

# Evaluation of Heavy Metals Levels and Pollution Status of Soils around Lead-zinc Mines in Oshiri, Southeast Nigeria.

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## ABSTRACT

Evaluation of the concentration and pollution status of heavy metals in soils around mine sites in Oshiri area has been carried out in this study. Hydrothermal mineralization in the Asu River Shales has led to the mining and related activities in the area. This work has evaluated the distribution and pollution status of arable soils in the area. Ten (10) samples of soil were systematically collected and analyzed using Buck scientific model 210 VGP Atomic Absorption Spectrometers (AAS), while pollution status were deduced using basic pollution indices including Geoaccumulation Index (Igeo), Contamination Factor (Cf) and Pollution Load Index (PLI). Geological mapping and studies of rock types show that the area is underlain by minor shales, mudstone and fine grained sandstone of the Asu River Group (Albian). Distribution of heavy metal concentration shows high concentration of Zn, Cu, Ni, Cd and Pd especially in the mining sites while pollution indices showed high pollution status for Cd>Zn>Pb>As > Hg>Ni > Ag>Cu>Cr in the area. Arable soils around the mine sites and stream sediments of rivers which serve as disposal channels are not suitable for food crop production as biomagnification can occur in the food chain. The adverse socio – environmental implications of mining in the area includes destruction of vegetation, environmental pollution, ecological disturbance and health hazards.

## I. INTRODUCTION

Environmental pollution and management problems are among the major challenges facing many developing countries of the world. These problems often emanate from both natural and anthropogenic sources. Natural sources may result from the host rocks (depending on the geology of the area), volcanic activities, and chemical evolution of hydrochemical facies, while anthropogenic sources often emanate from the challenges of waste disposal linked to human activities, including urbanization, industrialization, mining, municipal and domestic activities, among others (Obasi, 2020; Igweet al, 2021; Eyankware, et al, 2020; Nnaboet al., 2011; Obasi and Akudinobi, 2015). These activities often lead to the pollution of the environment (Eyankware, et al, 2021. Kamau, 2001, Obasi and Akudinobi, 2019a). Pollution of soil, surface and groundwater by heavy metals such as mercury, cadmium, lead, copper, zinc, nickel, molybdenum, vanadium, cobalt and selenium, globally constitutes a major threat to the environment and the quality of human health (Kisheet al, 2003; Obasi and Akudinobi, 2020). Recent studies has shown that lead – zinc mineralization and mining in the Abakaliki area increases the potential for environmental pollution (Obasi and Akudinobi, 2019; Obasi, 2020; Igweet al, 2021; Eyankware et al, 2021 Obiora, et al, 2016). Mining is the extraction of minerals and other geological materials of economic value from deposits on the Earth. The process adversely affects the environment by inducing loss of biodiversity, soil

erosion, and contamination of surface water, groundwater, and soil. Mining can also trigger the formation of sinkholes. The leakage of chemicals from mining sites can also have detrimental effects on the health of the population living at or around the mining site (Obasi and Akudinobi, 2020). In some countries, mining companies are expected to adhere to rehabilitation and environmental codes to ensure that the area mined is eventually transformed back into its original state. However, violations of such rules are quite common.

Mining also causes water pollution which includes metal contamination, increased sediment levels in streams, and acid mine drainage. Pollutants released from processing plants, tailing ponds, underground mines, waste-disposal areas, active or abandoned surface or haulage roads, etc., act as the top sources of water pollution. Sediments released through soil erosion cause siltation or the smothering of stream beds. It adversely impacts irrigation, swimming, fishing, domestic water supply, and other activities dependent on such water bodies. High concentrations of toxic chemicals in water bodies pose a survival threat to aquatic flora and fauna and terrestrial species dependent on them for food. The acidic water released from metal mines or coal mines also drains into surface water or seeps below ground to acidify groundwater. The loss of normal pH of water can have disastrous effects on life sustained by such water. Dispersion and dissolution of hydrochemical facies increases the ease of pollutant and contaminant transport in the aqueous medium.

The study area consists of Oshiri and environs in Onicha Local Government Area of Ebonyi State. It lies between longitudes 7°50'E and 7°57'E and latitudes 6° 05'N and 6° 10' N (Fig 1). It extends from Amaokpara- Ishieke in the north to Amankahu in the south and Umunboke and Ezeama communities in the east and west respectively. The communities include Amaokpara, Umuorie, Agbabi, Ishieke, Umumboke, Umuiman and Amanckaha (in Onicha Local Government Area), Ebonyi State, Southeastern Nigeria. The area is endowed with lead – zinc mineralization which occurs as lodes and veins traversing the area. The subsequent indiscriminate and illegal mining which has resulted in random citing of excavations and waste dumps, and unplanned disposal of mine wastes is prominent in the area. Active and abandoned mines abound in the

area. Private and communal ownership of mine pits was observed in the study area.

The carbonaceous shale of the Albian Asu River Group hosts the hydrothermal Pb-Zn mineralization which is a product of the Santonian orogeny (Kogbe, 1976, Obaje, 2009). These Cretaceous black shales contain enhanced background values of Cd, Pb, and Zn, especially close to mineralized zones, where there is strong enrichment due to primary dispersion (Nnabo et al, 2009, Oti and Nwabue, 2013; Obasiet al, 2018). Geologically, it has been noted that in weathering environment, many minerals are unstable and will break down as a result of weathering and other chemical reactions (Obiora et al, 2015; Obasi and Akudinobi, 2019). This results in the dispersion of ore and indicator elements in solution, run off sometimes in groundwater enables the occurrence for a relatively long distance within the drainage basin. Moreover, the existence of well pointed, massive mining, which resulted in the weathering and erosion/leaching, facilitated the preliminary assessment of the level of trace (heavy) elements in the bed sediments of the area. Heavy metal effluents from the weathering of the mineral deposits may have adverse consequences on soil and water 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, this can affect plants' growth and subsequent low agricultural yield or high heavy metal content in food crops. Mine wastes and tailings are directly discharged into farmlands, streams and river channels. Numerous health challenges such as miscarriages, selenosis in infants, decline in fertility, physiological and mental imbalance are commonly encountered in various communities (Obasiet al., 2015, Ezehe et al., 2009). It is against this background that a systematic assessment of the quality of the environment (especially in the area of agricultural soils) in the mineralized and mining affected areas of Oshiri, Ebonyi State, Nigeria has been carried out. Emphasis has been placed on qualitative assessment of the soils in the area, various input sources of hydrochemical significance have been assessed. Hence, providing valuable information in this regard may likely alleviate the numerous health problems in the area and constitute a vital planning tool to

healthcare providers, agro allied agencies and industries, environmental management and regulatory authorities and rural water supply agencies. This work is to establish the spatial distribution of Pb, Zn, Cu, Cd, Hg, Cr, Ag, Mn, Ni and As in the sediment beds of the area and evaluate the pollution status of soils in the area using the concepts of pollution index (I), geoaccumulation index and contamination factor (Cf) by organisms that form part of the food chain.

