

# Impact of heavy metal contamination on soil, rice plants and microbial communities within mining sites located in Ebonyi state, Nigeria

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## Abstract

The impact of heavy metals contamination on paddy soil and rice and soil microbial communities on six paddy farms in the vicinity of mine sites (Achara Nuhu, Enyigba, Ndufu-Alike, Ohankwu, Ishiagu and Afikpo) located across the three senatorial zones of Ebonyi State, Nigeria was estimated. Soil samples will be collected at a depth of 0-20 cm from 6 paddy farms between July- August for two farming seasons. Rice plant materials were collected. Heavy metals concentration of paddy soil and rice were analyzed using routine procedures with inductively coupled plasma-optical emission spectrometry. Soil microbial community structure and soil enzyme activity was carried out on soil samples using standard procedures. The soil P<sup>H</sup> in the mining site and the moisture content were 4.6-5.0 and 4.9-5.3. In the mining site, the available phosphorus, potassium, nitrates, nitrites, sulphur and Boron were 6.114-28.024, 0.123-0.157, 0.895-2.7943, 1.467-2.550, 1.319-1.512, and 2.216-2.425 ppm. The concentration of Zinc, Lead and Cadmium were 2.0-4.0 ppm, 0.0176-0.1068 ppm and 0.1335-0.6809 ppm in the mining sites. Results from the research helped to determine the bioaccumulation factors and showed that heavy metals contamination is a determinant of microbial community structure. The isolated microorganisms can be used in the bioremediation of heavy metal contaminated sites and measure soil enzyme activities which can serve as an indicator for soil quality.

**Keywords:** Mining sites, rice paddy, physicochemical, bioaccumulation, cation exchange capacity

## INTRODUCTION

Human activities such as mining, iron smelting, fossil burning and municipal and industrial waste have introduced large quantities of heavy metals such as lead, iron, manganese cadmium, cobalt and mercury into the soil. Soil pollution occurs when the concentration of these heavy metals become significantly higher than that of the background (Chen, 1996). Thus, it is important to safe guard soil health (Coppolecchin *et al.*, 2011). Heavy metals present soils pose serious threat to human and animal health. Paddy rice is considered as an important agricultural crop in Ebonyi State, Nigeria. Rice can be contaminated by heavy metals when grown in contaminated paddy soil (Zhao *et al.*, 2015). The consumption of heavy metal contaminated rice has detrimental effects on human health (Lugwisha and Othman, 2014). The risk of exposures of humans and the associated health effects depend on the extent of heavy metal contamination in rice and the quantity of the rice consumed by an individual. Heavy metals from the contaminated paddy soil may be taken up by the rice plant and accumulate in the grains (Payus and Talip., 2014); Nagarajan and Ganesh, 2014); although there are factors such as high PH of the soil that may hinder availability of heavy metals in the soil to be absorbed by plant roots (Lugwisha and Othman, 2014). According to Payus and Talip, (2014) the concentration of cadmium in rice was influenced by the level of cadmium in paddy soil. Positive correlation between the levels of cadmium and lead in collected from Yangtze river region of china with the levels of cadmium and lead in the corresponding

agricultural soils was shown by Liu *et al.*, (2016). However, soil heavy metal contamination has become a severe problem in many different parts of the world (Li *et al.*, 2014). Achara Nuhu and Enyigba in Ebonyi North, Ndufu-Alike and Ohankwu in Ebonyi Central while Ishiagu and Afikpo in Ebonyi South, Nigeria are well known for their long history of mining activities. Moreover, farms in this region also suffered severe heavy metals pollution due to careless discharge of wastes during smelting activities. The aim of this work is determine the concentrations of heavy metals on paddy soil, root, shoot and grains of rice plants and investigate its impact on soil physicochemical properties, soil microbial communities and soil enzyme activities.

## MATERIALS AND METHODS

### STUDY AREA

Two active mining sites each from the three senatorial zones in Ebonyi State was be used as the study area. Achara Nuhu and Enyigba from Ebonyi North, Ndufu-Alike and Ohankwu from Ebonyi Central while Ishiagu and Afikpo from Ebonyi South. The control sites were taken 10 kilometers from the mining sites in each of the three senatorial zones in Ebonyi State.

