

EFFECT OF ARTISANAL MINERAL MINING ON HEAVY METALS CONTENT AND CHEMICAL PROPERTIES OF SOILS OF AMEKA MINING AREA IN ABAKALIKI, EBONYI STATE

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Abstract

The study was conducted at Ameka mining area in Abakaliki, Southeastern Nigeria, to evaluate the effect of artisanal mineral mining activities on heavy metals (lead, Zinc and cadmium) concentrations and Chemical Properties of soils of Ameka mining area. Auger Soil Samples (0.20cm) were collected at the four compass directions from 0m to 100m and 2500m away from the mines sites at 10m intervals. At each sampling interval three samples were collected randomly, to make three replications three composites were obtained at each interval of the four compass directions. Unmined soil of Agbaja Unuhu community was used as control. The effect of artisanal mineral mining on lead, zinc and Cadmium concentrations in soils of the mineral mining area and soil chemical properties were assessed using randomized complete block design. The result showed that Lead, Zinc and Cadmium concentrations in soils of the mineral mining site were significantly ($p < 0.05$) higher than that of the unmined soil of Agbaja Unuhu. On average Lead concentration was 860.4% higher in soils of mining area than the unmined soil of Agbaja Unuhu and 215.1% higher than the maximum tolerable limit 100mg/kg of soil. Zinc concentration in soils of Ameka mining area was 290.3% higher than the unmined soil of Agbaja Unuhu, however it was still below the maximum tolerable limit of 300mg/kg of soil. Cd concentration in soils of mining area was 53100% higher in soils of the mining area than the unmined soil of Agbaja Unuhu and 177% higher than the maximum tolerable limit in the soil. The result equally revealed negative and significant correlations between concentrations of lead, zinc and cadmium and critical soil chemical properties such as; pH, Available phosphorous, total Nitrogen, Organic Matter content, and Cation Exchange Capacity, which is an indication that the concentrations of lead, zinc and cadmium have negatively impacted on the fertility of the soils of Ameka mineral mining area.

Keywords: Mining, Lead, Zinc, Cadmium and Soil Chemical properties

Introduction

It is well established that one of the primary anthropogenic sources of heavy metals is mine (Goyer, 1996). Mechanical mining in Nigeria started around 1939 by private owned foreign companies. However, the first legislation on mining was only reviewed in 1999 (Obaje *et al.*, 2005 and Aliyu *et al.*, 1996). For many years tin, coal, columbite and lead were being mined under the supervision of the defunct Nigeria mining corporation (Onyedika *et al.*, 2008). Thus, mechanized mining has been in practice for a long time at Enyigba. However, mechanized mining was abandoned at the areas alongside other mining areas in Nigeria in 1980 due to collapse of mining companies in the early 70s, thus negative environmental impact was significant (Aremu *et al.*, 2010). Cadmium in particular is an environmental protection agency (EPA) regulated heavy metal that is used as anti-corrosion and decorative coatings on the metal alloys. It is non-essential metal to living organisms and can become toxic by displacing zinc (IOCHIS, 1999). Epidemiological studies have revealed that cadmium may be a contributing factor in some forms of cancer in human (IARC, 1998). The

knowledge of Zn toxicity in human is minimal, the most important information reported is its interference with copper metabolism (Barone *et al.*, 1998). Ever since the mechanized mining was abandoned, the people of the mining area in Abakaliki had taken both the law and their destiny into their hands, as they resumed illegal and uncontrolled mineral from where the foreign companies stopped. According to Onyedika *et al.*, (2008) illegal and uncontrolled mining in developing countries have left a lot of environmental hazards and enormous of wastes and different types of pollutants are generated. The mining activities have left behind devastated landscape, exposed fertile lands, wells, streams, rivers and foods to mineral contamination. Heavy metals bioaccumulation in the food can be especially dangerous to human health, (Udoma *et al.*, 2003). Haphazard and artisanal mining activities across the Nigeria especially in Zamfara, Ebonyi and Nassarawa states have continued to wreck-havoc on the environment and have had a deadly impact on the health of children less than five years. In 2010, a serious lead poisoning situation was reported in Zamfara State, and hundreds of death and serious disabilities among children were related to high level lead exposures in many villages (CDCP, 2010). According to Fakayode *et al.*, (2003), for several years now lead has been the intense focus of environmental health research and this is understandable, considering the perennial effect of lead toxicity. Its pollution spans across the soil, water and air environments (Cobb, 2000 and Okoronkwo *et al.*, 2005). Lead (Pb) concentration in soils not only aroused the changes soil microorganisms, its activities result in soil fertility deterioration, but also directly affect the change in soil chemical fertility indices and therefore in crop yield decline (Majeret *et al.*, 2002).