## II. GEOLOGY, PHYSIOGRAPHY AND CLIMATE

Geologically, Oshire is located in the Lower Benue Trough. The Trough is generally believed to be an intracontinental rift valley formed during the separation of South America from the African plate in Mesozoic time through the Gulf of Guinea, South Atlantic. This is often referred to as the Benue triple junction (Kogbe, 1976). Hence it is an Aulacogen (Olade, 1989; 1976; Wright, 1988; Benkhelil, 1967; Ofodile, 1976). The Benue Trough is referred to as an Aulacogen formed as a failed arm of a Cretaceous triple rift system, since it failed to open into a proto-ocean and was filled with sediments (Burke et al, 1972). It hosts various economic minerals, especially lead and zinc which Farrington (1952) traced from south of Abakaliki to northeast of Gombe. More than fifteen mineral occurrences and small deposits (Lodes and veins) were known and mapped. They occur in a variety of host rocks including shales in Abakaliki, carbonates at Arufu and sandstone at Zurak and Gombe. The minerals occur in association with a variety of gangue minerals such as siderite, barite, calcite and quartz (Farrington 1952., Orajaka 1965). The mode of mineralization of lead-zinc lodes, according to Orazulike (1994), was largely by open space filling. According to Uzuakpunwa (1974) the tectonic history of the Abakaliki district shows that there was extensive faulting and folding, contemporaneous with igneous activities and mineralization. Field observation (Orazulike, 1979), and structural analysis (Ezepue, 1984) support this view. Micro-textures of the minerals according to Orazulike (1994) include incompletely filled vugs and calcite in mineralized zone and comb structures in which well-formed quartz crystals are observed projecting towards the centrevugs.

Locally, the area is composed of fine to coarse grained sandstone which belong to the Albian Asu River Group and hosts the hydrothermal Pb-Zn mineralization which is a product of the Santonian

orogeny (Kogbe, 1976, Obaje, 2009). This sandstone vary from milkish white to yellowish in colour. Outcrops are exposed variously in many places in the area. The rocks are well bedded and steeply dipping with the dip amount of about 12° to 30°. The rocks strike direction as NE-SW directions (fig 1). The sandstones are deeply weathered in some places. In some places, especially around Amaokpara the sandstones are consolidated and shows laminations. In hand specimen, the sandstones shows the presence of quartz and feldspars. These sandstones host the mineralized veins in the Oshiri area.

The physiography of the study area is controlled by the prevalent structural, lithologic and physico-chemical factors. The topography could be described as comprising irregular ridges and gentle sloping hills. The elevation of the highlands range from 45m to 65m above mean sea level, while the lowlands rise to an average of about 30m (Aghamelu, et al., 2011). The area is characterized by a uniform sloping drainage slightly tilted eastwards. This is due to the Basement complex rocks of the oban massif, Obudu hills and Mamfe Embayment, which bound the area to the east (Akandee et al., 1990). These topographic features are controlled by the bedrock geology. The Oshiri area is underlain by sedimentary rocks with pronounced intrusions of pyroclastic rocks with hydrothermal veins in many places. The lithology consists mainly of well-indurated shales, argillaceous siltstones and mudstones. The well indurated sandstones and siltstones are exposed at the hills and ridges while the shales and mudstones occupy the lowlands.

Surface drainage in the study area is controlled by the Ebonyi River. This river traverses the entire study area with its eminent tributaries and distributories transporting its hydrochemical attributes from one point to another. It flows predominantly southeast. Other major rivers in the area include Rivers Amankahu, Uguogu and Isiabor. These rivers and streams vary in sizes, colour, taste, flowpath and chemistry.

Oshiri lies within the tropical rainforest belt of South-East Nigeria. It is characterized by an average rainfall of 1750-2000mm/ annum (Aghamelu et al. 2011). Rainy season and dry season are the two major seasons that prevail in the area. The rainy season normally starts in March and ends in October, and has its peak in July through August and September. It is usually initiated by the SE trade wind, which blow across the Atlantic Ocean. The dry

season starts from November and ends in February and usually initiated by the NE trade wind, which blow across the Sahara desert. Temperatures in the dry season range from 20<sup>0</sup>c to 38<sup>0</sup>c, and during the rains from 16<sup>0</sup>c to 28<sup>0</sup>c, (Inyang, 1975). The vegetation cover in the study area is controlled by its climatic condition. The highlands are characterized by drought resistance grasses, along stream and rivers. The vegetation of the area is parkland, which is derived savannah. This is characterized by stunted trees and pockets of derelict woodland and secondary forests consisting of few shrubs with dispersed large trees and climbers.

### III. METHODOLOGY

#### 3.1 Sample Collection and Analysis

Ten (10) soil samples were collected from the major mine in Oshiri to assess the distribution of ionic species in the ecosystem within the mining area. (Table 1 and Fig 1). Pre – test systematic sample preparation was done for each soil sample analysed, including drying, screening, and digestion. Since the soils were damp, they were firstly dried and disaggregated prior to sieving. The samples were laid out in pre-numbered evaporating dishes and sun-dried for three days. Each sample was disaggregated and homogenized by the use of agate pestle and mortar. It was therefore decided to pass the homogenized samples through 100 micron sieve mesh. This helped to extract metals from 400mesh fractions which is considered the highly adsorptive fraction. The nylon screen was used to avoid contamination. After screening, 2.0g of each sample was weighed for digestion.

The samples were digested by the using aquaregia, which was prepared by the mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in the ratio 1:3. The advantage of this mixture is that it can be kept at higher temperature than other acids. The decomposition is also faster than most other techniques. The heavy metal analysis was conducted using Varian AA240 Atomic Absorption Spectrophotometer in line with American Public Health Association (APHA) (1998) specification. This analysis was done at Springboard Analytical Research Laboratory, Awka, Anambra

State. The result of the analysis was reported in mg/l and was converted to concentration of metal in mg/kg of dry sediment.

#### 3.2 Determination of Pollution Status

Geochemical studies of soils were carried out using various methods to determine the pollution/contamination status of soils. This includes:

##### 3.2.1 Pollution index (€)

Pollution index (€) as proposed by Powell (1992) is the ratio of individual metal concentration in soils to the ERM value for that particular metal. It expresses how many times the concentration of the individual metal is higher than the ERM for that metal in soil samples.

