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Assessment of Heavys Metals and Physicochemical Properties from Artisanal Mining Site at Rimin Zayam Toro Local Government Area of Bauchi State, Nigeria

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ABSTRACT
Artisanal and small- scale mining (ASM) activities are prevalent in many part of Nigeria and have been linked to significant environmental and public health concern. This study investigated the concentrations of heavy metals and the associated physicochemical properties of soil collected from an artisanal mining site in Rimin Zayam Toro Local Government Area of Bauchi State Nigeria. To assess the extended of environmental contamination and provide baseline data for environmental monitoring and remediation efforts. Soil samples were obtained from three different sites namely; abandoned mining site, active mining site and non - mining site respectively. The heavy metals concentrations were determined and quantified for Cd., Cr, Cu, Fe, Mn, Ni, Pb and Zn using Atomic Absorption Spectroscopy (AAS). Physicochemical properties such as the pH, total organic carbon, total organic matter, electrical conductivity and soil particle size were analyzed using standard methods. The soil examined under the following abandon, active and non-mining sites. From the results soils pH reveals slightly alkaline in nature for all mining sitesi.eabandon, active and non-mining site having 6.04, 6.45 and 6.35 respectively; with moderate electrical conductivity of 31.30, 42.66 and 26.75 (µS/cm) respectively; low to medium value of total organic carbon of 0.062, 0.423 and 0.452 (%); medium to high total organic matter value of 0.844, 0.729 and 0.780 (%) and ECEC values are 7.385, 4.003 and 3.994 for abandon active and non-mining sites respectively. All the values were lower than the maximum allowable concentrations in soils for mining sites. Although appreciable amounts of all the metals were detected in the various site but were within the permissible limit (WHO /FAO). Cd, Cu and Pb were below detectable limits in the three sites. The findings indicate the absence of environmental contamination from heavy metals and physicochemical properties due to early stage mining activities have not yet significantly impacted the surrounding environment. This is a wakeup call for a proactive environmental management. The current baseline data can serve as an essential environmental changes and guiding regulatory oversight in artisanal mining operations.

Keywords:
Heavy Metals, Physicochemical properties, Artisanal mining, Environmental contaminations, Mining pollution.

INTRODUCTION

The primary source of heavy metals contamination in the environment due to activities of mineral excavation, ore transportation, smelting, and refining (Igwe *et al.*, 2017). Among all mining wastes, tailings are a solid waste with especially high toxic heavy metals produced in the process of mining, mineral processing and smelting, which are considered the greatest threat to ecological stability due to their high content of heavy metals (Fawen *et al.*, 2020). When the tailings are discharged at random, heavy metals will be released into surrounding soils, streams, and groundwater mediated by erosion, weathering, and leaching over a long duration, which may pose serious environmental threats to the surrounding area (Lee *et al.*,2007). As a kind of persistent potentially toxic pollutant, heavy metals can easily accumulate in excessive amounts in soils and sediments.

The general importance of mining sectors has been documented to include foreign exchange, employment and economic development, (Obaje and Abas 2005; Ako *et al.*, 2014). Nigeria has a diverse geography, with climates ranging from arid to humid equatorial. The country has abundant natural resources, notably large deposits of petroleum and natural gas. Minerals mined in Nigeria include barite, coal, columbite (an iron-bearing mineral that accompanies tin), gold, gypsum, kaolin, lead, phosphates, rock salt, sapphires, tin, and topazes. Uranium deposits discovered in the north-eastern part of the country have not yet been exploited (Ako *et al*., 2014). Mining industry has often been perceived negatively because it can be hazardous to both public health and safety and cause damage to the surrounding environment, including the land, soil, water and forests at the local, regional and global levels (Choi and Song, 2016), such hazards include but not limited to land subsidence, soil contamination by heavy metal pollutants or mine tailing, water pollution, inundation by water, deforestation, slope failure, spontaneous combustion, explosion of released gas, inhalation of dust and poisonous gases, and abandoned facilities (Jangwon *et al*.,2017). Potential toxic elements (PTEs) in the soil at mine sites pose a risk to human health because of their potential to enter the food chain via direct ingestion of dust or the ingestion of crops from farm product (Carr *et al*., 2008).