Materials and Methods

The study was conducted at Ameka (latitude 09° 45'N, longitude 008° 37'E) in Abakaliki Southeastern Nigeria using completely randomized design. The area experiences bimodal patterns of rainfall (April-July) and (September-November) respectively, (Ofomata, 1975). The soils are over 1m deep and belong to the order ultisols, with shale as the predominant parent material and usually acidic in nature (FDALR, 1985 and Nwaogu and Ebeniro, 2009). Auger soil samples (0-20cm), were collected from the four compass directions: East, West, North and South from 0m to 100m and 2500m away from the base of the mining sites at 10m intervals and a composite sample of each distance interval of the four directions were obtained by quartering and cone methods. While a soil sample from neighboring Agbaja Unuhu collected in the same manner was used as a control. Particles size distribution of the soil was determined using the Bouyocous hydrometer method as described by Benton (2001). Total organic carbon was determined by wet oxidation method according to Nelson and Sommers (1986) and converted to organic matter by multiplying by 1.724. The available phosphorus was determined using Bray-2 method (Jones, 1998). The soil pH in water was determined with a pH meter using a 1:2.5 soil/water ratio (McClean, 1982). Total nitrogen determination was by micro Kjeldahl digestion procedure (Simmone, *et al.*, 1994). Exchangeable basic cations (K⁺, Ca²⁺, Mg²⁺ and Na⁺) were determined by ammonium acetate leaching method and exchangeable acidity by back titration, effective cation exchange capacity was obtained by summation of all the exchangeable cations (Tucker, *et al.*, 1997). Soil samples for heavy metals (lead, zinc and cadmium) were extracted by the wet digestion method of Benton (2001). 0.5g of soil samples were weighed into 50mls conical flask, then 10mls of nitric acid (HNO₃) was added and heated to dampness in fume cupboard, and then the samples were removed and allowed to cool before 10mls of perchloric acid (HClO₄) was added to it, after which the samples were heated again in the fume cupboard until it formed profused fume. The samples were removed from the cupboard allowed to cool and then made up to 50ml with distilled water. The digest were filtered with Whatman No 42 filter paper into transparent plastic containers for onward AAS elemental reading. AAS variance spectrAA 220FS model was used to read the elemental

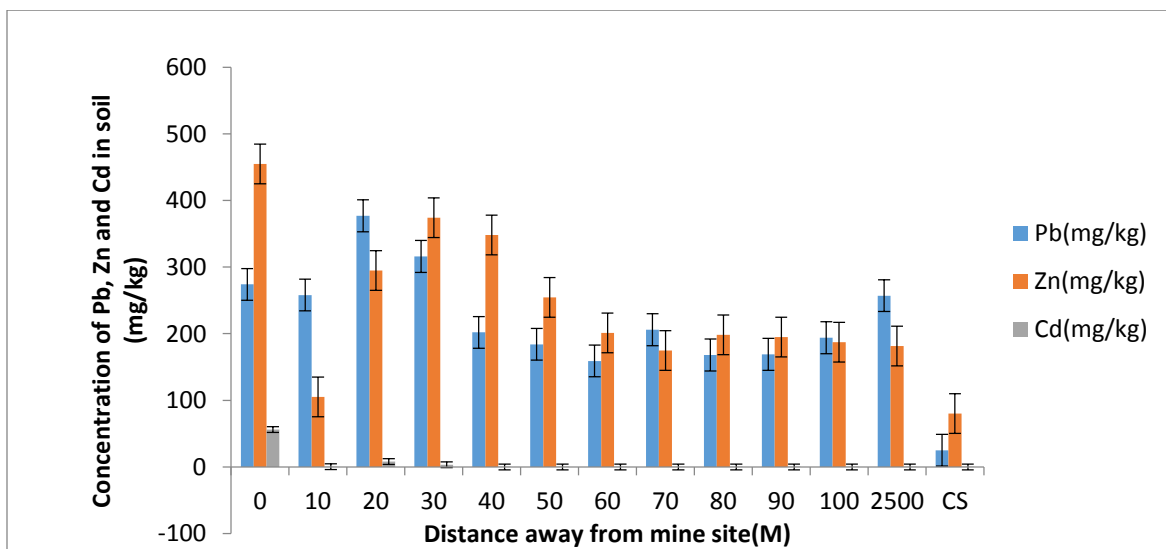
concentration values of the three elements (Pb, Zn and Cd) in soil digests, following Horneck and Hanson method in Benton (2001). Data generated were subjected to statistical analysis using SAS software, while Fisher's least significant differences (FLSD) were used to compare means at 5% probability level.

