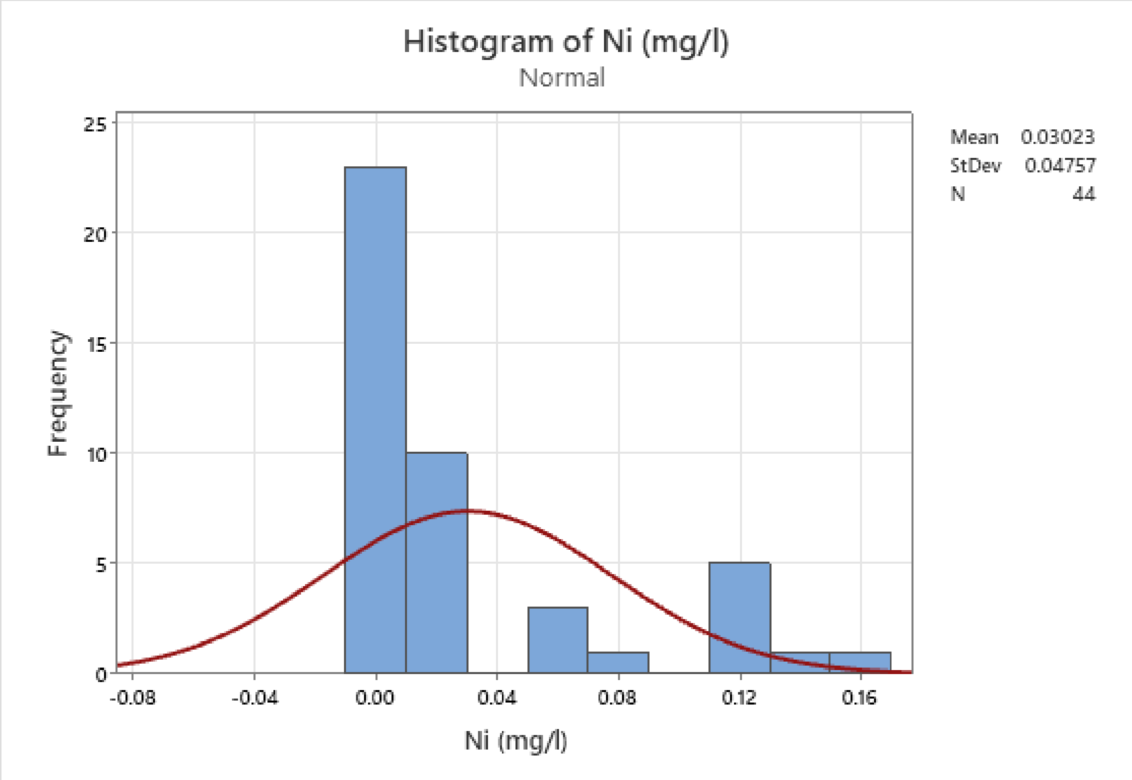

Figure 4.7: Histogram of Ni concentration in surface water and ground water

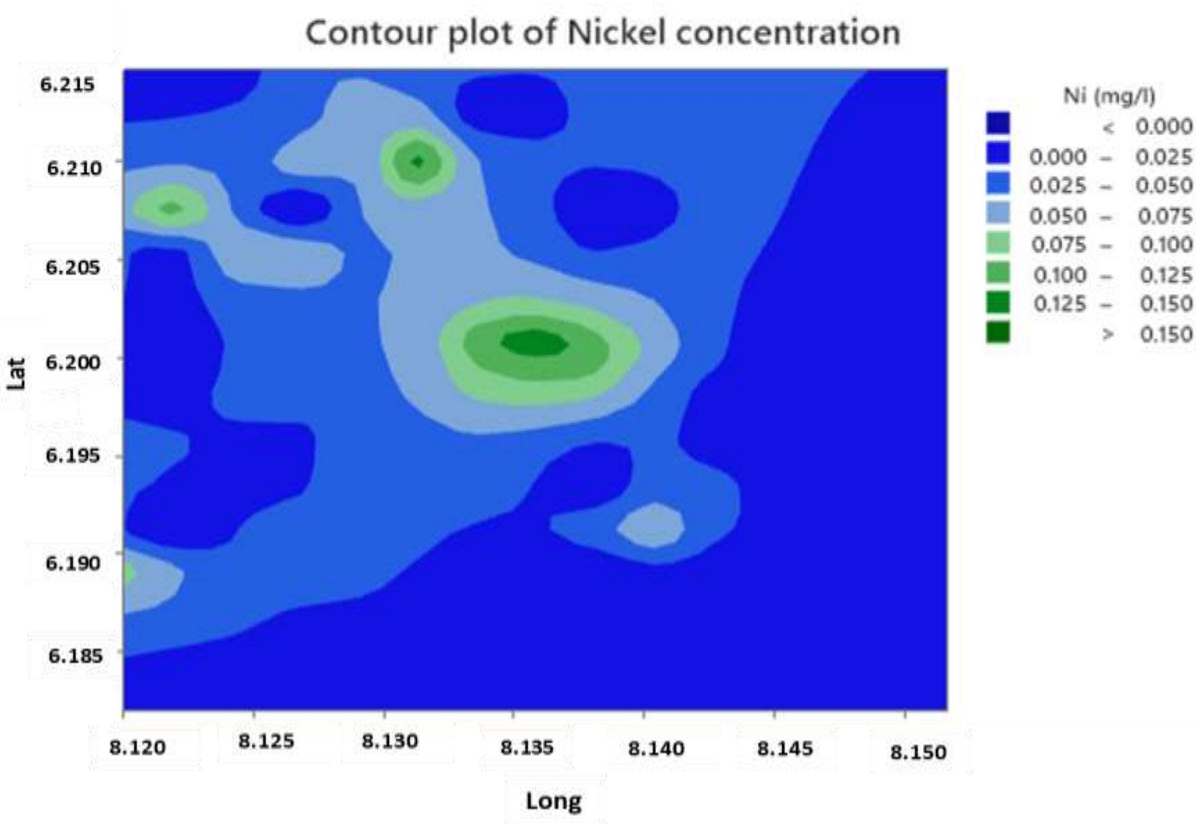

Figure 4.8: Contour plot of Ni concentration in surface water and ground water

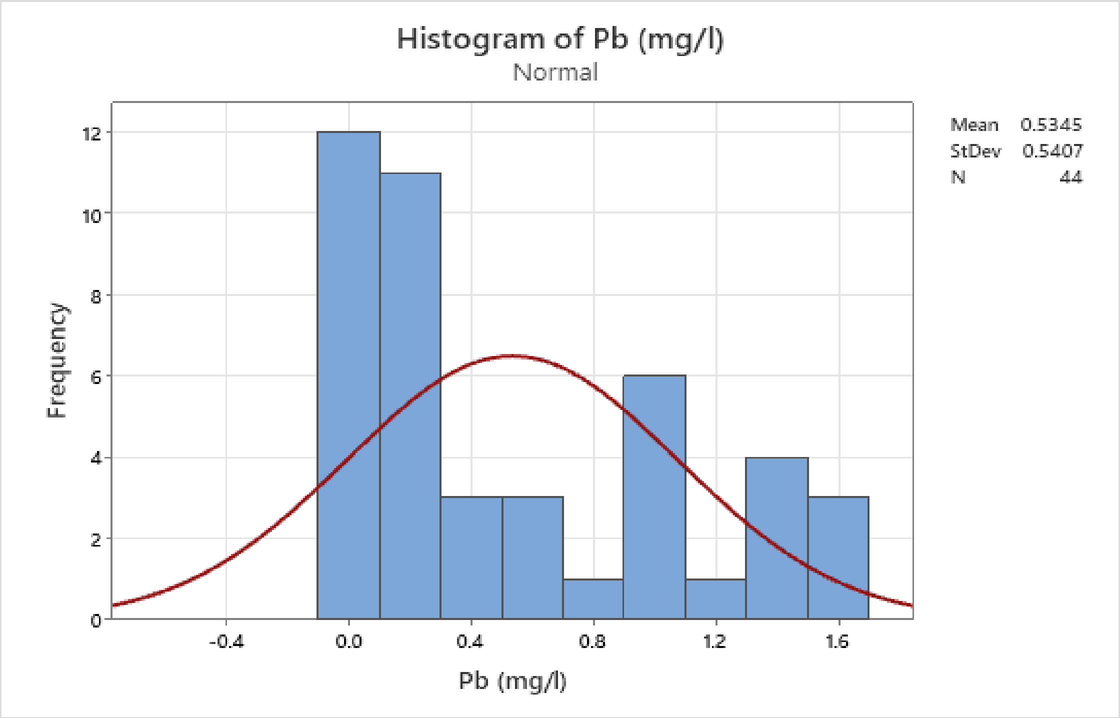

Figure 4.9: Histogram of Pb concentration in surface water and ground water

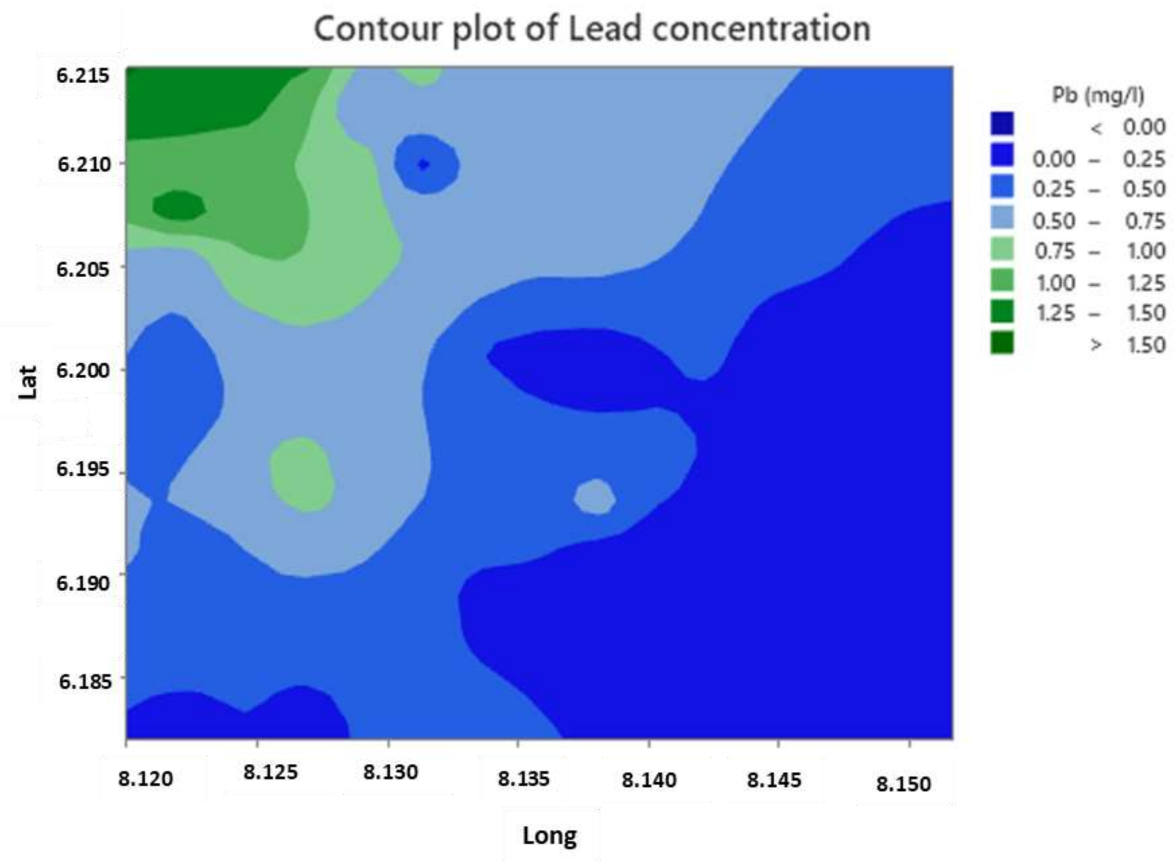

Figure 4.10: Contour plot of Pb concentration in surface water and ground water

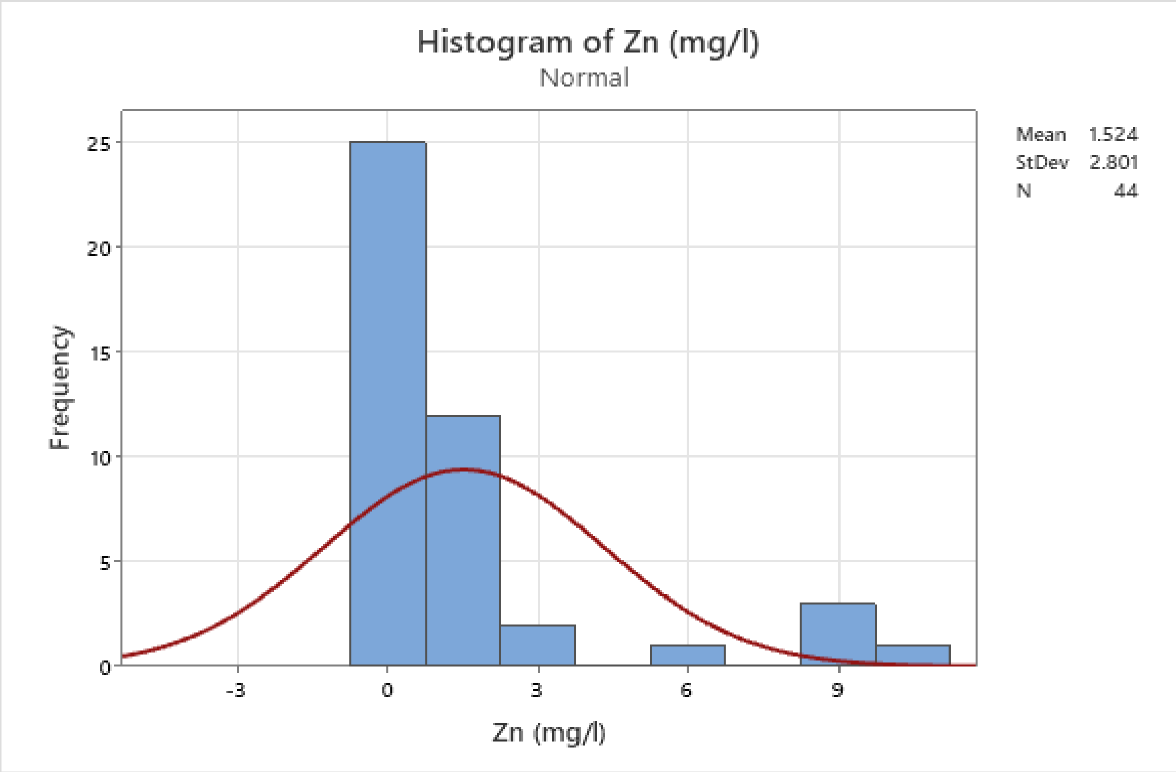

Figure 4.11: Histogram of Zn concentration in surface water and ground water

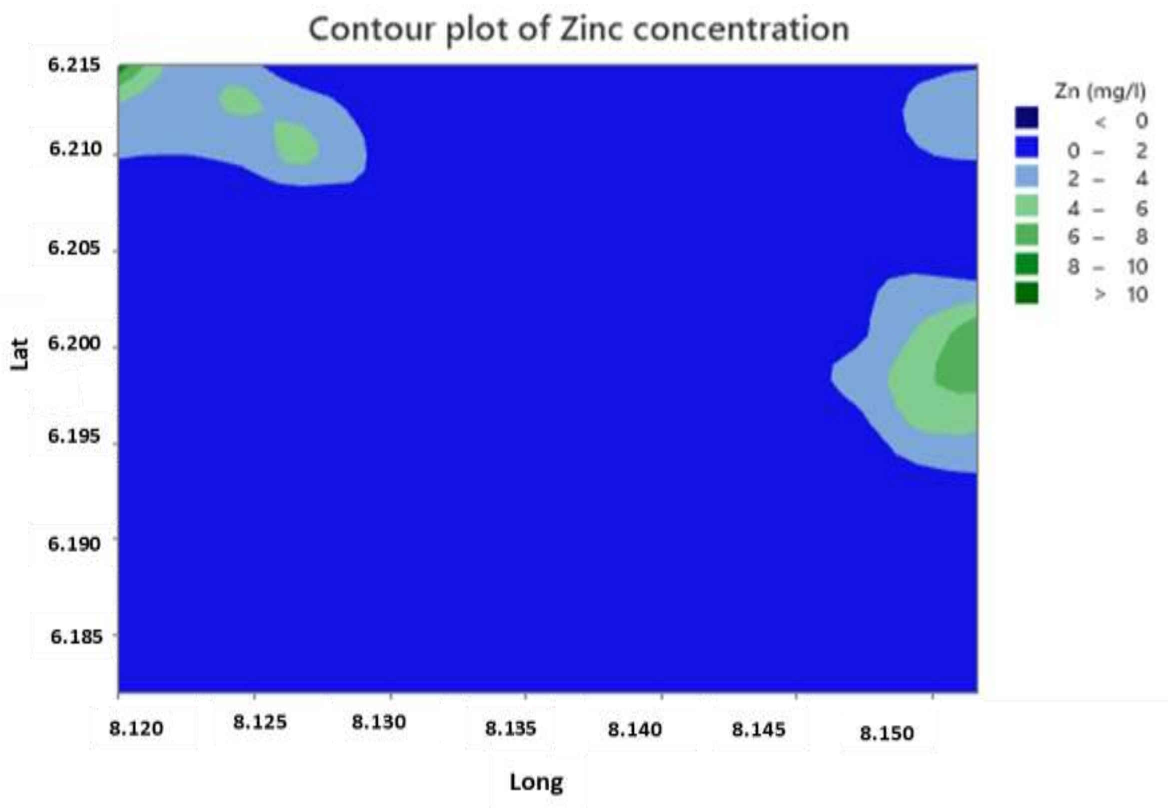

Figure 4.12: Contour plot of Zn concentration in surface water and ground water

Table 4.6: Descriptive statistics of the physical properties of groundwater