Mathematically; pollution index (€) = C/ERM - - - - - (1)

Where C is the concentration of the individual metal in bed sediments (in Mg/Kg), ERM is the effect Range Median (in Mg/Kg).

##### 3.2.2 Geoaccumulation index (Igeo)

Geoaccumulation index (Igeo) is defined by the formula

$$I_{geo} = \frac{\log 2C_n}{1.5B_n} - - - - - (2)$$

Where C<sub>n</sub> is the measured concentration of metals in politic sediment fraction and B<sub>n</sub> is the geochemical background value for shale

##### 3.2.3 Contamination factor

Determination of pollution status of heavy metals in the stream bed sediment/ soils was also assessed using the contamination factor.

Mathematically, contamination factor is expressed as:

$$CF = \frac{C_n^F}{C_n^F} - - - - - (3)$$

Where C<sub>n-1</sub><sup>F</sup> is the mean content of the metal from sampling locations. C<sub>n</sub><sup>F</sup> is the concentration of the heavy metals in the Earth's crust as a reference value.



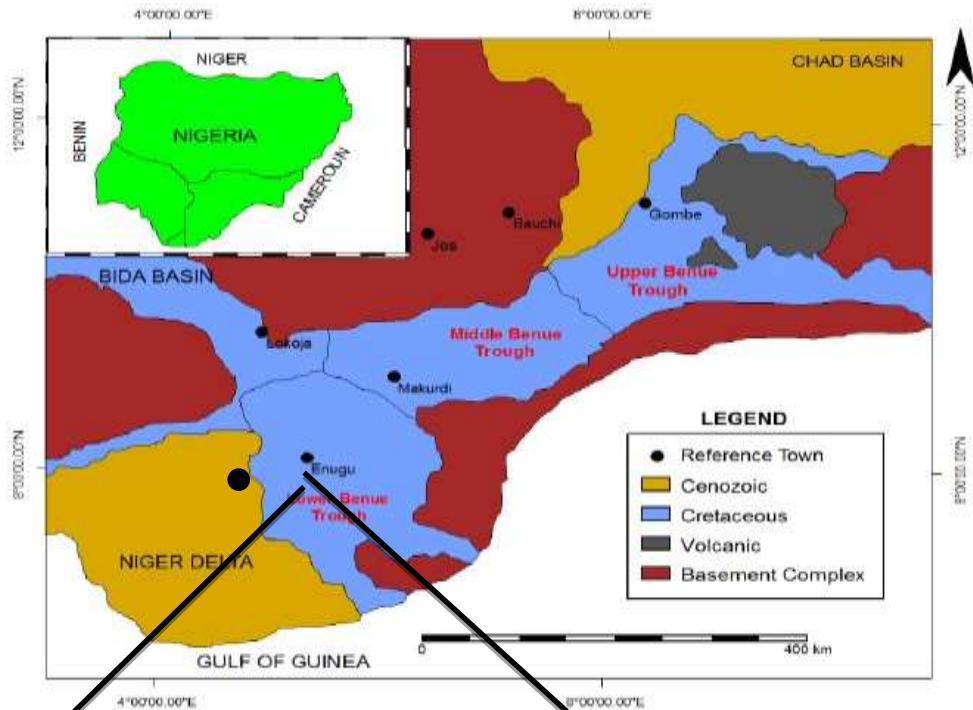
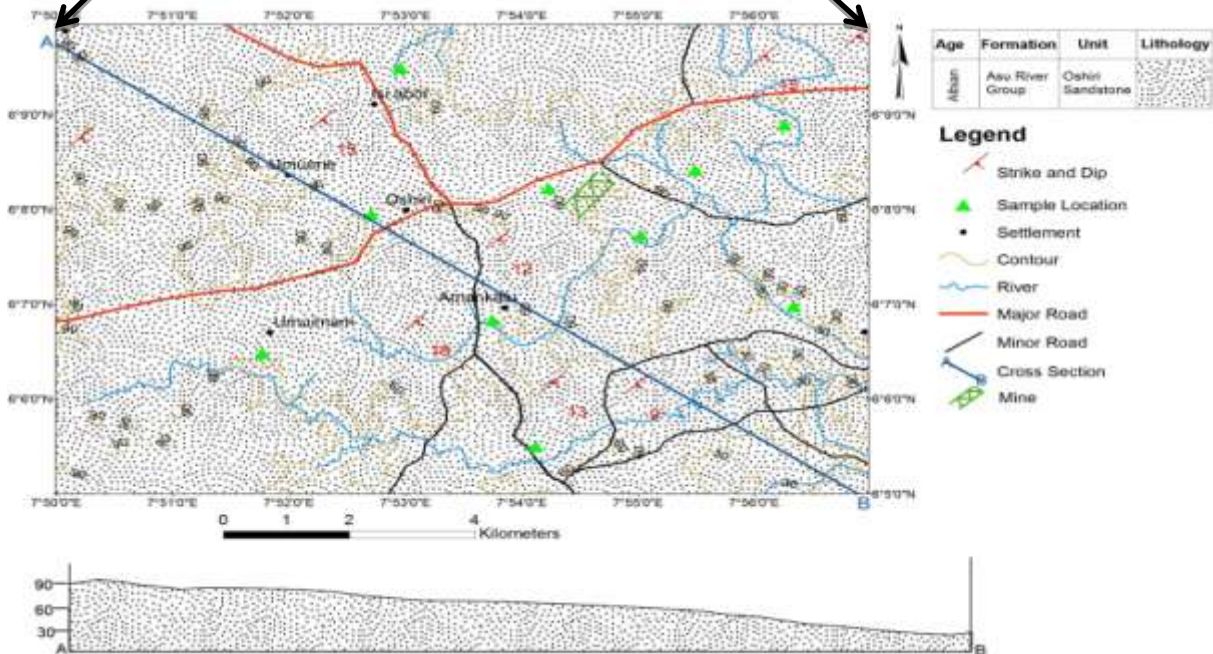


Fig 14: Geologic map of the study area.