Results and Discussion

Lead, zinc and cadmium concentrations in surface soils of Ameka mineral mining area

The results of lead, zinc and cadmium concentrations in surface soils of Ameka mineral mining area is presented in Figure 1. The results indicate that the concentrations of Pb in soils at Ameka mineral mining areas at all sampling intervals were significantly ($P < 0.05$), higher than that of unmined soil of Agbaja Unuhu. Pb concentration in soils of Ameka mineral mining area ranges from 159 mg/Kg to 377 mg/Kg. The highest Pb concentration within the area was observed at 20 meters away from the mine base. The Pb concentration at 2500 meters away from the mine base was observed to be higher than the concentrations at closer distances of 40, 50, 60, 70, 80, 90 and 100 meters away from the mine base. It was also observed that Pb concentrations at all sampled points around both mining sites are higher than the 70mg/kg maximum tolerable limit of Pb in soil (FAO/WHO, 2002). The Zn mean concentrations in soils of the mining area at all sampling intervals were significantly ($P < 0.05$) higher than Zn concentration in the soil of Agbaja Unuhu. Zn concentration in soils Ameka mining area ranges from 105.19 mg/Kg to 454.95 mg/Kg. The highest concentration was observed at mine base (zero meter), while the lowest concentration was observed at 10 meters away from the mine base. However, except for the concentrations at 0, 30, and 40 meters away from the mine base, Zn concentrations in surface soil are still below maximum tolerable limit of 300 mg/Kg according to (FAO/WHO 2002). The highest concentration of Cd in soils of Ameka mineral mining area (56.2 mg/kg) was observed at the mine base, while the lowest concentration of 0.01 mg/Kg each were observed at 50, 60, 70, 80, 90, 100, and 2500 meters away from the mine base. The concentrations at 0m, 10m, 20m, 30m and 40m away from the mine base were significantly ($P < 0.05$) higher than the concentration of Cd in Agbaja Unuhu soil. When the mean concentration of Cd at both sites was compared with the maximum tolerable threshold in soil, it was observed that Cd concentration in soil of Ameka mining area was higher than 3.0mg/kg maximum tolerable limit, (FAO/WHO, 2002). The elevated concentrations of these heavy metals observed in the soils of Ameka mining area were similar to that reported by Aremu, *et al.*, (2010) and were also strongly supported by the findings of Ayodele and Modupe (2008). The artisanal mining activities expose the geological materials (the shale and the ores), which are the sources of these heavy metals to intensive weathering. When these geological materials are broken down either by chemical or mechanical weathering, the composite metals are released into the soil either as aqueous species or in dispersed forms of the constituting mineral or as precipitates of new minerals. In this way, mining especially artisanal method contribute immensely to high levels of heavy metals concentration in the surface soil. And once heavy metals especially lead has been deposited in the soil, it moves very slowly down the profile and can persist for a long time at the surface. Thornton (1998) reported that in Britain alone an estimated area in excess of 400km² of land was polluted by lead as a result of mining activities dating from Roman times. Thus, the high levels of heavy metals pollution of Agricultural soils at Ameka mineral mining area might be attributed to artisanal mineral mining activities. The distribution trends of these metals along the sampling distances from the mine base were not consistent. This could be attributed to the nature of relief in the area, which could also influence the transportation and deposition of the heavy metals by air. Gerrard (1990) reported that the greatest concentration of certain soil minerals would be expected on the gentle slope at the top and bottom of the slope. This he said is because upper slopes appear to be associated with processes of erosion and transport and lower slopes with deposition. However, contrary to this finding,