Statistic	pH	TDS (mg/l)	Temperature (^{0}C)
No. of observations	13	13	13
Minimum	4.680	0.800	25.000
Maximum	7.530	71.580	28.000
1st Quartile	6.250	16.900	26.000
Median	6.610	34.200	26.000
3rd Quartile	6.770	53.000	27.000
Mean	6.476	32.768	26.462
Variance	0.430	508.947	1.018
Standard deviation	0.656	22.560	1.009

Table 4.7: Descriptive statistics of the physical properties of surface water

Statistic	pH	TDS (mg/l)	Temperature (ºC)
No. of observations	13	13	13
Minimum	1.250	2.260	25.000
Maximum	9.730	195.000	29.000
1st Quartile	3.345	13.300	26.000
Median	5.140	68.230	27.000
3rd Quartile	6.245	74.295	28.000
Mean	5.010	57.109	27.032
Variance	4.727	1676.757	1.063
Standard deviation	2.174	40.948	1.031

Table 4.8: Descriptive statistics of the analysis of Pb, Zn and SO_4^{-2} of groundwater

Statistic	Pb (mg/l)	Zn (mg/l)	SO_4^{-2} mg/l
No. of observations	13	13	13
Minimum	0.000	0.000	25.000
Maximum	38.000	1.720	864.200
1st Quartile	0.950	0.000	72.000
Median	2.310	0..020	258.000
3rd Quartile	2.770	0.086	358.700
Mean	5.248	0.171	269.062
Variance	98.060	0.202	48252.965
Standard deviation	9.903	0.450	219.666

Table 4.9: Descriptive statistics of the analysis of Pb, Zn and SO_4^{-2} of surface water

Statistic	Pb (mg/l)	Zn (mg/l)	SO_4^{-2} mg/l
No. of observations	31	31	31
Minimum	0.010	0.040	27.000
Maximum	10.210	10.620	300.600
1st Quartile	0.245	0.240	53.500
Median	0.900	0.960	71.000
3rd Quartile	2.525	1.450	85.500
Mean	1.921	2.091	85.758
Variance	5.502	9.707	3465.263
Standard deviation	2.346	3.116	58.866

4.4 Discussion of Result

4.4.1 Physical parameters

a. pH