**Table 1: Concentration of geochemical elements in (mg/kg) of soil samples analysed**

		Coordinates		Concentration of parameters in mg/kg.									
S/n	Samples	Latitude	Longitude	Zn	Cu	Pb	Mn	Cd	Cr	Hg	Ag	As	Ni
1	NR/S1	6° 08' 44.9"	007° 55' 99.0"	198.4	3.94	20.74	195.7	12.65	0.012	9.57	5.16	0.22	12.31
2	NR/S2	6° 08' 44.6"	007° 55' 58.2"	188.7	1.72	21.03	54.5	0.00	0.016	8.07	3.48	0.016	3.52
3	NR/S3	6° 08' 44.6"	007° 55' 58.2"	196.1	1.13	24.61	189.2	0.05	0.10	0.65	1.64	0.18	2.57
4	NR/S4	6° 08' 44.6"	007° 55' 58.1"	195.9	2.26	24.31	119.8	0.25	0.014	0.12	1.14	0.36	4.47
5	NR/S5	6° 08' 46.1"	007° 55' 58.8"	194.0	1.28	21.23	86.2	0.00	0.009	0.38	0.68	0.012	2.05
6	NR/S6	6° 08' 46.1"	007° 55' 58.7"	196.7	0.24	35.64	195.1	17.56	0.06	0.17	0.28	0.22	7.88
7	NRS7	6° 08' 45.2"	007° 56' 00.2"	196.1	1.05	28.76	195.8	9.42	0.08	0.54	0.38	0.19	6.93
8	NR/S8	6° 08' 45.2"	007° 56' 00.3"	195.7	1.45	32.59	200.1	4.45	0.012	1.01	0.00	0.22	5.58
9	NR/S9	6° 08' 42.5"	007° 56' 00.1"	195.5	1.87	22.31	111.4	0.00	0.009	1.24	0.18	0.48	4.43
10	NR/S10	6° 08' 42.5"	007° 56' 00.1"	196.0	1.34	19.80	129.5	3.31	0.018	0.34	0.11	0.28	9.24
	Min c			188.7	0.24	19.80	54.50	0.00	0.009	0.120	0.00	0.016	2.050
	Max con			198.4	3.94	35.64	200.1	17.56	0.10	9.57	5.16	0.48	12.31
	mean			195.3	1.628	25.10	147.7	4.769	0.033	2.209	1.305	0.218	5.898
	Range			9.7	3.7	15.84	145.6	17.56	0.091	9.45	5.16	0.218	10.26

### 3.3 Levels of Heavy Metals

#### 3.3.1 Zinc (Zn)

Zinc is also a chalcophile metallic element and forms several minerals, including sphalerite, ZnS, the commonest Zn mineral, smithsonite, ZnCO<sub>3</sub> and zincite, ZnO, but is also widely dispersed as a trace element in pyroxene, amphibole, mica, garnet and magnetite.

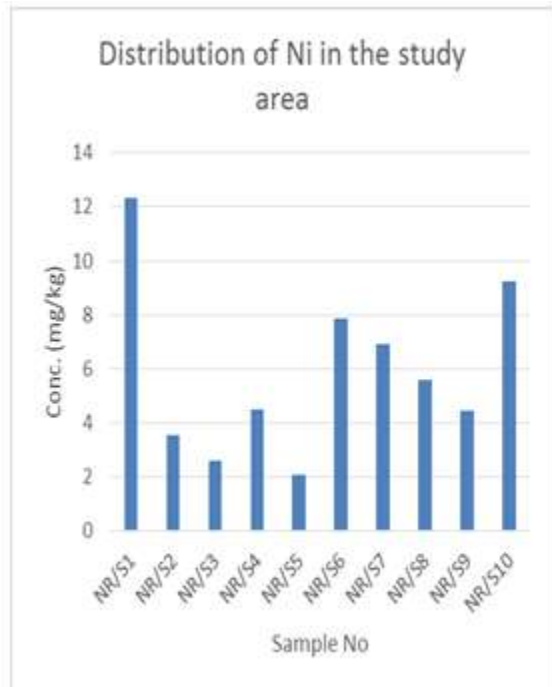
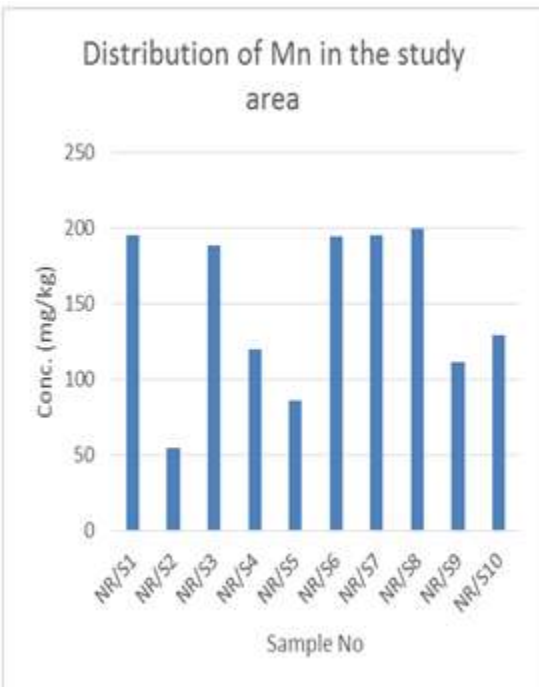
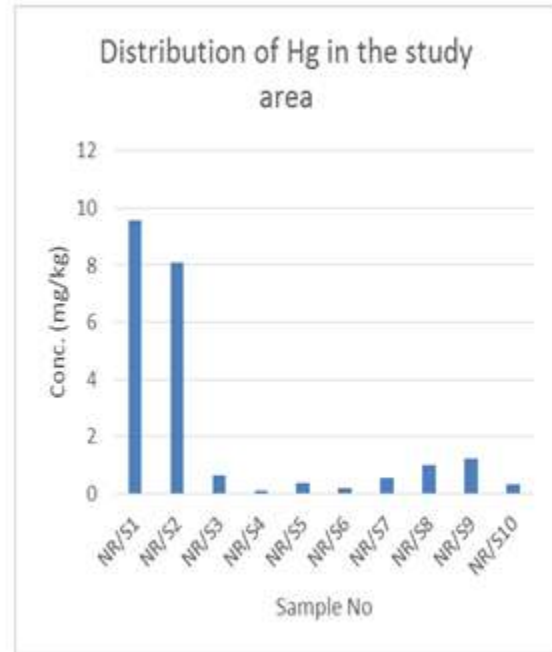
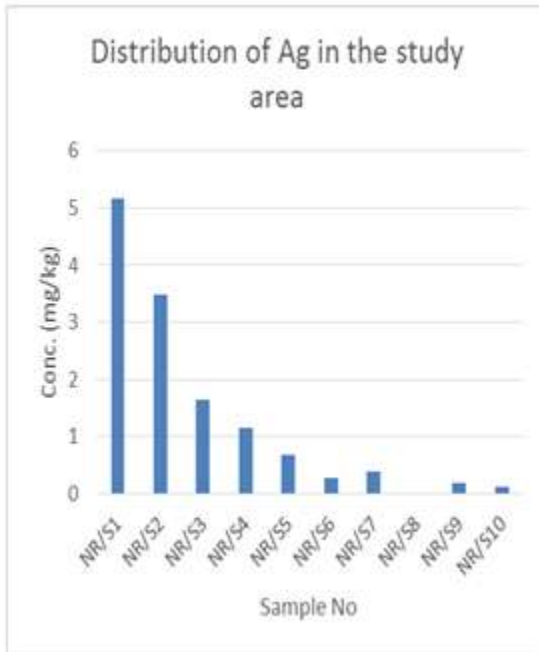
Analysis for Zinc in all ten soil samples showed positive results, with values ranging from 188.7 to 198.4 mg/kg, with mean concentration of 195.31 mg/kg. Zinc has a geochemical background value of 70 mg/kg in the Earth's crust and 90 mg/kg for Shale. Natural background of total zinc concentration is usually from 10- 300mg/kg dry weight in soils (Buchauer, 1973). ATSDR (2005) stated that increased levels of zinc in soils can be attributed to natural occurrence of zinc enriched ores (as in the study area), anthropogenic sources including the disposal of zinc wastes from metal manufacturing industries and coal ash from electric utilities, sludge and fertilizer or even through abiotic and biotic processes. Toxicity in human may occur if zinc concentration in water approaches 400mg/kg.