### SOIL SAMPLING

Sampling of paddy soil and paddy rice were carried out between July-August before harvesting time. Paddy soil was collected from paddy farms in the vicinity of each of the active mining communities from the three senatorial zones, Ebonyi North, Ebonyi Central and Ebonyi South. The upper soil layer was stripped before fresh

underground soil sample was collected at a depth of 0-20 cm from rice cultivated farms at the same locations where the plant materials were sampled. Each sample was collected using the plum blossom five sub sample method. Five sub soil samples were crushed, mixed and amalgamated in the field into one by sample quatering. The soil samples were placed and marked in a labeled polyvinyl chloride bags and brought to the Microbiology Laboratory of University of Nigeria, Nsukka. The samples were divided into two equal parts. One part was air-dried, sieved through a 2 mm mesh and tested for physicochemical properties and heavy metal analysis. The other part was stored at 4°C for subsequent soil enzyme analysis. For microbiological analysis, soil sample were collected from rhizosphere soil, homogenized and stored at -20 °C until analysis.

#### **RICE PLANT ANALYSIS**

Rice plant was harvested at the maturity. Rice plant was collected and washed thoroughly with distilled water and then with diluted HCl. Rice plants were cut and separated into root, shoot and grain sub samples. All sub samples were oven-dried at 60 °C for constant weight and the dried samples were weighed.

#### **PHYSICOCHEMICAL ANALYSIS OF SOIL**

Soil particle size analysis was determined using the hydrometer method (Bouyoucos, 1962). Soil pH was determined in 0.0 1 M CaCl<sub>2</sub> extracts using a glass electrode. Organic carbon was determined by chromic acid oxidation method (Walkley and Black, 1934). Total nitrogen was determined using micro Kjeldal procedure followed by steam distillation (Bremner and Keeney, 1966). Available phosphorus was extracted using the Bray method (Bray and kurz, 1945). Exchangeable cations (calcium, magnesium, potassium and sodium) was determined with extracting solution. The concentrations of potassium (K<sup>+</sup>) and sodium (Na<sup>+</sup>) were determined using a Gallenkamp model FH 500 flame photometer.

#### **HEAVY METAL ANALYSIS OF SOIL AND RICE PLANT MATERIALS**

One gram of the fine-powdered samples (soil, root, shoot and grain) were weighed into a flask and digested in a mixture of concentrated HNO<sub>3</sub> and HClO<sub>4</sub> in a 5:1 ratio at 100 °C on a hot plate in a fumehood until a clear solution was obtained. The resulting solution was left over night and made up to 50 ml with double distilled water and filtered with filter paper and diluted to 50 ml with double distilled water. The concentration of heavy metals (lead, zinc, cadmium, chromium, cobalt, copper) in the digested solution was measured using inductively coupled plasma - optical emission spectrometry.

#### **MICROBIAL ENUMERATION**

Standard spread plate method will be used to determine the total heterotrophic culturable bacteria count. Nutrient Agar and 10% Tryptic Soy Agar (TSA) with was used to isolate bacterial strains. Soil samples were rehydrated in 10 ml sterile distilled water in MacCartney bottles with some glass chips inserted (10% w/v). Ten fold serial dilutions of the soil extract was made in a set of test tubes containing 9.0 ml of sterile distilled water and aliquots of the resulting solutions plated on appropriate Nutrient Agar

and 10% Tryptic Soy Agar. The culture plates were incubated aerobically at 35 °C for 36-48 hours. Potato dextrose agar (PDA) medium with Rose Bengal (30 µg/ml) and streptomycin (30 µg/ml) were used to screen for the fungal strains and the estimation of total heterotrophic bacteria were done after incubation at 30°C for 3-5 days.

#### **IDENTIFICATION OF SOIL MICROORGANISM**

Bacterial and fungal isolates gotten from microbial enumeration were sub cultured on 10 % Tryptic Soy Agar with nystatin and Potato Dextrose Agar medium with Rose Bengal (30 µg/ml) and Streptomycin (30 µg/ml) respectively for further assays. Identification of bacteria were based on colony characteristics (elevation, texture, pigmentation, morphology arrangement and shape) Gram reaction and biochemical tests. Moulds and yeasts isolates were identified by their growth characteristics such as pigmentation, form, texture and spore formation. Cultural and morphological characteristics were compared with those described by Robert *et al.*, (1984).

