



RESEARCH PAPER

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Heavy metal concentration and physicochemical properties of soil in the lead-zinc mining area of Ishiagu, Nigeria

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Abstract

The study assessed heavy metal (lead, zinc, cobalt, chromium and cadmium) and physicochemical properties (pH, cation exchange capacity, electrical conductivity, organic carbon and clay content) of soil samples in Ishiagu lead-zinc mining area. Soil samples were collected at depths of 0-15cm, 16-30cm and 31-45cm from abandoned pit, active pit, artificial lake and tailing in the study area, and from a control site. Results of laboratory analysis indicated that heavy metal concentration followed the order zinc>lead>cobalt>chromium>cadmium with the control site having the least concentration. Heavy metal concentration was above normal limits in soil. Variations were also observed in soil physicochemical properties. Statistical analysis showed significance differences in both heavy metal content and physicochemical properties of soil between sites ($p < 0.05$). There were no significant differences ($p > 0.05$) with respect to depth. There is high risk of heavy metal contamination of water and vegetation from the tailing area due to its low pH, while the higher clay content at the mining area may help impede metal dissolution. However, the high content of these toxic metals in the soil may have adverse effects on soil quality and on human health if they get into the food chain. In order to reduce the likelihood of this occurring, illegal artisanal mining and the consumption of contaminated plant and water should be strongly discouraged.

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Introduction

Metals occur naturally in the earth's crust but increasingly higher quantities are released into the environment by anthropogenic activities (Ross, 1994; Lorenz *et al.*, 1997; Chaudhury and Srivastara, 2001, Humphries, 2007). Mining is an important source of heavy metal contamination of the environment (Huton and Symon 1986).

In Ishiagu, Southeastern Nigeria, lead and zinc mining has been going on for over fifty years, and in recent times its exploration has been intensified. Heavy metals are known to contaminate areas surrounding mine sites as well as posing serious threats to ecosystems and to human health (Ogwuegbu and Muhanga, 2005; Duruibe *et al.*, 2007). The sources of contamination include mine tailings, heap leach areas, mine effluents, active and abandoned pits and spoil banks (Nwaugo *et al.*, 2008). In soils, heavy metals may remain in solution, could be taken up by plants or retained by soils in soluble or insoluble forms (Andrea and Gimeno – Garcia 1999). The retention time of heavy metals in soils may reach thousands of years (Salomons, 1993). Soil biota which plays important roles in soil fertility and primary production, are sensitive to metal stress (Fritze *et al.*, 1989; Zak *et al.*, 1994; Schimel and Guilledge 1998; Olivera and Pampulha, 2006). These effects lead to the disruption of soil enzyme function and symbiotic nitrogen fixation (Struczynski *et al.*, 2007). It was the view of Humphries (2007), that all of these may translate into higher soil ecosystem level effects.

In the developing world, only few sites near mining areas have been characterized in terms of metal contamination and risk assessment (Obiekezie, 2005). Where this has been done, it is necessary that data are regularly updated to generate a reliable database to aid environmental planning and management. High heavy metal content has been reported in water sources in the Ishiagu area (Akubugwo *et al.*, 2012). The aim of this study therefore is to assess heavy metal content and

physiochemical properties of soils in Ishiagu lead-zinc mining area and their environmental implications.

Materials and methods

Study area

The study area, Ishiagu is situated in Ivo Local Government Area of Ebonyi State, South Eastern Nigeria. It is located between latitudes 5° 52' to 5° 60' N and longitudes 7° 30' to 7° 37" E. Four sampling locations within the mining site namely, abandoned pit (05.55.695 N and 007.29.909 E), active pit (05.55.726 N and 007.30.030 E), artificial lake (05.55.711 N and 007.30.000 E) and tailing (05.55.694 N and 007.29.846 E) were used for the study.

Mean annual rainfall in the study area ranges from 1750mm to 2000mm with double maxima in July and September. Mean relative humidity is 70 percent and mean annual temperature 27°C. (Oguntoyinbo, 1982 - Oguntoyinbo, 1987). The study area is located in the tropical rainforest, but due to intensive human modification has been replaced with the so called forest savanna characterized by grasses, shrubs and few trees (Areola, 1983). The soil of the study area is red ferrasols or red- brown gravelly and pale clayey soils derived from shale (Ofomata, (1975). The study area is part of the region referred to geologically as the Cross River Basin.

Sample Collection

Soil samples were taken from, abandoned pit (ABP), active pit (ACP), artificial lake (AL) and tailing (TL) and from the botanical garden of Abia State University, Uturu. Samples were collected in June, 2012. The coordinates of the sampling locations were obtained using GARMIN GPS map model 76CS. At each of the four sampling locations, three different soil samples were collected using a soil auger and pooled to give a composite sample for that location. Samples were collected at depths of 0-15cm, 16-30cm and 31-45cm, in polythene bags which were

labelled at site of collection before they were sent for analysis.