Nigeria's artisanal and small-scale mining sector continues to grow in size and significance. Its contribution to wealth, creating employment and the economy makes it one of the nation's most important livelihood activities. However, the majority of mining activities are carried out illegally and informally. This informality has given rise to a host of environmental and social problems some of which include land degradation, water and air pollution and health hazards to the populace.

Mining industry, as with other extractive industries is an economically viable enterprise, enhancing employment opportunities, lubricating livelihoods and among others, supporting national income. Many countries have taken to mining as a means of expanding their economic bases. Nigerian Government recognized the economic importance of mining activities when it set up a new mineral policy, the mineral and mining act of 2007, with the ultimate aim of orderly and sustainable development of the solid mineral sector (NMMA, 2007).

MATERIAL AND METHOD

Description of the study site

Bauchi state occupies a total land area of 549,260 km^2 representing about 5.30 % of Nigerian's total land mass. Rimin Zayam, Toro Local Government of Bauchi is on GPRS locations of 9º18'18" at active mining area, 9º18'36" at abandoned mining area and 9º18'54" at non–mining area.

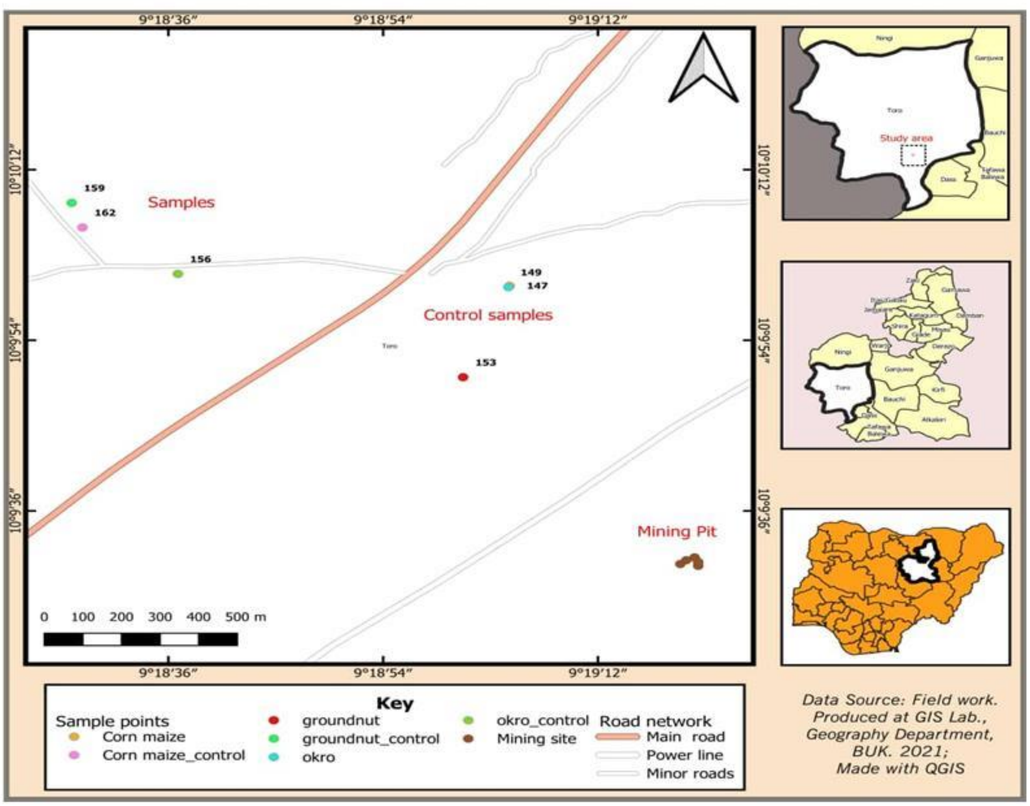

Figure 1: Map of Bauchi State Showing Sampling Locations of Rimin Zayam Mining Areas