#### **BIOACCUMULATION FACTOR (BAF)**

The Bioaccumulation factor (the ratio of the concentration of the element in the grain to that in the corresponding soil) was calculated for each rice sample to quantify the bioaccumulation effect of rice on the uptake of heavy metals from the soil (Liu *et al.*, 2005). The bioaccumulation factor is an index of the ability of a plant to accumulate a particular metal with respect to the soil (Ghosh and Singh, 2005). The BAF was computed as follows

$$\text{BAF} = \text{Cr/Cs}$$

Where Cr and Cs represent the heavy metal concentrations in rice grains and soils respectively.

#### **SOIL CATALASE ACTIVITY**

Volumetric method for measuring soil catalase was carried out according to methods described by Zhou and Zhang, (1980). Twenty grams of the soil sample was placed in a 100 ml conical flask, injected with 40 ml distilled water and 5 ml 0.6% (mass fraction) hydrogen peroxide solution. The flask was sealed with a cork and oscillated in a reciprocating shaker for 20 minutes. The reaction was stopped by adding 5 ml, 1.5 mol/L sulfuric acid. Finally, the liquid in the bottle was filtered with a filter paper and 25 ml of the 0.02 mol/L liquid was titrated from mineral chameleon to reddish colour.

#### **SOIL UREASE ACTIVITY**

Soil urease activity was determined using methods described by Feng *et al.*, (2008). One gram of dry soil sample was placed in a 100 ml triangle flask and 0.5 ml toluene was added. After 15 minutes, 10 ml urea solution 10 % (mass fraction) and 20 ml citrate buffer (pH = 6) was added and mixed evenly. Subsequently, the flask was placed in a constant temperature incubator (28 °C) for 24 hours. After filtration, 1 ml of the solution was put into a 50 ml volumetric flask and 20 ml of distilled water added. Then, 4 ml sodium phenate solution and 3 ml sodium hypochlorite was added successively and mixed thoroughly. After 20 minutes, it was subjected to colorimetric analysis at 578 nm using a spectrophotometer within 1 hour.

## STATISTICAL ANALYSIS

Data collected was analysed statistically by Analysis of Variance (ANOVA) Procedure. Means were compared by the least significance difference (LSD) test ( $P \leq 0.05$ ) (Hoshmand, 1993). Correlation and cluster analysis were used to determine interrelationships between the parameters.

## RESULTS

The soil pH in the mining site was strongly acidic ranging from 4.6-5.0 while the soil pH at the control site ranged between 4.9-5.3. The moisture content in the mining site ranged from 5.110-5.800 while the moisture content in the control site ranged from 52.250-56.110.

Soil textural class of the mining site was loamy from 10-30 cm and Sandy Clay Loamy from 40-50 cm. In the control site, the textural class was Sandy Clay Loamy from 10-20 cm, loamy at 30 cm and Sandy Clay Loamy from 40-50 cm. Clay, silt, fine sand, coarse sand varied

from 21-23 %, 27-33 %, 42-48 %, 2-4 % respectively in the mining site while in the control site, the percentage clay, silt, fine sand, coarse sand varied from 21-23 %, 26-32 %, 43-48 %, 3-5 % respectively.

Status of available calcium, sodium and magnesium in the soil ranged between 0.012-0.152 %, 0.0623-0.083 % and 0.0525-0.0912 % respectively while status of available calcium, sodium and magnesium in the soil ranged between 0.0136-0.278 %, 0.0968-0.1442 % and 0.0336-0.1056 % respectively. Available aluminium and hydrogen ion varied from 1.60-3.00 mg/100 g and 0.40-2.40 mg/100 g respectively at the mining site while available aluminium and hydrogen ion varied between 2.60-4.60 mg/100 g and 0.72-1.80 mg/100 g respectively in the control site. In the mining site, the cation exchange capacity ranged from 14.20-19.70 meq/100 g while the cation exchange capacity at the control site ranged from 8.40-12.60 meq/100 g.

**Table 1: Determination of pH and Moisture**

Sample Description	pH (H <sub>2</sub> O)		pH (KCl)		Moisture	
	Control Site	Mining Site	Control Site	Mining Site	Control Site	Mining Site
10 cm	5.000	4.700	6.200	5.100	52.250	5.110
20 cm	5.000	4.900	6.400	5.300	53.270	5.360
30 cm	5.300	4.600	6.000	5.600	55.060	5.680
40 cm	5.000	5.200	6.400	5.600	55.870	5.680
50 cm	4.900	5.000	6.000	5.800	56.110	5.800