pH is defined as the measurement of hydrogen ion (H^+) concentration in a water sample. The pH of water is essential because it affects the solubility and availability of nutrients and their utilization by aquatic organisms (Osman and Kloas, 2010). Chapman and Kimstach (1989) proposed that the health-based guideline value proposed for pH usually depends on the direct impact on consumers, and they regarded it as one of the most important operational water quality parameters.

The pH of groundwater within the study area ranges from 6.03 to 7.17; it has an average of 6.545. The pH of surface water varies from 4.13 to 7.32, with a mean of 5.71. the mean values show that the groundwater within the study area is generally neutral while the surface water is acidic. The acidic water with pH ranging from 4 to 6 are distributed in tributaries and ponds within Enyigba, Ameri, and Amachara areas. The high pH is observed majorly within active mines and abandoned pits, now ponds of water serving the communities. The high acidic nature of the surface water system (rivers and ponds) places is way above the WHO guideline for drinking water. Acidic highs most have resulted from the poorly planning mining projects taking place within the study area.

b. Total Dissolved Solid (TDS)

Total dissolved solids (TDS) comprise inorganic salts and small amounts of organic matter dissolved in water (Batram and Balance, 1996). Concentrations of Total dissolved solid in water vary in different geological regions due to the differences in the solubilities of minerals. Analytically, TDS represents the solids remaining as the filtrate after all the suspended solids have been removed using filter paper (Batram and Balance, 1996).