Sampling and Sample pre-treatment

Bulk soil samples at abandoned mining site were collected randomly at a depth of 0-30 cm from different locations in already mined areas well as from the non-mining site (control) from Rimin Zayam Toro Local government of Bauchi State. Soil samples of mining site and non-mining sites were homogenised separately to form a composite soil sample, air-dried, ground using a wooden pestle and mortar, sieved through a 2 mm mesh in order to remove the "not-soil and impurities". The sieved soil samples were stored separately in plastic bottles and labelled appropriately prior to laboratory analyses.

Methods

Modified triacid digestion of pre-treated soil samples

A volume of 1.00 cm^3 of 30.00 % H_2O_2, 7.00 cm^3 of concentrated HNO_3 and 2.00 cm^3 of concentrated HCl were added to 1.00 g of pretreated soil sample in a digestion flask and placed in Advanced Microwave Digestion system (Ethos Easy). The digest was filtered using Whatman Filter Paper Number 1 into a 100 cm^3 volumetric flask and made up to the mark with water. The resulting solution was transferred into a labelled polyethylene bottle. The metals were determined at their respective wavelengths using Micro Plasma Atomic Emission Spectrophotometer Model OMP –AES Number 4200 Model (Olufemi *et al*., 2014; Paulinus, 2015).

Determination of Selected Soil Physicochemical Parameters

Determination of soil texture

The particle size distribution of the soil was determined using the Hydrometer Method adopted by Juo, 1979; Umeri *et al*., 2017. A volume of 2.50 cm^3 of 5.00 % sodium hexameta-phosphate solution and 400.00 cm^3 of water were added to 50.00 g of soil sample in a pre-weighed polyethylene bottle. The mixture was stirred with a magnetic stirrer for 15 minutes and quantitatively transferred into a 1.00 cm^3 plastic measuring cylinder and made to volume with water. Hydrometer was placed in the suspension and the hydrometer reading taken at 40 seconds and 2 hours intervals respectively. A blank determination was similarly carried out. The temperatures of the suspension were noted for each reading. The calculation of the percentage of each of the soil constituent was evaluated:

$$HR = (HR- BR) + 0.36T \qquad (1)$$

and at 2 hours:

$$CHR = (HR – BR) + 036\ T \qquad (2)$$

Where CHR = Corrected Hydrometer reading

BR = black hydrometer reading, 0.36 is a constant and

T = sample temperature minus 20 ^{0}C respectively

$$\%\ clay = \frac{CHR\ at\ 2\ hours\ x100}{mass\ of\ soil\ sample} \qquad (3)$$

$$\%\ slit = \frac{CHR\ at\ seconds\ x\ 100 - \%\ clay}{mass\ of\ soil\ sample} \qquad (4)$$

$$\%\ sand = 100 - \%\ (clay + slit) \qquad (5)$$

(Davidescu and Davidese, 1982).

Determination of soil pH

A soil water ratio of 1:2 was used for the determination of soil pH using apH meter glass electrode (Mclean 1982; Bamgbose *et al*., 2000; Umeri *et al*., 2017). A mass of 10.00 g of soil was weighted into a 100 cm^3 beaker and 20.00 cm^3 of water was added and the mixture allowed to stand for 30 minutes and stirred with a glass rod. The electrode was calibrated at pH 7.00 and pH 4.00. The pH meter electrode was inserted into the partially settled suspension and the pH of the soil was measured using a JENWAY pH Meter Model 3520.

Determination of soil electrical Conductivity

A mass of 10.00 g of the soil sample was weighted into a100 cm^3 beaker and 50.00 cm^3 of water was added (1:5). The mixture was allowed to stand for 15 minutes and stirred occasionally with a glass rod. The electrode was calibrated with 0.01 mol/dm^3 of KCl solution, inserted into the mixture and the electrical conductivity of each sample was recorded using electrical conductivity meter JENWAY 4520.At the end of each measurement, the electrode of the conductivity meter was thoroughly rinsed with distilled water before the next measurement (Ajai *et al*., 2016).