Angelova *et al.*, (2009) observed that total Pb, Zn and Cd concentrations in soils 1-15 km away from non-ferrous metal work site decreased from 913.5 to 24.6 mg/kg, 1903.8 to 33.9 mg/kg and 26.2 to 2.7 mg/kg respectively. This may as well be due to the relief nature of the site, if the site is a flat land, then there is tendency that there will be consistent decrease as distance away from the site increases, but, if the site is undulated or slopy topography as was the case in this study, then a tendency towards inconsistency in the trends of concentration of these heavy metals as distance from the point of activity increase will be observed. The high heavy metals concentration, especially, the Pb in soils of the study sites portend a great risk to human health in these areas, as soil is a veritable source of heavy metals entrance into food chain. The deleterious effects of high concentration of these heavy metals due to artisanal mining activities on human population is further aggravated by the fact that cassava root which is the major staple food and source of dietary calories of the people in the study area was planted as close as less than 10 meters from the mine site. Therefore, high concentrations of the heavy metals in soils of the study area expose human population to the risk of food poisoning.



cs; control soil.

Fig 1: Heavy metals (Pb, Zn and Cd) concentration in of surface soil of Ameka mineral mining area

Effect of Mineral Mining on Chemical Properties of Soils of Ameka

The result of chemical properties of the soils of Ameka mineral mining area is presented in Table 1 below.

Soil pH and exchange acidity

The pH of soils at both locations were determined using water and kCl. The results showed that pH in both water and KCl of soils Ameka mining area were significantly ($p < 0.05$) lower than that of Agbaja Unuhu soil. The pH in water and KCl of soils Ameka mining area range from 4.5 to 5.7 and 3.23 to 3.89 respectively. Highest pH in water and KCl values were observed at 20, 60 meters away from mine base and at mine base respectively, while lowest pH in water and KCl values were observed at 100 and 2500 meters away from the mine base respectively. The results of exchange acidity (EA) showed that the EA of all the sampling intervals at Ameka mining area were significantly higher ($p < 0.05$) when compared with EA of Agbaja Unuhu soil, except for 40m away from the mine base. The EA of Ameka soils ranges from 1.36 mg/kg to 12.8mg/kg, expectedly the

highest EA was observed at the mine base, whereas, the lowest EA was observed at 40 meters away from the mine base. This result indicates that the soils of the area were more acidic than the control soil of Agbaja Unuhu. When the mean of values of soil pH and EA of both areas were compared with FDALR (2004) acidity rating for natural soil fertility, the soils of area belong to a strongly acid soil class. This is in agreement with the report of Japony and Young (1994) which established a relationship between total soil lead content, solution lead content and soil pH. So, the elevated level of heavy metals concentration in the soils of these areas due to mineral mining might have contributed to strong acidic nature of soils of these areas.

Available phosphorus

The results showed that available P from all the sampling intervals at Ameka mining area ranges 1-8ppm. The highest available P was observed at 20 meters away from the mine base, while lowest available P was at 50, 90, 100 and 2500 meters away from the mine site. The available P obtained from the soils Ameka mining area was significantly ($P < 0.05$) lower than that of Agbaja Unuhu soil. The strong acidic nature of the soils of the areas is indicated by low soil pH, low soil pH is one of the important factors that determine P availability. Strong acidic soils have been reported to have the tendency to immobilize the P and thereby reducing available P content in the soil. Beside the effect of low pH, the presence of these heavy metals in high concentrations can directly influence availability of P in the soil. Example, the bioavailability of lead ions can be decreased by complexation with various materials in order to decrease their toxicity. Lead chemical immobilization using phosphate addition is a widely accepted technique to immobilize Pb from aqueous solution and contaminated soils, (Miretzky and Fernandez-Cirelli, (2008). The interactive reactions involved in this process can also lead to chelating of available P there by reducing the available P content in the soil.

Nitrogen (N)

The results showed that the N content of soils of Ameka mineral mine location were significantly ($p < 0.05$) lower than that of Agbaja Unuhu, except for the N content of samples obtained at 40 meters away from the mine site. The N content of Ameka mineral mine surroundings ranged from 0.042 to 0.168. The highest N content was observed at 40 meters away from the mine site, while the lowest N content was observed at 30 meters away from the mine location. When the mean values of N content Ameka soils were compared with FDALR (2004) soil natural fertility rating for N content, Ameka soil belongs to low N content class. This is similar to the findings reported by Ogbodo (2006). Soil N is prone to leaching and volatilization and requires to be continuously replenished in the soil, this would have been achieved with adequate vegetation cover. But the mineral mining activities have created both physical and chemical impact on the soils of the locations which might have led to sparse vegetation of these areas. Greater proportion of soil N has been reported to be in organic form, relatively denser vegetation would have ensured higher level of soil organic matter from decomposition of vegetation debris and consequently mineralization to release more nitrogen in organic form into the soil. Volatilization N due to exposure of surface soils of the mining areas may also be another factor responsible for low N content in the soils of the area.