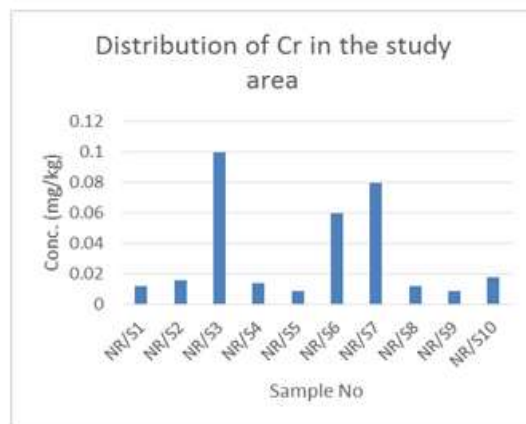
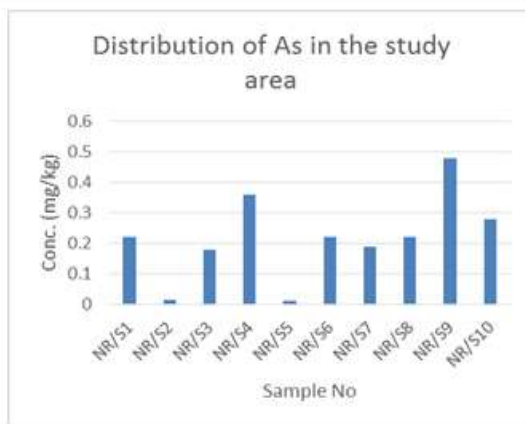
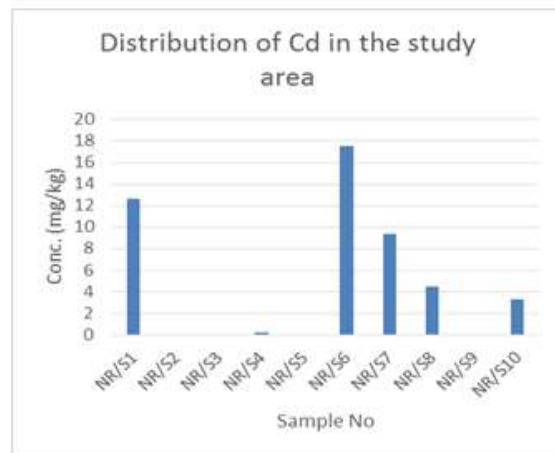
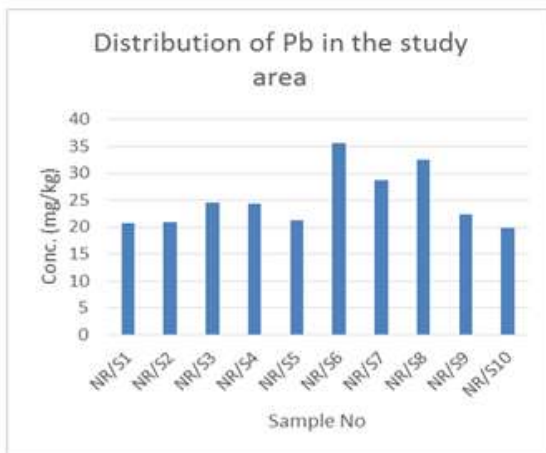
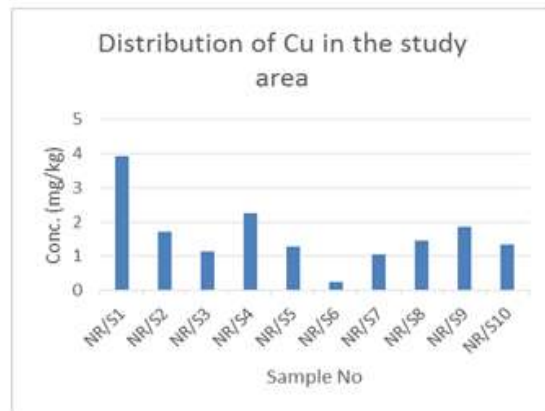
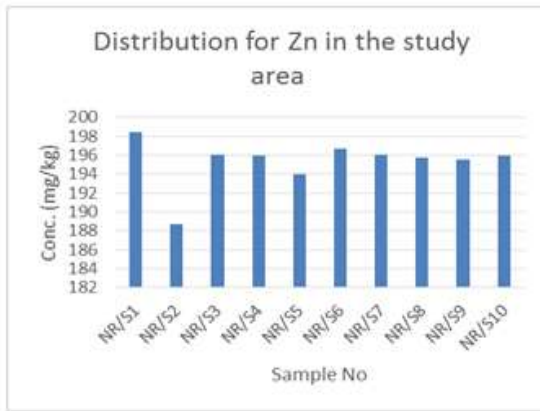
This is characterized by symptoms of irritability, muscular stiffness, pain, loss of appetite and nausea.

#### 3.3.2 Copper (Cu)

From the results of the analysis, copper was observed in all the ten samples analysed. It has a mean concentration of 1.628 mg/kg, and a range of 3.7 mg/kg. The minimum and maximum concentrations were 0.24 mg/kg and 3.94 mg/kg respectively (fig 2). The high concentrations of copper can be attributed to the mining activities and the chemical behavior of copper. Tyler and McBride (1982), observed that most copper deposited in soil from the atmosphere, agricultural use, and solid waste and sludge disposal will be strongly adsorbed and remain in the upper centimeters of soil. In general, copper will be adsorbed to organic matter, carbonate minerals, clay minerals, orhydrous iron and manganese oxides (Callahan, et al. 1979; Fuhrer, 1986). Copper binds to soil much more strongly than other divalent cations, and the distribution of copper in the soil solution is less affected by pH than other metals (Reddy et al 1995).