Determination of soil organic matter

The soil investigated (5.00 g) was weighed into a pre-weighed porcelain crucible and heated in a muffle furnace maintained at a temperature of 550 ^{0} C for as long as a constant mass was obtained. The loss on ignition at that temperature was considered as the organic matter content (Angeloni *et al.*, 2006 and Ramalingam, 2010).

Determination of organic carbon

The organic carbon content of the soil was determined using wet oxidation of Walkley and Black method (Todorovi *et al*., 2001). Soil sample (1.00 g) was placed in a block digester tube and 5.00 cm^3 of 0.50 mol/dm^3 of potassium heptaoxodichromate (VI) solution and 7.50cm^3 of tetraoxosulphate (VI) acid were added. The tube was placed in a preheated block maintained at 145 to 155° C for 30 minutes, removed and allowed to cool to room temperature. The digest was quantitatively transferred into a 100 cm^3 conical flask and 0.30 cm^3ferroin indicator was added and mixed thoroughly using a magnetic bar stirrer. The digest was titrated with 0.25 mol/dm^3 of ferrous sulphate solution and the end point was a colour change from greenish to brown coloration. A blank titration was similarly carried out without the sample. The percentage organic caution is given by the equation (Todorovi *et al*., 2001).

Determination of effective cation exchange capacity (ECEC)

Exchangeable cations (Ca^{2+}, Mg^{2+}, $K^{+}$and Na^{+}) where determined using 1.00 mol/dm^3 NH_4OAC (Ammoniummactate) buffered at pH 7.0 as extractant (Thomas, 1982). The K^+ and Na^+ concentration in soil extracts were read on Flame photometer while Ca^{2+}, Mg^{2+}concentration in soil extracts were read using atomic absorption spectrophotometer (AAS). The exchangeable acidity [H^- + Al^{3+}] isn soil was extracted with 1.00 mol/dm^{3}KCl (Thomas, 1982). Solution of extract was titrated with 0.05 mol/dm^{3}NaOH to a permanent pink endpoint using phenolphthalein as indicator. The amount of base (NaOH) used is equivalent to the total amount of exchangeable acidity [H^- + Al^{3+}] in the aliquot taken (Adewole and Adesina, 2011). The total sum of exchangeable bases (Ca^{2+}, Mg^{2+}, K^+ and Na^+) and acidity [H^- + Al^{3+}] gave the effective cation exchangeable capacity (ECEC) (Juo, 1979);

i. e. ECEC = (Ca^{2+}, Mg^{2+}, K^+ and Na^{++} H^+ + Al^{3+} (6)

RESULTS AND DISCUSSION

Levels of Some Physicochemical Parameters of Soil

Table 1 depicts the results of some physicochemical parameters of soil samples collected from abandoned mining site, active mining site and non -mining site (control) respectively of Rimin Zayam.

Table 1: Some Physicochemical Parameters of Soil

Parameters	ABM	ACM	NMS
pH	6.04± 0.016	6.45 ± 0.024	6.35± 0.016
EC (µS/cm)	31.30 ±1.86	42.66 ± 1.40	26.76 ±0.09
% TOC	0.061± 0.01	0.423 ±0.02	0.452 ±0.02
% TOM	0.844 ± 0.409	0.729 ± 0.004	0.780 ±0.004
ECEC (cmol/kg)	7.385 ± 0.046	4.003 ± 0.001	3.994 ±0.015

Values are mean ± standard deviation (n=5). ABM = Abandoned mining site, ACM= Active mining site and NMS= Non-mining site (control).