Soil organic matter (SOM)

The organic matter content of soils of Ameka mineral mine surroundings were significantly ($P < 0.05$) lower than that of Agbaja Unuhu soil. It ranged from 0.69 to 3.39. The highest organic matter content was observed at 2500 away from the mine site, while the lowest organic matter was observed at 30 meters away from the mine base. When the mean value of 1.92%OM content in

Ameka soils was compared with organic matter content for soil natural fertility rating of FDALR (2004), it was observed that Ameka soil belongs to low %OM content class. This was supported by similar findings of Ano et al (2007). Who also reported that mining activity reduced SOM content of soil of a mining area. The low organic matter content of these soils could also be attributed to sparse vegetation of the areas, which is an indication of highly mineralized soil and poor fertility status

Exchangeable bases

The concentration of Calcium (Ca), magnesium (Mg), Potassium (K) and Sodium (Na) in the soils of Ameka mining area were significantly ($P < 0.05$) lower than that of Agbaja Unuhu soil. Concentration of Ca ranges from 2.8 to 12 Cmol/kg. The highest concentration of Ca was observed at the mine base. Mg concentration ranges from 0.4 to 5.2 Cmol/kg. Highest Mg concentration was obtained at 60 meters away from the mine base, while lowest Mg concentrations were observed at 40, 50, 70 and 90 meters away from the mine base. K concentration ranges from 0.1 to 1.4 Cmol/kg. The highest K concentration was observed at 80 meters away from the mine base, while the lowest K concentration at Ameka mining area was observed at 2500 meters away from the mine base. While concentration ranges from 0.2 to 2.4 Cmol/kg within Ameka mine vicinity. Highest concentration was observed at 30 meters away from the mine site, whereas, the lowest concentration was obtained at 2500 meters away from the mine base. When the mean concentration of these elements was compared with FDALR (2004) soil natural fertility rating, it was observed that Ca, Mg and K the mean values concentration in Enyigba soil was rated moderate. The relatively lower concentrations of these basic cations at the mining area, when compared with the control soil of Agbaja Unuhu could be attributed to the effect of low pH content of the soils of both areas. It could be that low pH which depicts strong acidity might have resulted in preponderance of exchangeable acidic cations that have displaced most of the basic cations in the soils of the mining area.

Cation exchange capacity (CEC)

The CEC of the soils of the mine location were significantly ($P < 0.05$) lower than that of Agbaja Unuhu soil, except for the CEC of the soil sample obtained at the mine base. The CEC of the soils of Enyigba mineral area ranges from 9.44 to 22.6 Cmol/kg. CEC ranges from 9.5 to 30.26 Cmol/kg. Expectedly highest CEC was observed at the mine base, whereas, lowest CEC was observed at 2500 meters away from the mine site. Comparing FDALR (2004) CEC rating for soil natural fertility with CEC of the soils of the mine location, Ameka soils belong to low CEC class. The low level of CEC at the mining area could be related to low soil pH and organic matter content of soils of the mining area. The level of exchangeable cations in the soil is often an indicator of the nutrients status of the soil. The observed low level of organic matter within the mining area might have adversely affected the nutrients availability level in soils of the area, since organic matter is often regarded as a reservoir of nutrient elements. Therefore low organic matter could suggest low cation exchange capacity, since soils nutrient storing and exchange capacity lies on the nature and quantity of organic matter. Soil pH is also another critical factor that influences chemical reactions and determines the nutrient elements availability in the soil. It therefore follows that minerals mining activities in these areas is negatively affecting these critical soil fertility factors, thereby keeping the agricultural soil in a poor fertility status that has been observed at the areas. This result is in agreement with the findings of Ogbodo (2006).

Percentage base saturation (%BS)

The %BS in the soils of Ameka mining location were significantly (0.05) lower than that of Agbaja Unuhu soil, except for the %BS of the soil sampled at 40 and 50 meters away from the mine base.