WHO (2011) guideline value for TDS in drinking water is 1000 mg/l; therefore, higher values are harmful to consumers.

The TDS of groundwater within the study area ranges from 0.8 to 71.58. it has an average of 41.77. The TDS of surface water varies from 2.26 to 195, with a mean of 62.52. The mean values show that the ground surface water within the study area has TDS below the WHO limit for drinking water. The spatial distribution of pH in both ground and surface water indicates that the higher TDS is within the mining areas/sites.

c. Temperature

Temperature is the measure of the degree of hotness or coldness of a body. The temperature of water sources of the area ranges from 26^{o} C to 29^{o}C for both surface and groundwater samples. The groundwater temperature has an average of 26^{0}C, while surface water has an average temperature of 26.7^{o}C. Surface water samples show higher temperatures than due to natural variations and exposure to atmospheric temperatures at the surface. Cool water is generally more palatable than warm water, and temperature will impact the acceptability of several other inorganic constituents and chemical contaminants that may affect the taste. High water temperature enhances the growth of microorganisms and may increase taste, odour, colour and corrosion problems (WHO, 2011). The higher temperature is recorded within the mining sites in the study area.

4.4.2 Major chemical parameters

The chemical parameters include the concentration of dissolved chemical constituents in water. Some might be of organic or inorganic origin. For easy discussion of this analysis, the selected chemical parameters measured in this study are those with a direct link to the mining operation in the study area, they are;

a. sulphate ion (SO4)
b. lead (Pb)
c. Zn (Zn)

a. Sulphate Ions ($SO4^{2+}$)

Sulphate ions are a natural constituent of water. They mainly occur due to the oxidation of sulphide ores, gypsum and anhydrite (Obasi *et al*., 2015). They can also happen as leachates from their ores and other pyrite minerals. Sometimes they originate from the atmospheric deposition of oceanic aerosols. The sulphate ion is commonly less than 300mg/l in natural waters except in wells influenced by acid mines (Todd, 1980). Sulphate concentration greater than 400mg/l makes drinking water unpleasant (Pipkin, 1994), while concentration above 500mg/l imparts a bitter taste in water (Todd, 1980). Sulphate could constitute an oxygen source for bacteria, which chemosynthetically converts it to hydrogen sulphide (H_2S) in anaerobic conditions (WHO, 2008); This process causes odour in water.

The sulphate ion is divided into three population groups. Group A is comprised of sulphate concentration below 120mg/l, group B is formed of sulphate concentration ranging from 120mg/l to 250mg/l and group C comprises of sulphate concentration greater than 250mg/l.

The analysed result shows that 50% of groundwater sample falls within group A population, 12.5% falls within group B population, and 37.5% falls within group C. Surface water has 86.6% of sample analysed under group A, and 13.4% falls within group B. Above 250mg/l sulphate ion concentration in drinking water could result to health challenges (WHO, 2011), therefore, groundwater systems needs to be monitored within the study area. High sulphate ion concentration is observed majorly around the active and abandoned mine sites in Enyigba, Ameri and Amanchara (Figure 4.10 and 4.13). Therefore, the sulphide mineral ores (galena, chalcopyrite and siderite) are the primary source of sulphate ores in the study area, primarily due to water interaction with the ore, tailings and stockpiles of mining sites, weathering (oxidation) and transportation of these ions by both precipitation and surface runoff into groundwater and surface water respectively.

b) Lead (Pb)

The amount of lead dissolved in water depends on several factors, including pH, temperature, water hardness and standing time of the water, with soft, acidic water being the most plumb solvent (WHO, 2008). WHO (1984) proposed a health guideline value of 0.05 mg/l and in 1993 reviewed it to 0.01mg/l: This review was necessary because lead is a cumulative poison and that there should be no accumulation of lead in the body.

Based on the analysis of water samples from the study area, the groundwater sample has 25% of its sample below the WHO (1993) limit of 0.01mg/l; while, 75% groundwater sample is above the limit. The water analysis also shows that 100% of the surface water sample is above the WHO (1993) Pb in drinking water limit of 0.01mg/l.