The observed pH values as can be seen from Table 1 ranging from 6.04 (found at abandoned mining site) to 6.45 (determined at active mining site). A pH value of 6.35 was found at non- mining site between these lowest and highest values. This therefore shows that soil samples at the three locations investigated are slightly acidic. The observed pH values are in close agreement with pH values of 6.20 to 6.58 found in Dass, Bauchi State, Nigeria (Hassan *et al.*,019) The observed pH values are within literature values of 5.17 to 8.28 found in physicochemical characteristics of anthropogenic sites in Abeokuta, Nigeria (Oslayinka *et al.,* 2017). The experimental values are higher than the values of pH 4.20 to 5.80 reported in literature from farmlands along major highways in Delta State, Nigeria (Osakwe and Okolie, 2015). The observed pH values are lower than literature values of 7.80 to 9.20 found in soil from dumpsites reported by Sani *et al.*, 2012. Soil pH is an important parameter as it helps in ensuring availability of plants nutrients such as Fe, Mn, Zn and Cu which are more available in acidic than alkaline soils (Deshmukh, 2012). Soil pH is important to all living organisms in the soil. Some diseases tend to thrive when the soil is either acidic or alkaline (Hassan *et al.*, 2019). Soil pH indicates sign to maintain equilibrium between nutrients in soil. It is important for detecting plant and other living organism, available nutrients, cation exchange capacity and organic matter content (Deshmukh, 2012).

The electrical conductivity of the soils investigated range from 26.76 to 42.66 µS/cm. An analytical electrical conductivity value of 31.30 µS/cm was found between the extreme values at abandoned mining site. The observed values are higher than reported literature values of 4.0 to 4.2 µS/cm found in soil from dumpsites (Sain *et al*., 2017). The experimental values also are higher than literature values of 3.54 to 13.97 µS/cm determined in soil farmlands along major highways in Delta State, Nigeria (Osakwe and Okolie, 2015). The high values obtained in this research might be due to mining activities associated with the studied locations. The observed values are within threshold values of 1000 µS /cm (WHO, 2008; NASERA, 2010). Electrical conductivity can affect soil properties such as the soil texture, cation exchange capacity, drainage condition, level of organic matter, salinity and subsoil characteristics. It is also used to estimate the concentration of soluble salts in soil and commonly used as a measure of salinity (Osakwe and Okolie, 2015). The electrical conductivity values are rated as : less than 1.00µS/cm (normal soil), 1.00 – 2.00 µS /cm (critical for germination), >2 .00 -3. 00µS/cm (critical for growth of salt sensitive crops) and > 3.00 µS/cm (severely injurious to crops) as reported by Deshmukh, 2012. Based on this classification, the soils in the three locations investigated as said to be severely injurious to crops.

Table 1 shows that the levels of total organic carbon (TOC) investigated range from 0.061 to 0.452 % (0.61 to 4.52 g/kg) found at abandoned mining site and non-mining site respectively. An observed % TOC of 0.423 (4.23 g/kg) was found at active mining site between the extreme observed values. The results from this research are slightly lower than literature values of 0.28 to 1.15 % found from soils in mangrove swamp zones of Delta State (Umeri *et al* 2017). The observed values are within literature values of 0.02 to 8.48 % found in soil from anthropogenic sites in Abeokuta, Nigeria reported by Olayinka, *et al.,* 2017. Soil are classified as having low, medium and high soil fertility when the TOC contents are less than 10.00, 10,00 to 15.00 and greater than 15.00 g/kg (Kolo *et al*., 2009). It is therefore evident that soil samples from the studied locations can be classified as having low soil fertility. Soil organic carbon is important for monitoring physical and chemical parameter sused in nutrient management in tropical farming systems. The soil parameter provides integrative benefits in protecting the environment and sustaining agriculture. Some scientists have described soil organic carbon as a ‘universal keystone indicator’ in soil fertility management (Musinguzi *et al*., 2013).