The %BS of soils of Ameka mining area ranges from 45.27 to 90.19. Highest %BS was observed at 40 meters away from the mine base, while lowest %BS was expectedly observed at the mine base. The relatively lower %BS of the soils of the mineral mining location than the unmined soil of Agbaja Unuhu could be attributed to preponderance of acidic cations at the mining location. The further lower %BS of soils at both mine sites compared to %BS of soils of other distances away from the mine sites could also be attributed the above mentioned reasons. This is supported by higher Exchangeable acidity observed at the mine site.

Particles size distribution in soils of ameka mining area affected by mining activities

The sand fraction at 20 and 40 meters away from the mine site were significantly higher, while the sand fraction at 80 and 100meter away from the mine were significantly ($P < 0.05$) lower at than the percentage sand fraction of Agbaja Unuhu soil. The sand fraction ranged from 61.2% to 79.2%. The highest sand fraction was observed at 40m away from the mine base, where as lowest percentage sand fraction was observed at 2500m away from the mine base. Percentage silt fraction distribution ranges from 12.8% to 24.8%. The highest % silt fraction was observed at 70m and 80m away from the mine, while the lowest was observed at 40meter away from the mine base. Except for silt fraction at 20 and 40 meter away from the mine site, silt fractions at every other sample point away from mine site were significantly higher at ($P < 0.05$) than that of Agbaja Unuhu soil. Percentage clay fraction distribution within Ameka mining area ranged from 8 to 10%. The highest proportion of clay was observed at 80 and 90 meter away from mine site. The clay fraction of all the sampled points around Ameka mining site were significantly ($P < 0.05$) lower than that of AgbajaUnuhu soil. A distinct trend in textural grouping was observed with regard to distance away from the mine base. The soils from zero to 50m away from Ameka mine base belong to loamy sand textural class with exception of soil at 10m away from the mine base, which was observed to be sandy loam, while soils from 60 to 2500m away from the mine base belong to sandy loam textural class. These results indicate that physical artisanal mining operation might have impacted more on the soils closer to Ameka mine base. The miners might have covered the top soils at mine base with sands excavated in the process of digging out commercial mineral of interest which is often located at lower soil profile, which may be responsible for higher proportion of sand particles in soils closer to the mine base. Ano et al, (2007) reported similar textural class their similar study.

Table 1: Effect of mineral mining on chemical properties of soil of Ameka mining areas

Distant from site (m)	pH (H ₂ O)	pH (KCl)	P Mg/kg	%N	%OM	CaCmol/kg	Mg Cmol/kg	K Cmol/kg	Na Cmol/kg	EA Cmol/kg	CEC Coml/kg	%BS
0	5.6	3.89	4.0	0.112	1.43	12.00	1.20	0.40	1.10	16.56	30.26	45.27
10	4.5	3.54	4.0	0.098	1.71	6.00	2.00	1.10	0.30	1.60	11.00	85.46
20	5.7	3.41	8.0	0.070	1.49	4.80	1.60	1.10	2.00	4.40	15.90	72.33
30	5.3	3.81	4.0	0.042	0.69	3.60	1.60	1.10	2.10	5.68	15.98	64.46
40	5.5	3.44	7.0	0.168	1.43	7.20	0.80	0.50	1.80	1.12	11.42	90.19
50	5.6	3.39	1.0	0.126	2.12	6.80	0.80	0.20	0.90	1.20	9.90	87.85
60	5.7	3.39	3.0	0.084	1.84	4.80	3.20	0.20	1.50	1.44	9.70	85.16
70	5.6	3.25	2.0	0.098	1.53	3.20	0.80	0.50	2.00	1.28	8.76	85.39
80	5.5	3.28	7.0	0.154	2.12	4.00	1.20	1.40	2.40	1.76	9.76	81.98
90	5.4	3.55	1.0	0.098	1.89	2.80	0.80	0.40	2.30	5.12	11.42	55.17
100	5.3	3.23	1.0	0.112	1.95	3.60	1.20	0.40	1.20	1.92	8.32	76.92
2500	5.3	3.81	1.0	0.112	3.39	6.00	1.60	0.10	0.20	1.60	9.50	83.16
CS	6.22	5.12	23.0	0.238	3.67	18.70	7.40	2.10	2.70	1.15	33.05	96.52
mean	5.43	3.59	3.83	3.159	1.920	5.72	1.573	0.5341	1.897	3.421	13.07	76.9
FLSD	2.514	1.144	1.100	0.3324	0.2980	1.239	0.9031	0.1030	0.3452	0.8470	1.711	13.76