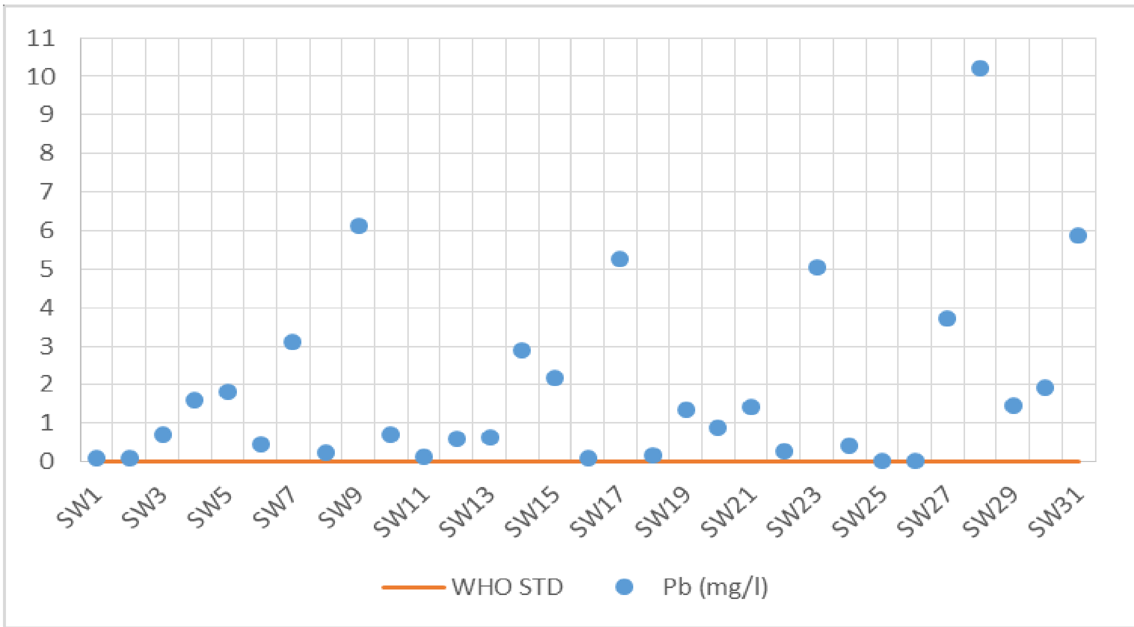

Figure 4.13: Concentration of Pb in surface water of the study area as compared with the WHO standard.

The high Pb concentration is attributed to the occurrence and mining of lead ore (galena) within the study area; higher values (>2mg/l) concentrations are observed within and around the mining area is. This is mainly due to the high immobility of lead in water. The analysis also shows that other factors like pH, Salinity and CO2 in water also resulted in the quick dissolution of lead in water (ATSDR, 2007). The quality of water within the study area is generally classified as poor due to its Pb concentration.

c) Zinc

Zinc is a chalcophile metallic element and forms numerous minerals (Sphalerite (ZnS). The most standard Zn mineral in water is Smithsonite (ZnCO3) and Zincite (ZnO). Zn is also widely dispersed as a trace element in pyroxene, amphibole, mica, garnet and magnetite minerals (Andrews and Sutherland, 2004). Its source into the environment is natural and anthropogenic, but anthropogenic sources play a higher role in introducing Zn into the environment.

The analysis shows that zinc has a range of 0.05mg/l to 8.92mg/l with an average of 1.64mg/l in surface water. Zinc has a range of 0mg/l to 1.7mg/l with an average of 0.25mg/l in groundwater. WHO (2011) did not limit zinc in drinking water, but concentration between 3mg/l to 5mg/l is good for healthy living (ATSDR, 2007). A high concentration level of up to 8.92 mg/l was recorded at the abandoned pit in Ameri, currently used as a water reservoir serving the community.