Please note that N/A means not available.





### 3.3.3 Lead (Pb)

Lead is a chalcophile metallic element forming several important minerals including galena, PbS, anglesite, PbSO<sub>4</sub>, cerussite, PbCO<sub>3</sub> and minium Pb<sub>3</sub>O<sub>4</sub>. It is also widely dispersed at trace levels in a range of other minerals, including K-feldspar, plagioclase, mica, zircon and magnetite. It is one of

the seven metals known in antiquity, because of its relative ease of extraction as a metal.

All of the ten samples analysed were observed to contain Lead (fig 2) in contents ranging from 19.8 to 35.64 mg/kg with a mean concentration of 25.10 mg/kg and the geochemical background value has been set as 12.5mg/kg for the Earth's



crust and 20 mg/kg for Shale. Apart from the ores which occur in the study area, the chemistry of lead contributes to its higher concentration. Once lead falls onto soil, it sticks strongly to soil particles and remains in the upper layer of soil (ATSDR, 2007). Reddy, et al; (1995) concluded that the mobility of lead will increase in environments having low pH due to the enhanced solubility of lead under acidic conditions.

### 3.3.4 Cadmium (Cd)

Cadmium is found in minor amounts in sphalerite. It is also found in secondary minerals such as hawleyite (CdS) and greenockite (CdS).

Cadmium was observed in only seven samples with values ranging from 0 mg/kg to 17.46 mg/kg (fig 2). Mean value was at 4.77 mg/kg. Geochemical background value was set as 0.15 mg/kg on the Earth's crust and 0.3 mg/kg in Shale. This high concentration of cadmium is because cadmium is commonly associated with zinc, lead, and copper ores (as in the study area) (ATSDR, 2007). In soils, pH, oxidation-reduction reactions, formation of complexes and the availability of organic matter are important factors affecting the mobility of cadmium (Herrero and Martin, 1993). Cadmium in soil tends to be more available when the soil pH is low (acidic) (Elinder, 1992).

### 3.3.5 Arsenic (As)

Arsenic is both a chalcophile and lithophile element. Its principal ore mineral is arsenopyrite. It is also usually found as a nickel-arsenide assemblage.

The amount of concentration of Arsenic when compared to the other heavy metals in the study area is low (fig 2). Mean concentration is 0.218 mg/kg with a range of 0.464 mg/kg. Geochemical background value is at 1.8 mg/kg in the earth's crust and 10 mg/kg in Shale. Arsenic occurs naturally in soil and in many kinds of rock, especially in minerals and ores that contain copper or lead, volcanic eruptions are another source of arsenic (ATSDR, 2007). Arsenic may enter the environment during the mining and smelting of these ores. Davies et al. (2005) noted that arsenic in soil may be transported by wind or in runoff or may leach into the subsurface soil. However, arsenic cannot be destroyed in the environment. It can only change its form, or become attached to or separated from particles (ATSDR, 2007).

### 3.3.6 Chromium (Cr)

From the analysis, chromium was evenly distributed in the study area. The maximum concentration is 0.10 mg/kg, lowest concentrations were recorded in samples from NR5, NR9 and NR10 (fig 2). This low concentrations can be attributed to the fact that chromium is not a major component of the Pb-Zn ore. The total mean value of Cr is 0.033 mg/kg with range of 0.091 mg/kg. Geochemical background value was set as 100mg/kg in Earth's crust and 73mg/kg in shale. Chromium occurs naturally in rocks, animals, plants, and soil, where it exists in combination with other elements to form various compounds, however, anthropogenic activities like the manufacture of chromium-based products, leather tanning and the burning of natural gas, oil, or coal can release chromium in the environment (ATSDR, 2012). The mobility of chromium in soil is dependent upon the speciation of chromium, which is a function of redox potential and the pH of the soil (Ashley et al; 2003).

### 3.3.7 Mercury (Hg)

The result indicates that apart from sample NR1 (centre of the mine pit 9.57mg/kg), low concentration of mercury was observed in the study area (fig 3). The mean concentration of this metal was 2.209 mg/kg with the range of 9.45mg/kg. The low concentrations in other points may be due to moderate dispersion of the metal in soils of the area. Mercury has long been known to cause various cancers. Sources of mercury in the environment include water, rocks and very importantly, biodegradable waste dumps. The long and short term toxicity effect is on the kidney.

### 3.3.8 Silver (Ag)

From the result obtained, silver was also evenly distributed in the study area. This is due to the fact that silver is a major composition of the Pb – Zn ores. A maximum concentration of 5.16 mg/kg was recorded at the center of the mine pit. Silver occurs naturally mainly in the form of its insoluble and immobile oxides, sulphides and some salts. ATSDR (1990) also noted that the factors governing the environmental fate of silver are not well characterized. While silver and its compounds are transported in the air, water, and soil, and are partitioned between these media, the mechanisms of transport and partitioning are not well-defined. No

partition coefficients or constants have been determined for silver or its compounds (Dissanayake et al, 1983). The transport and partitioning of silver in surface waters and soils is influenced by the particular form of the compound.

### 3.3.9 Manganese (Mn)

From the results of the analysis manganese was also observed in all the (ten) 10 samples analysed with a total mean concentration of 147.73 mg/kg, and range of 145.6 mg/kg (fig 3). The minimum and maximum concentrations were 54.5 mg/kg and 200.1mg/kg respectively. Mn is highly concentrated in the mine because it is a major component of the pb – zn. Moreover, Mn is highly immobile and has low dispersion especially in the tropical regions (Buchauer, 1973).

### 3.3.10 Nickel (Ni)

Analysis for Nickel in all ten soil samples showed positive results, with values ranging from 2.05 to 12.31mg/kg, a mean concentration of 5.898 mg/kg. Ni is highly dispersed in the study area has its highest concentration in NRS1. This reflects high concentration for nickel. ATSDR (2005), stated that

effluent water generated from mining and smelting operations, runoff from tailing piles, or from utility water used for mine operations can lead to higher concentrations of nickel in mining areas. Barcan, (2002) showed that these discharges consist mostly of less-soluble silicates and sulfides that readily settle out. Tailing effluents from sulfidic ores are acidic due to the bacterial generation of sulfuric acid from the sulfidic minerals in the tailings, and very high concentrations of soluble nickel sulfate may be released (Mann, et al. 1989). Also the presence of iron-(di)sulfides in wetland sediments has been associated with increased mobilization of nickel into soils during periods of drought (Lucassen, et al. 2002).