Significance at 0.05 probability level

Table 2: Particles size distribution in soil at Ameka as affected by mineral mining

Distant from site (m)	% sand	% silt	% clay	texture
0	73.2	18.8	8.0	Loamy Sand
10	67.2	24.8	8.0	Sandy Loam
20	77.2	14.8	8.0	Loamy Sand
30	75.2	16.8	8.0	Loamy Sand
40	79.2	12.8	8.0	Loamy Sand
50	75.2	16.8	8.0	Loamy Sand
60	69.2	22.8	8.0	Sandy Loam
70	67.2	24.8	8.0	Sandy Loam
80	65.2	24.8	10.0	Sandy Loam
90	69.2	22.8	8.0	Sandy Loam
100	61.2	26.8	8.0	Sandy Loam
2500	71.2	18.8	10.0	Sandy Loam
Cs	71.2	20.8	9.0	Sandy Loam
Mean	77.0	20.1	9.1	Loamy Sand
FLSD	5.3	4.3	1.9	

Significant difference at 0.05 probability level

Relationship between Heavy Metals (Pb, Zn And Cd) Content in the Soil and some Soil Chemical Properties

The correlation coefficient (r) of relationship between soil heavy metals (Pb, Zn and Cd) concentration and some soil chemical properties are presented in Table 3. Negative significant correlation coefficient was observed between soil Pb and nitrogen ($r = 0.606^*$) and CEC ($r = 0.640^*$). While, Zn showed negative significant correlation ($r = 0.642^*$) with cation exchange capacity. Positive and significant correlation ($r = 0.576^*$) was observed between soil cation exchange capacity and Cd. This result contrasts the findings of Ano *et al.*, (2007), but agreed with the reports of Onweremadu and Mbah (2009) and Oti, *et al.*, (2012). The implication is that as these heavy metals (Pb, and Zn) concentrations levels increase in soil, the nitrogen and cation exchange capacity decrease. The importance of optimum nitrogen in soil and soil cation exchange capacity cannot be over emphasized with regard to the roles of these two factors in soil fertility and productivity. When these critical soil fertility factors are reduced below natural minimum level as a result of increased heavy metal concentration, the natural capacity of the soil to support crop production is invariably reduced. Hence, this result further confirms the earlier suggestion that soil heavy metals pollution as result of mineral mining activities is responsible for poor natural fertility status and consequently sparse vegetation of the area. Thus heavy metals polluted soils were not only a danger to environmental health, but also, was a danger to Agricultural soils productivity. This study has shown that the soils of the study areas will soon lose their natural capacity to support crop production, if nothing is done to remedy the situation. The positive significant correlation observed between cadmium and CEC also indicated that cadmium can replace some of the basic cation in the soil exchange site, therefore, increase in cadmium concentration can lead to increased soil CEC, but since cadmium cannot perform the same biochemical roles as these cations. It can constitute harm to both the crop and animals, including humans.

Table 3: Correlation coefficient of the relationship between soil (Pb, Zn and Cd) content and chemical properties at Ameka mining area

	Pb	Zn	Cd
pH	-0.344	0.190	0.094
Avail.P	0.437	-0.187	0.148
N(%)	-0.606*	-0.434	-0.142
OM(%)	-0.009	0.252	-0.094
CEC	-0.640*	-0.642*	-0.576*

*Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0, 01 level (2-tailed)

Conclusion

The findings of this study indicate that the soils of Enyigba mineral mining area are polluted with Pb and contaminated with Zn as a result of mineral mining in the area. It was also found that the pollution is wide spread within the area, as far as 2500m away from the mine base and has impacted negatively on the soil natural fertility. Finally it can be concluded that the level of Pb, Zn and Cd concentrations in soil as result of mineral mining activities in the area have constituted a great threat to agricultural soil productivity and environmental health of animal and human populations in the area. Since the major economic activity of the people of the area is agricultural production and soil heavy metal is the major source of heavy metals entrance into the cycle of food chain. Therefore, it is pertinent that phytoremediation is urgently employed to clean up the soils of Enyigba mining area, in order to restore the productivity of the soils of the area and prevent possible heavy metal food poisoning of humans and animals in the area.

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