Keys: H<sub>2</sub>O = Water ; KCl = Potassium Chloride

**Table 2: Result of Particle Size Distribution**

Sample Depth	% Clay		% Silt		% F.S		% C.S		T.C	
	Control site	Mining site	Control site	Mining site	Control site	Mining site	Control site	Mining site	Control site	Mining site
10 cm	22	21	30	33	43	42	5	4	SCL	L
20 cm	21	21	27	29	46	46	5	4	SCL	L
30 cm	21	23	32	31	44	44	3	2	L	L
40 cm	23	23	26	27	48	48	3	2	SCL	SCL
50 cm	22	23	26	27	48	48	4	2	SCL	SCL

Keys: F.S = Fine Sand, C.S = Coarse Sand, T.C = Textural Class, L = Loamy, SCL = Sandy Clay Loamy

**Table 3: Exchangeable Cations and Cation Exchange Capacity**

Sample Description	Ca (%)		Na (%)		Mg (%)		Al (Mg/100g)		H <sup>+</sup> (Mg/100g)		CEC (Mg/100g)	
	Control Site	Mining Site	Control Site	Mining Site	Control Site	Mining Site	Control Site	Mining Site	Control Site	Mining Site	Control Site	Mining Site
10 cm	0.20	0.120	0.1332	0.0623	0.1056	0.0525	4.603	3.000	1.800	2.400	12.600	14.200
20 cm	0.080	0.1520	0.0968	0.0713	0.0336	0.0672	3.000	2.000	0.806	1.200	10.400	16.400
30 cm	0.0136	0.1280	0.1442	0.070	0.0528	0.0768	2.600	2.000	0.720	0.400	11.600	18.400
40 cm	0.104	0.1440	0.1328	0.083	0.0528	0.0912	2.800	2.800	1.606	1.600	9.000	18.630
50 cm	0.2780	0.1440	0.1332	0.083	0.0576	0.0864	2.600	1.600	0.743	1.200	8.400	19.700

**Table 4: Soil Available Nutrients**

Sample Depth	P (ppm)		K (%)		Nitrates (ppm)		Nitrites (ppm)	
	Control site	Mining site	Control site	Mining site	Control site	Mining site	Control site	Mining site
10 cm	39.360	6.1440	0.2460	0.1230	3.324	2.743	2.220	2.743
20 cm	37.920	11.424	0.3630	0.1375	2.986	2.943	2.427	2.943
30 cm	24.480	3.168	0.2750	0.1550	2.743	2.463	2.298	2.463
40 cm	27.840	9.024	0.2890	0.1482	3.143	2.786	2.558	2.786
50 cm	26.016	28.024	0.2280	0.1570	2.712	0.895	2.712	0.895

Table 5: Changes in C and N Storage and Light Fraction SOM for 0-10, 10-20, 20-30, 30-40, 40-50 cm depths of soil samples

Sample Depth	C storage		N storage		SOM	
	Control site	Mining site	Control site	Mining site	Control site	Mining site
10 cm	1.199	1.197	0.490	0.322	2.0671	2.064
20 cm	1.197	0.1596	0.3080	0.1121	2.0636	0.275
30 cm	1.197	2.2394	0.3220	0.2242	2.0636	3.861
40 cm	0.598	2.3140	0.336	0.2382	1.0309	3.989
50 cm	0.3990	0.399	0.280	0.1261	0.6878	0.6878

In the mining site, available phosphorus (ppm) ranged between 6.144-28.024 while in the control site the available phosphorus ranged between 24.48-39.36. The % K at the mining site ranges from 0.123-0.157 while the % K ranges from 0.228-0.363 at the control site. The concentration of nitrates (ppm) at the mining site ranges from 0.895-2.7943 while the value of nitrates ranges from 2.712-3.324. The concentration of nitrites (ppm) at the mining site ranges from 1.467-2.550 while the value of nitrites (ppm) ranges from 2.220-2.712. In the control site, the quantity of sulphur varied from 1.319-1.512 while in the mining site, the quantity of sulphur varied from 1.131-1.272. In the control site, the quantity of boron varied from 2.216-2.425 while in the mining site, the quantity of boron varied from 2.133-2.596.

The organic carbon content ranged from 0.399-2.314 at the mining site while the organic carbon content in the control site ranged from 0.399-1.99. The total nitrogen content varied from 0.1121-0.322 in the mining site while in the control site, the total nitrogen content varied from 0.280-0.490. The soil organic matter in the mining site varied from 0.6878-3.9893 while the soil organic matter in the control site varied from 0.6878-2.0671.