### 3.4 Pollution Status of the Oshiri mine

#### 3.4.1 Pollution Index (PI)

Pollution index (€) (Equation 1), with the ERM values as standards (see Table 3), it is possible to consider the pollution levels in terms of pollution index. Table 2 shows the calculated pollution index for the soil samples. When  $\epsilon \geq 1$  = Significant Contamination (SC), when  $\epsilon \leq 1$  = Insignificant Contamination (IC).

**Table 2: Pollution index for soils in the Oshiri mine.**

Samples	Zn	Cu	Pb	Cd	Cr	Hg	Ag	As
NR/ S1	0.484	0.015	0.094	1.318	0.00003	13.47	1.395	0.0031
NR/S2	0.460	0.006	0.096	0.000	0.00004	11.36	0.941	0.0002
NR/S3	0.478	0.004	0.112	0.005	0.0003	0.916	0.443	0.0026
NR/S4	0.478	0.008	0.111	0.026	0.00004	0.169	0.308	0.0051
NR/S5	0.473	0.005	0.097	0.000	0.00002	0.535	0.184	0.0002
NR/S6	0.480	0.001	0.162	1.829	0.0002	0.239	0.076	0.0031
NR/S7	0.478	0.004	0.131	0.981	0.0002	0.761	0.103	0.0027
NR/S8	0.477	0.005	0.148	0.464	0.00003	1.423	0.000	0.0031
NR/S9	0.477	0.007	0.101	0.000	0.00002	1.747	0.049	0.0069
NR/S10	0.478	0.005	0.090	0.345	0.00005	0.479	0.030	0.0040

**Table 3: The ERL and ERM limits for metals (US –EPA – MAIA 1998)**

Metals	ERL values in mg/kg	ERM values in mg/kg
Zinc (Zn)	150	410
Copper (Cu)	34	270
Lead (Pb)	47	220
Cadmium (Cd)	1.2	9.6
Chromium (Cr)	81	370
Mercury (Hg)	0.15	0.71
Silver (Ag)	1	3.7
Arsenic (As)	8.2	70

The ERM value of Zinc is 410mg/kg, the concentration of Zinc in many of the samples locations is above the ERL and below the ERM value in many locations, its pollution index ranges (0.460 – 0.484€). Zinc has highest enrichment of 0.484€ in sample from the center of the mine. The pollution index for zinc is below the toxic level and indicates insignificant contamination.

The ERM value for Copper is 270mg/kg. Copper is below the ERL and ERM value in all the samples locations and its pollution index is below the toxic level (0.001 – 0.015€). This is insignificant contamination.

The ERM value for lead is 220mg/kg and ERL value is 47mg/kg. The concentration of lead is below the ERL value in all the samples. Pollution index status shows insignificant contamination as it ranges from (0.090 – 0.162€). For Cadmium, the ERM value is 9.6mg/kg and ERL value is 1.2mg/kg. Cadmium is below ERL in some of the samples and above the ERM value in sample NRS1 and sample NRS6. Pollution index ranges between (0.00 – 1.829€). This attains its toxic level in the two samples above. It has 20% significant contamination. Chromium has ERL value of 81mg/kg and ERM value of 370mg/kg. The values are below the ERL and ERM values in all the samples analysed. It shows insignificant contamination with pollution index ranges (0.00002 – 0.00016€). Mercury has ERM

value 0.71mg/kg and ERL of 0.15mg/kg. 90% of the samples are above the ERL while 40% are above the ERM value. It has pollution index range of (0.169 – 13.48€). This is significant contamination. Silver has ERM value of 3.7mg/kg and ERL of 1mg/kg, 20% of the samples are above the ERM. This indicates significant contamination for only sample NR/S1 but this is insignificant for the entire area. Pollution index for silver range between (0.000 – 1.395€). Arsenic has ERM of 70mg/kg and ERL of 8.2 mg/kg. All the samples are below the ERM and ERL values. Pollution index ranges between (0.0002 – 0.0069€). This shows insignificant contamination in the study area.

The results of the analysis showed that pollution index (€) for Zn, Cu, Pb, Cr and As are less than 1 (<1) while those of Cd (20%), Hg (40%) and Ag (10%) are greater than 1 (>1) in some samples.

### 3.4.2 Geoaccumulation Index (Igeo)

Following the geoaccumulation index values from Table 5, it can be deduced that Zn, Cu, Pb, Cr, As and Ni satisfy class (0) (practically uncontaminated) of Table 4 (classes of geoaccumulation index) except Cd. 30% Cd was observed to be extremely contaminated, 20% moderately contaminated, 20% uncontaminated to moderately contaminated while 30% is practically uncontaminated.

**Table 4: Classes of geoaccumulation index (Boskeet al., 2004)**

Class	Value	Soil/sediment quality
0	$I_{geo} < 0$	Practically uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately contaminated to heavily contaminated
4	$3 < I_{geo} < 4$	Heavily contaminated
5	$4 < I_{geo} < 5$	Heavily contaminated to extremely contaminated
6	$5 < I_{geo} < 6$	Extremely contaminated

**Table 5: Geoaccumulation index values for soils from the Oshiri mine.**

Samples	Zn	Cu	Pb	Cd	Cr	As	Ni
NR/S1	0.442	0.016	0.208	8.46	0.00004	0.004	0.03
NR/S2	0.421	0.007	0.211	0.00	0.00006	0.0003	0.009
NR/S3	0.437	0.247	0.247	0.03	0.03716	0.004	0.006
NR/S4	0.437	0.009	0.244	0.17	0.00005	0.007	0.006
NR/S5	0.433	0.005	0.213	0.00	0.00003	0.0002	0.005
NR/S6	0.378	0.0019	0.358	11.75	0.00022	0.004	0.029
NR/S7	0.437	0.004	0.289	6.30	0.0003	0.004	0.017
NR/S8	0.436	0.006	0.327	2.98	0.00004	1.004	0.014

NR/S9	0.436	0.008	0.224	0.00	0.00003	1.01	0.011
NR/S10	0.437	0.005	0.199	2.21	0.00007	0.006	0.023

### 3.4.3 Contamination factor

The pollution status of heavy metals in the soils of the Oshiri minewas also assessed using the contamination factor. According to Hakanson, 1980, contamination factor (Equation 3) expresses the mean

concentration with reference to the concentration of the metal in the earth crust. Table 6 shows categories of contamination factor, while calculated values are represented in table 7.