Table 4.10: WHO 2011 Guidelines/Nigerian Standard and Health Impact of Drinking

S/N	Parameters	WHO NIG. Health Guidance Standard	Impact Nig.
1.	Appearance	Clear	None (aesthetics)
2.	Colour (Hz)	5	None (aesthetics)
3.	Qualitative odour	Unobjectional	None
4.	Qualitative Taste	Unobjectional	None
5.	Temperature	Ambient	None
6.	Copper (mg/L)	2.0	Gastrointestinal disorder
7.	Zinc (mg/L)	3-5	None
8.	Lead (mg/L)	0.01	Diarrhea, brain damage, blood tissue disintegration
9.	Sulphide (mg/L)	NS	None
10.	Sulphate (mg/L)	250	INA
11.	TDS (mg/L)	1000	None
12.	Ph	6.5-8.5	None

(Obasi et al., 2015)
Key: INA = Information not Available = No Standard ND = Not Done

High element concentration of Pb and sulphate ion observed in water that drains the tailings and abandoned pits within the study area show that the mine tailings and open cast mining operations are significant environmental risks because the sulphide mineral association with them are causing acid mine drainage and contamination of the study area. High metal and sulphate contents and low pH are some of the environmental effects observed in the study area. The relationship between elements concentration and physical properties of water draining both active and abandoned mining areas indicate that acid mine drainage is taking place in the water system of the study area. The water draining from the mining areas into surface water by runoff and groundwater by precipitation gives rise to metal contamination, already above the WHO drinking water guideline (as observed in Pb concentration). The extent of the contamination can be achieved by evaluating water systems beyond the study area.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The hydro-geochemical analysis of the water system within and around the mining areas of Enyigba, Ebonyi State, Eastern Nigeria, was carried out to evaluate the impact of mining activities and the heavy metal pollution levels within both groundwater and surface water systems.

Reconnaissance survey and geologic mapping of the study area revealed distinct natural and mining-related environmental risks. These risks result from heavy metal contamination in water systems of the study area, especially in the locations closest to where sulphide minerals (Pb and Zn) were mined. Oxide precipitation of heavy metal concentrations in both surface and groundwater within areas of both active and mining operations indicates that natural acid rocks drainage occurs as observed in the low pH values measures from the analysis of water samples.

Results from the analysis of sulphate ion, lead, and zinc metals in surface water and groundwater samples revealed that the concentration levels of sulphate ion and lead-heavy metal are above the WHO, (2011) acceptable guidelines for drinking water. Especially for surface water and areas close to the active mines for groundwater. The results were presented graphically using bar charts. Compared with reference literature and WHO standard for water quality, the analysis reveals dangerous lead levels in surface water samples, especially around the active mining pits and abandoned pits. The highest zinc concentration was observed at an abandoned pit in Ameri, which has now been converted to a community water reservoir.

5.2 Recommendation

a. Mining laws and Policies

The effect of poor mining practices is evident from this study resulting in environmental degradation and could lead to a significant ecological disaster as observed in Zamfara in 2010. The Federal Government needs to provide and be more pressing on mining companies to evaluate environmental impact assessment health and safety protocols to manage environmental degradation. One of the major causes of contamination is illegal unskilled miners operating in some parts of the study area, which needs to be cut off or managed to reduce environmental degradation.

Government should provide policies that will mandate mining companies to carry out an environmental impact assessment (EIA) and, most importantly, land reclamation to stop the formation of dangerous, unplanned and unanalyzed water reservoirs within the study area.

b. Groundwater development and waste management

Due to the contamination of water systems within the study area, it is paramount to carry out groundwater and waste management planning for the rural dwellers for sustainable water supply. Borehole for quality water supply is needed for the host communities of the mining operations. Both surface and some poorly planned groundwater systems can be seen to be contaminated by heavy metals. Also, comprehensive studies of the surface water system are highly recommended to avoid destroying the aquatic environment and aquatic life.

5.3 Contribution to knowledge

The area is underlain by very high levels of lead (as high as 1.68mg//l), zinc (10.62mg/l), and other associated metals such as iron (57.1mg/l) nickel (0.16mg/l) in water sources around Enyigba. These values observed are above the NSDWQ and WHO recommended standard for drinking water, lead (0.01mg/l) and zinc (5 mg/l) iron (0.3mg/l) nickel (0.02mg/l). So the water sources in the area are unsuitable for consumption.

The heavy metals in the environment greatly degrades soil and water quality, agricultural produce and eventually the health of organisms. The relationship between elements concentration and physical properties of water draining both active and abandoned mining areas indicate that acid mine drainage is taking place in the water system of the study area.

The water draining from the mining areas into surface water by runoff and groundwater by precipitation gives rise to metal contamination, already above the WHO drinking water guideline.

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