#### DISCUSSIONS

Soil pH in the mining site was very strongly acidic and varied from 4.60-5.00. On the other hand, the soil pH was strongly acidic and varied from 4.90-5.30 in the control site. The lowest pH 4.60 however was obtained from the mining site at depth 20-30 cm (Table 1). The higher the values of pH the higher the concentration of heavy metals and vice versa. This is because heavy metals form basic oxides in solution with water, thereby increasing the tendency towards alkalinity. Low pH however, reduces metal solubility and speciation (Blaylock, 1997). The highly acidic (low pH) nature of the mining site imply that the heavy metals there may be less soluble and bio-available. Low pH in heavy metal polluted soil have been reported by Lee *et al.*, (2002); Osuji and Adesiyani, (2005) and Onyeobi and Imeokparia, (2014). The texture of the soil samples did not vary substantially. Soil textural class in the mining site varied from loamy 10-30 cm to sandy clay loamy 40-50 cm while in the control site, the textural class varied from sandy clay loamy 10-20 cm, loamy 30 cm and sandy clay loamy 40-50 cm. Clay, silt, fine sand, coarse sand varied from 21-23 %, 27-33 %, 42-48 %, 2-4 % respectively in the mining site while in the control site, the percentage clay, silt, fine sand, coarse sand varied from 21-23 %, 26-32 %, 43-48 %, 3-5 % respectively (Table 2). Clay content is the most important textural

property affecting metal bioavailability in soils. Differences in the % clay content in both the mining and the control site could be attributed to the nature of the parent rock from which they were formed. Particle size distribution of mining soils is directly inherited from their parent rocks. Hu *et al.*, (1992) are of the opinion that soil with stone content greater than 50% should be rated as poor quality. Stone content of coal mine overburden dumps has been reported to be as high as 80-85% (Maiti and Saxena, 1998). Maiti and Ghose, (2005) reported stone content in overburden dumps in range of 35%-65%, with an average value of 55%. The clay fraction of the soil mineral phase adsorbs metals through ion exchange and specific adsorption. Adsorption is pH dependent, but this could vary for different types of clay minerals. Although the percentage clay content was slightly higher in the mining site, the higher pH and clay content at the control site imply more metal bioavailability and hence higher quantity of heavy metals. The low porosity of clayey soils hampers metal dissolution. This agrees with Sizmur (2007). From table 3, the exchangeable cations (Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>) in the mining and control site were generally low ranging from 0.012-0.152 %, 0.0623-0.083 % and 0.0525-0.0912 % respectively in the mining site and 0.0136-0.278 %, 0.0968-0.1442 % and 0.0336-0.1056 % respectively in the control site. Also, the concentration of aluminium and hydrogen ion varied from 1.60-3.00 meq/100 g and 0.40-2.40 meq/100 g respectively at the mining site while available aluminium and hydrogen ion varied between 2.60-4.60 meq/100 g and 0.72-1.80 meq/100 g respectively in the control site and were slightly higher than the exchangeable cations. However, as soils become more acidic these cations are replaced by H<sup>+</sup> and Al<sup>3+</sup> (exchange acidity) lowering the cation exchange capacity. The cation exchange capacity is crucial for soil metal bioavailability (Jung, 2008) and fertility (Obasi, 2012). The control site has a low cation exchange capacity ranging from 8.40-12.60 meq/100 g. On the other hand, the mining site has a slightly low cation exchange capacity at 10 cm and normal cation exchange capacity ranging from 16.40-19.70 meq/100 g at 20-50 cm. CEC values at the mining and control site were not surprising since CEC is affected by soil pH, soil texture (% clay) and organic matter (Brady and Weil, 1999). The low CEC values at the mining and control site was due to the low values of percentage clay and organic matter content which are major factors that affect the CEC of soils. Also, the lower the pH, the lower the CEC. The % potassium in the mining site ranges from 0.123-0.157 while the % potassium ranges from 0.228-0.363 in the control site.