**Table 6: Categories of Contamination Factor (CF) after Hakanson, 1980**

CF < 1	Low contamination factor indicating low contamination
1 < CF < 3	Moderate contamination factor
3 < CF < 6	Considerable contamination factor
6 < CF	Very high contamination factor

**Table 7: Contamination factor for soils from the Oshiri mine**

Sample N0	Zn	Cu	Pb	Cd	Cr	As	Ni
NR/S1	2.2044	0.0788	1.0370	42.17	0.0002	0.022	0.1539
NR/S2	2.0967	0.0344	1.0515	0.00	0.0003	0.002	0.044
NR/3	2.1789	0.0226	1.2305	0.17	0.002	0.018	0.0321
NR/S4	2.1767	0.0452	1.2155	0.83	0.0003	0.036	0.0559
NR/S5	2.1556	0.0256	1.0615	0.00	0.0002	0.001	0.0256
NR/S6	2.1856	0.0048	1.782	58.53	0.001	0.022	0.0985
NR/S7	2.1789	0.0210	1.438	31.40	0.0015	0.019	0.0866
NR/S8	2.1744	0.0290	1.6295	14.83	0.0002	1.022	0.0698
NR/S9	2.1722	0.0374	1.1155	0.00	0.0002	1.048	0.0554
NR/S10	2.1778	0.0268	0.990	11.03	0.0003	0.028	0.1155

From table 7above, analysis of contamination factor shows that the contamination factor (CF) of Zn is moderate ( $1 < CF < 3$ ), Cu is low ( $CF < 1$ ), Pb is moderate ( $1 < CF < 3$ ) and Cr is low ( $CF < 1$ ), As is low ( $CF < 1$ ), Ni is ( $CF < 1$ ). Cd has very highcontamination factor ( $6 < CF$ ).

### 3.5 Effects of Heavy Metals on the Ecosystem

According to Gerhatet al., 1992, during high stream flow, stream sediments are mobilised and transported downstream, resulting to transportation and re-deposition in downstream.. Through this, contaminants are introduced into new areas of the stream ecosystem, thereby becoming available for ingestion by greater numbers of aquatic organisms. Heavy metals can accumulate in the environment and cause damage to ecosystems and human health. Strategies to reduce these impacts have to be developed. It is however difficult to tackle this problem because analysis and actions are usually addressed from separate areas such as air, water or soil.

Concentration of heavy metals in rocks, water and soils spans across through vast areas. Some of the concentrated metals have no significant physical or biological action except for the toxic effects in relation to inhabiting certain enzymes (Finsteret al., 2004).

Some metals in small quantities support life and are referred to as trace elements, on the other hand in excess, they become toxic and can lead to damage to the internal organs, reduce energy levels, mental and central nervous function etc. The effects of long-term exposure may result in slowly progressing physical, muscular and neurological degenerative processes that mimic Alzheimers’s disease, Parkinsons disease, muscular dystrophy and multiple Sclerosis(Gerhatet al., 1992). Human activities to a large extent upset the natural cycle of these metals and help increase the content of these metals in the various media to toxic levels.

Toxicity of Zinc in human may occur if zinc concentration in water approaches 400 mg/kg. This is characterized by symptoms of irritability, muscular stiffness and pain, loss of appetite and nausea. Zinc



appears to have a protective effect against the toxicities of both cadmium and lead (Fergusson, 1990). Zn has been shown to exert adverse reproductive biochemical, physiological and behavioural effect on a variety of aquatic organisms as concentrations exceed 20 mg/kg. Toxicity is however influenced by many factors such as the temperature, hardness and pH of the water [World Health Organisation (WHO, 2001). Zn toxicity in plants generally causes disturbances in metabolism.

Cu deficiency in soils can generally lead to serious reduction in yield in cereals (Barcan, 2002). Cu deficiency in humans may cause anaemia, poor growth, degeneration of the nervous system and bone demineralisation leading to osteoporosis and bone fractures (Lech et al., 2004).

Lead poisoning has dominated the environmental agenda for several decades. Nonetheless, environmental lead remained a mere curiosity until the 1960s. Lead does not undergo biomagnifications in food chain and also not toxic to plants (Hakanson, 1980). Some of the known effects on higher plants include dark green leaves, stunted foliage and increased amounts of shoots (Ferguson, 1990). It is not known to be of any known function in the human body (Essa, 1999). The inorganic forms of lead in soil have the same toxic endpoints (National Environmental Policy Institute, 2000). The common symptom of lead poisoning is anaemia because lead interferes with the formation of haemoglobin. It prevents iron uptake (Akande et al., 1990). High levels of lead may produce permanent brain damage and kidney dysfunction. Over time lead will substitute Ca in bone which acts to store the lead. Then in old age the lead is reactivated by slow dissolution of the bone.

This is a heavy metal of major environmental concern because of its high mobility and the small concentration at which it can adversely affect plants and animal metabolism. Furthermore it has adverse impact on soil biological activity (Kabata – Pendias and Pendias, 1984). Toxicity of cadmium results from cadmium substitution for zinc in enzymes (Elinder, 1992). The critical toxic endpoint after ingestion is kidney damage (Davies et al., 2005), because of bioaccumulation in the liver and kidney. Cd poisoning may result in the Cd substitution for Ca in bones producing itaiitai, a degenerate bone disease.

Arsenic as one of the trace elements that occurred in Nigeria soils, have toxic endpoints

regardless of its valence state (EPA, US 2000), and are potentially carcinogenic (Finster et al., 2004). The Ancient Greeks used arsenic for therapeutic purposes. Arsenic has long also been used as poison. Skin cancer is believed to be related to exposure to arsenic contaminated sources. Sources of Arsenic include water, medical drugs and food materials.

#### **IV. CONCLUSION**

Evaluation of heavy metals levels and pollution status of soils around mine sites in Oshiri area was carried out. The area is located in the Lower Benue Trough, southeastern Nigeria where mineralization and both artisanal and mechanized mining has been on-going for over three decades. Heavy metals can emanate from the deterioration of mine dumps, gangues and wastes. All these can affect the environment. Ten (10) samples of soil were systematically collected and analyzed using Buck scientific model 210 VGP Atomic Absorption Spectrometers (AAS), while pollution status were deduced using basic pollution indices. Geologically, the area is underlain by the fine grained Sandstone of the Abakaliki Shale Formation which belongs to the Asu River Group (Albian). These rocks host the hydrothermal veins that bears the metalliferous minerals.

Geochemical results indicates high concentrations of Zn, Cu, Ni and Pb, while pollution index shows  $Cd > Zn > Pb > As > Hg > Ni > Ag > Cu > Cr$ . Samples from mine sites and within mine dumps has higher concentrations than other areas. There is high possibility of health risk in the area.

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