The experimental values of organic matter found at abandoned mining site, active mining site and non-mining site are 0.844 %, 0.729 % and 0.780 % respectively. Abandoned mining site has the highest (0.844 %), while active mining site has the lowest (0.729%). The observed values from this research are within the literature values of 0.09 to 16.01 % found in soil from anthropogenic sites in Abeokuta, Nigeria (Olayinka *et al.,* 2017).Polluted soil have higher significant levels of organic matter and organic carbon. Organic matter greater than 2.00 % or organic carbon greater than 1.50 % can create conductive medium for heavy metal chelation formation. (Dawaki *et al*. 2013). The content of organic matter in a soil can maintain soil structure. It also affects the available water capacity and infiltration rate (Musinguzi *et al*., 2013). Soil organic matter can determine the uptake of heavy metals by plants; higher organic matter might be due to over-fertilization especially organic fertilizers (Emurotu and Onianwa 2017). Organic matter can influence buffering and exchange capacity of soils and increases nutrient availability for crops. (McCauley 2009).

The observed result for effective cation exchangeable capacity ranges from (3.994 cmol/kg) found in non-mining site to 7.185 cmol/kg determined in abandon mining site with that of active mining site in between the extremes levels. The observed values slightly falls within literature values of 2.069 to 8.901 cmol/kg found in soil contents in farmlands alone major highways in Delta state, Nigeria reported by Osakwe and Okolie, 2015. The experimental values are within literature values of 4.95 to 9.12 cmol/kg determined in pollution assessment of granite querying operation at Ikole Ekiti, Nigeria reported by Olufemi *et al*., 2014.

Mechanical properties of soil

Table 2: Percentage Mechanical Properties of Soil

Particles size (%)	ABM	ACM	NMS
Clay	27.10 ± 1.57	20.04 ± 0.7 0	20.29 ± 0.83
Silt	12.58 ± 1.21	10.56± 0.72	9.42± 1.07
Sand	60.32 ± 1.41	69.40 ± 1.19	70.29 ±1.07

Values are mean ± standard deviation (n=5).

The soil of mining site was separated into particles of clay, silt and sand in Table 18. Clay particles ranges from 20.29 % determined in non- mining site to 27.10 % found in abandoned mining site with active mining site (20.04 %) in between the extreme values. The silt particle ranges from 9.42 % in non- mining site to 12.58 % in abandoned mining site with others observed value in between the extreme values. The sand particles ranges from 60.32 % in abandoned to 70.29 % found in non-mining site with other value in between the extreme values. The particle distribution in this study showed that sand fractions were predominant while silt particles are the lowest. The obtained distribution follows same pattern of sand > clay > silt as those reported by Osakwe and Okolie, 2015. Soil texture directly influences soil-water relation, aeration and root penetration. It also affects the nutritional status of soil. Soil texture can be expressed significantly through electrical conductivity. Clay textured soil is highly conductive while sandy soil are poor conductors (Deshmukh, 2012).

Effect of the physico–chemical properties of the soils on bioavailability ofheavy metals present in the soil sampled from the mining.

Effect of Soil texture on the bioavailability of heavy metals presen in it

Generally, Acosta *et al*. (2011) established that the accumulation of metals in soils increases with the decreasing particle size, hence soil texture rich in clay fraction or organic matter have higher contents of trace elements than sandy horizons and vice visa. This is based on the metals accumulate in fine-particle size fraction of soils due to high surface areas and negative charges associated with clay minerals and humic substances.

Kabata–Pendias (1993) have observed that copper and chromium are present in higher concentrations in the topsoil than in the parent material. Nickel tends to be more concentrated in minerals from the parent material than is appear in the surface horizon of soil. Thus, explaining the higher mobility of copper and chromium under chemical weathering. In all these, the main factors controlling the behaviour of trace metals in soils are organic matter content, iron and manganese hydroxides and redox potential. Metals fixed by Al, Fe and Mn hydrous oxides and other crystalline solid components are hardly mobile. (Ku, Smita and Dr, Sangita, 2015).