Plant roots absorb sulphur in the form of sulphate ( $\text{SO}_4^{2-}$ ) from the soil solution. In the control site, the quantity of sulphur varied from 1.319-1.512 ppm while in the mining site, the quantity of sulphur varied from 1.131-1.272 ppm. From table 4, the sulphate concentration decreased down the soil profile (soil depth) and alongside the heavy metal concentration in both the mining and control site. Heavy metals such as Pb, Zn, Cd and Cu co exist in sulphide ores. Fuller *et al.*, (1987) reported that the oxidation of reduced sulphur such as pyrite and atmospheric deposition of sulphur compounds are the major sources of sulphate. Keeping this fact in view, the soil under study may be classified as deficient as per the categorization given by Hariram and Dwivedi, (1994). According to Horneck *et al.*, (2011), when the concentration of sulphate sulphur is less than 2 ppm it is very low. The total nitrogen content varied from 0.1121-0.322 in the mining site while in the control site, the total nitrogen content varied from 0.280-0.490. The soil organic matter in the mining site varied from 0.6878-3.9893 while the soil organic matter in the control site varied from 0.6878-2.0671. The soil organic matter in the control and mining sites were generally low. This agreed with Lee *et al.*, (2002) who also observed low organic matter content in soil contaminated with heavy metals. The concentration levels of Zinc (Zn) was highest in respect of the heavy metals measured and ranged from 2.0-4.0 ppm and 1.06-2.0 ppm; followed by lead (Pb) which ranged from 0.0176 to 0.1068 and 0.1335 to 0.6809 ppm and cadmium (Cd) which ranged from 0.053-0.085 and 0.063-0.075 ppm respectively in the mining and control sites respectively. The concentration distribution sequence trend were  $\text{Zn} > \text{Pb} > \text{Cd}$ , and is consistent with the findings of Ma and Rao, (1997) in the order  $\text{Zn} > \text{Cu} > \text{Cd} > \text{Ni}$ , with Zn having the highest respect to the relative abundance in topsoil. There was decreasing gradient in concentrations of the measured metals from top soil 0 – 10 cm to depth 50 cm. The concentration levels of Cd, Zn, and Pb in Table 6 showed that, the concentration of all the heavy metals at the depth of 0-30 cm (top soil) were higher than the concentration of heavy metals found at the depth of 30-50 cm (sub soil or surface). It can be assumed that the sub soil is considerably less influenced by soil forming process and anthropogenic supply than the top soil. The concentration of lead varied from 0.0176 to 0.1068 and 0.1335 to 0.6809 respectively in the mining and control sites respectively. With respect to lead, concentrations above 100 mg/kg are considered high in soil (Kabata –Pendias and Pendias, 2000). The concentration of lead in the mining and control sites was within the acceptable limits of  $\text{Pb} = 1$  to 500 mg/kg (average = 50 mg/kg) recommended by the Interdepartmental Committee on Reclamation of Contaminated Land (ICRCL, 1987) for heavy metals in soil used for agriculture, but much lower than the maximum tolerable levels proposed for agricultural soil (90-300 mg/kg DW) by Kabata-Pendias and Pendias (2000). None of the test sites had lead level greater than the recommended average. Zn occurs chiefly as single sulfides ( $\text{ZnS}$ ) in soil, when weathered give  $\text{Zn}^{+2}$ , so organic soil is non to capable of bonding Zn in stable form

and Zn accumulate in organic rich soils. Mean total Zn contents in surface soils ranged from 17 to 125 ppm according to Kabata-Pendias, and Pendias, (2001). Zinc concentration in the soil ranged from 1.06-2.0 ppm and 2.0-4.0 ppm in the control and mining site respectively. The highest value was obtained at depth 30-40 cm (4.0 ppm) and 0-10 cm (2.0 ppm) in mining and control site respectively while the lowest value was obtained at depth 0-10 cm (2.0 ppm) and 10-20 cm (1.06 ppm) in mining and control site respectively. Mobility of Zn is moderately high, limited by tendency to be absorbed by Fe – Mn oxide and insoluble organic matter (Levison, 1980). Low pH generally favours mobility of Zn. It was noted generally that the mining and control sites have low pH values in the study area (4.7-5.3). Zn is relatively soluble and tends to be transported out of the oxidizing, low pH value of the weathering environment. There is growing environmental concern about Cadmium (Cd) as being one of the most ecotoxic metals that exhibit highly adverse effects on soil biological activity, plant metabolism, and the health of humans and the animal kingdom.