Effect of pH on the bioavailability of heavy metals present in the soil at mining sites

The physicochemical properties of pH measured for the soil sediments taken from the study areas were relatively low within the ranges of 6.04–6.45 see (Table 7). This variation in these values of the soil pH of the three areas could be attributed to the nature of the soils especially as it related to the bioavailability. Alkorta *et al*. (2004) had observed that soil pH is considered one of the most important factors determining the concentration of metals in the soil solution, their mobility and hence, bioavailability. The increase of hydrogen ion concentration was noted to affect the mobilization intensity of heavy metals. Hence, in highly acidic soils, the mobility of metallic elements is much higher than in soils with neutral and alkaline reaction. Generalizing Vamerali *et al*. (2010) stated that mobility of metals in soils with low pH decreases in the order of: Cd > Ni > Zn >Mn> Cu >Pb. Also, noted that the effect of pH on the mobility of metallic elements in the soil is highly variable and dependent on the content and type of organic matter. Alkorta, *et al*. (2004) also noted that just as anthropogenic factors, are linked with heavy metal introduction into the soils, so also is with soil pH to their bioavailability.

Levels of the heavy metal present in soil samples

The levels of heavy metal composition in the soil taken from abandon, active and non – mining sites in modified triacid (data) obtained are presented in Table 3. All the soil samples considered in this study were found positive for all the heavy metals analyzed, except for cadmium and copper those were observed to be below detection limit (BDL) in all the locations.

Table 3: Levels of the Heavy Metal (mg/kg) Present in Soil Samples

Location	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
AB M	BDL	0.71	BDL	119.51	1.63	10.72	BDL	5.99
ACM	BDL	0.73	BDL	168.91	1.25	0.92	BDL	6.58
NMS	BDL	0.75	BDL	185.26	2.51	1.47	0.15	4.69

Values mean ± standard deviation (n = 5) BDL = Below Detection Limit; ABM =abandoned mining site, ACM= active mining site, NMS= non-mining site (control).

The levels of cadmium and copper were found to be completely below detection limit in all the locations sampled. The result obtained in this research agreed with that reported by Safana and Taiu (2018) in the study of comparative analysis of heavy metals in irrigation soil and vegetable, cadmium was below detectable limit. The result obtained is not in agreement with Sanusi *et al*. (2017), where cadmium ranges from 12.62 to 20.70mg/kg in soil and water around abandon Pb-Zn mines in Yelu, Akaleri Local Government Area, Bauchi State and Olayinka *et al* reported values ranging from 0.25 to 1.63 (mg/kg). The WHO 2008, maximum permissible limit for cadmium at 0.35 mg/kg.

The mean levels of lead in the soils were below detection limit at location of active mining and abandoned mining sites, but found to be 0.15 mg/kg, for soil sediment in the non–mining area. This level of lead obtained in *the* soil sediment collected from the non – mining area is noted to be much lower than ranging reported by Sanusi *et al*., (2017) of 65 mg/kg - 658mg/kg, and even much more lower than the 1162 mg/kg reported by Ezeh and Chukwu, (2011) in soils from South East Nigeria.

The concentration of chromium in soil samples taken from the active mining, abandoned mining sites and non–mining area were found to 0.73, 0.71 and 0.75 mg/Kg, respectively. These levels as obtained are far lesser than the safe limit and of 100 mg/kg recommended value for agricultural soil as reported by (Sharma *et al*. 2007). The concentration of iron in soil samples taken from the active mining, abandoned mining sites and non–mining area was found to 168.91, 119.51 and 185.26 mg/Kg, respectively. The outcome of the analysis done on the soil sediments clearly indicated that all the samples are enriched with elevated concentrations of iron, which are attributed to the ferrilitic nature of the soil, which is characteristic of the land in the tropics, and as such was used as the reference metal in subsequent data analysis.

CONCLUSION

The findings indicating the absence of environmental contamination from heavy metals and physicochemical properties at the new artisanal mining site. This suggest that early-stage mining activities have not yet significantly impacted the surrounding environment. This presents a critical opportunity for proactive environmental management and sustainable mining practices to be implemented before degradation occurs. Continuous monitoring and the adoption of environmentally responsible techniques can help preserve soil and water quality, thus mitigating long-term ecological damage. The current baseline data serve as an essential reference point for assessing future environmental changes and guiding regulatory oversight in artisanal mining operations.

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