In soil developed under humid condition Cd accumulated down soil, while accumulation of Cd in top soil related to contamination effect. The lowest concentration of cadmium was 0.063 ppm at depth 10-20 cm in the control site and 0.053 ppm at depth 10-20 and 40-50 cm in the mining site. Thus the range of concentration of cadmium at the control and mining site varied from 0.063-0.075 ppm and 0.053-0.085 ppm respectively. The maximum permissible limit of Cd in the soil according to the Dutch standard is 0.8mg/kg. This low level of Cd suggests little anthropogenic activities. The metal levels were probably nature influenced by Enyigba's geological environment, and source input from the waste mine and mined area as a result of weathering processes and or dispersed metal bearing mining wastes of the past exploratory mining. Soil contamination by mining and other metallurgical processes have been variously reported (Bunzl *et al.*, 1999; Gardea-Torresday *et al.*, 2000; Taylor *et al.*, 2002). The results of this study showed lower concentrations levels of the determined heavy metals in the mining and control sites when compared with the findings from elsewhere. Gardea-Torresday *et al.*, (2000), Taylor *et al.*, 2002 and Demetriades *et al.*, 1996 who reported the contamination of surface soils of Lavreotiki Peninsula Greece, with Cd,  $11.9 \pm 0.9$ ppm; Mn,  $2092.0 \pm 71.0$ ppm; Cr,  $368.0 \pm 11.0$ ppm; Ni,  $189.0 \pm 6.0$ ppm; Cu,  $89.0 \pm 5.0$ ppm; Zn,  $1956.0 \pm 178.0$ ppm; and Pb,  $2883.0 \pm 240.0$ ppm, due to Lavreotiki mining activities. Thus heavy metal mining and other metallurgical activities are potential sources of heavy metal pollution and therefore a threat to environment. The concentration levels of heavy metals detected in soils around Enyigba mining environments was low within the natural background levels for the metals in contaminated soils when compared with Kabata-Pendias and Pendias (1984), Alloway (1995) and the recommended maximum allowable concentration in agricultural soils set by European Economic Community (EEC) (1993). It is therefore apparent from the results that surface soils around Enyigba mining site contain concentration levels

below phytotoxic level range of Cd, 3-8mg/kg, Mn, 1500-3000mg/kg; Cr, 75-100mg/kg; Ni, 100 mg/kg; Cu, 60-125mg/kg; Zn, 70-400mg/kg and Pb, 30-300mg/kg recommended by Boularbah *et al*, (2006) and Kabata-Pendias and Pendias, (1984). The overall contents of these metals in the root are much higher than those in stem, following the order root>stem. Cadmium enters the body via the gastrointestinal tract by eating food products grown on contaminated soil, although smokers may receive a considerable part of their cadmium intake by inhaling cigarette smoke (Corbett *et al*, 2002). Cadmium is a mobile element, easily absorbed by roots and transported to shoots where it is uniformly distributed in plant (Sekara *et al.*, 2005). The concentrations of Cd in all the investigated roots and stem from Enyigba were below WHO Maximum Limit which is 0.1 mg/ kg (CODEX, 2001). This is similar to the work done by Oti and Nwabue, (2013), who reported the concentration of Cd in vegetables obtained from Enyigba below the WHO Maximum Limit, which is 0.1 mg/ kg. Highest concentration of Cd in the plant was observed in the roots 0.086 in the mining site.

#### CONCLUSION

Lead is the main cause for concern in terms of contamination of rice plants in Enyigba lead Mine by heavy metals. Lead is toxic and can be harmful to plants, though the plants usually show ability to accumulate large amounts of lead without visible changes in their appearance or yield. In many plants, Pb accumulation can exceed several hundred times the threshold of maximum level permissible for human (Wierzbicka, 1995). Pb in the rice plant roots and stems in the mining and control sites exceeded the WHO maximum limit which is 0.3 mg/kg (CODEX, 2001). There was an elevated concentration of lead in all the vegetable samples ranging from 0.105 mg/kg to 0.826mg/kg. Consumption of these plants will certainly result to health disorders. Among all metals, Zn is the least toxic and an essential element in the human diet as it is required to maintain the proper functions of the immune system, normal brain activity and is fundamental in the growth and development of the foetus. Zinc deficiency in the diet may be more detrimental to human health than too much zinc in the diet. Although the average daily intake of Zinc is 7-16.3 mg Zn/day, the recommended dietary allowance for it is 15 mg Zn/day for men and 12 mg Zn/day for women. In the present study, the concentrations of Zn in all the investigated roots and

stem from Enyigba mining town were far below WHO Maximum Limit which is 100 mg/ kg (CODEX, 2001).

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