Sample Preparation and Treatment

Soil samples were air dried, sieved and then stored in clean plastic bottles at room temperature before analysis. Soil pH was determined with a pH meter (Jenway, HANNA 1910) as described by Neyak *et al.*, (1996). Cation exchange capacity (CEC) of the soil samples was determined by the NH_4OAc , pH 7 extraction method. The electrical conductivity of the soil extract was determined with the conductivity bridge. The method of Walkey and Black (1934) was used in the determination of total organic carbon (TOC). Particle size analysis was determined according to Agbenin (1995). The method of AOAC (2005) was adopted for analysis of heavy metals. Exactly 1g of each soil sample was wet digested using aqua regia (1: 2vol of NH_4O_3 , HCl) and extracted with deionised water. The extract was aspirated into the Spectra AA 220 FS spectrophotometer after inserting the hollow cathode lamp for the various heavy metals. The result of lead content of the various samples is as hereafter presented.

Analysis of variance was done using *Minitab version 14* at 95% confidence level.

Results

The result of soil physiochemical properties are presented in Table 1. while those of heavy metal content of soils are presented in Fig.(1.-5.). Soil pH ranged from 4.45 to 7.54 with the tailing (31-45cm) and abandoned pit (16-30cm) having the lowest and highest pH values respectively. Electrical conductivity ranged from $0.52\mu\text{s}/\text{cm}$ to $91.00\mu\text{s}/\text{cm}$. The lowest value for electrical conductivity was at the control (31-45cm) while the highest value was at the tailing (0-15cm). Cation exchange capacity ranged from $8.52\text{mg}/100\text{g}$ to $66.35\text{mg}/100\text{g}$ with the control (31-45cm) and the abandoned pit (31-45cm) having the lowest and highest values respectively. Total organic carbon ranged from 0.47% at the tailing (16-30cm) to 2.96% at the artificial lake (0-

15cm). Percentage clay ranged from 0.10% at the artificial lake (31-45cm) to 17.30% at the tailing (16-30cm).

Heavy metal contents of soils are presented in Fig.(1.-5.). Cobalt content of soil ranged from $14.75\text{mg}/\text{kg}$ at the control (16-30cm) to $300.90\text{mg}/\text{kg}$ at the artificial lake (16-30cm). Lead content of soil ranged from $0.01\text{mg}/\text{kg}$ to $266.75\text{mg}/\text{kg}$. Lead content was lowest at control (31-45cm) and highest at the active pit (16-30cm). Zinc content of soil ranged from $15.85\text{mg}/\text{kg}$ to $725.73\text{mg}/\text{kg}$. The zinc content of soil was lowest and highest at the control (31-45cm) and at the active pit (31-45cm) respectively. Chromium content ranged from $37.50\text{mg}/\text{kg}$ at the control (16-30cm) to $149.00\text{mg}/\text{kg}$ the tailing (31-45cm). Cadmium content ranged from $0.45\text{mg}/\text{kg}$ at the control (0-15cm) to $45.00\text{mg}/\text{kg}$ at the artificial lake (16-30cm). The result of statistical analysis showed that for pH, significant differences exist between sites ($p\text{-value} = 0.00 < 0.05$) but not between depth ($p\text{-value} = 0.29 > 0.05$). The mean values are summarized as follows; Mean ABP = 7.45 > mean ACP = 6.87 > mean AL = 6.397 > mean Control = 5.43 > mean TL = 4.993. No significant differences exist between the various depths. Significant differences did not exist in ECEC with respect to depth ($p\text{-value} = 0.894 > 0.05$). Differences however exist with respect to the various sites ($p\text{-value} = 0.00 < 0.05$).

For percentage TOC, no significant difference exists between the various depths ($p\text{-value} = 0.70 > 0.05$) and among the various sites ($p\text{-value} = 0.21 > 0.05$). Significant differences were not found in EC with respect to site ($p\text{-value} = 0.30 > 0.05$) and depth ($p\text{-value} = 0.68 > 0.05$).

With respect to clay content of soil, significant differences exist with respect to site ($p\text{-value} = 0.007 < 0.05$) but not to depth ($p\text{-value} = 0.17 > 0.05$). In terms of mean contents, mean TL = 13.10 > mean ABP = 9.50 > mean ACP = 5.47 > mean Control = 0.867 > mean AL = 0.30. There was no significant

difference between heavy metal content with respect to depth (p-value =0.56>0.05). However, heavy metal content varied significantly (p-value=0.00<0.05), where mean Zn =329.40>mean Pb=144.30>mean Co=128.50>mean Cr>107.78>mean Cd=10.60. Significant differences

also exist between soil heavy metal contents at study area and control (p-value =0.00<0.05) Mean metal contents with respect to site are summarised as follows; mean AL=242.80> mean ACP=187.50> mean TL=168.30> mean ABP=104.60> mean control =17.48.

Table 1. Physicochemical properties of soils at various depths.

S/N		AL			ABP			ACP			TL			CONTROL		
		A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
1	pH	6.52	6.07	6.60	7.52	7.54	7.29	6.89	6.63	6.88	5.18	5.35	4.45	5.67	5.95	4.67
2	EC(μS/CM)	33.00	25.00	55.00	21.00	21.00	23.00	29.00	51.00	71.00	91.00	6.00	3.00	5.00	2.29	0.52
3	ECEC(Meq/100g of soil)	32.33	56.89	36.06	33.66	40.31	66.35	63.21	48.47	44.06	56.64	31.03	48.89	19.47	12.01	8.52
4	TOC(%)	2.96	1.58	1.83	0.64	1.36	1.11	1.09	1.73	2.29	1.03	0.46	1.07	2.49	1.32	0.85
5	% Clay	0.60	0.20	0.10	6.10	7.20	15.20	0.30	10.10	6.00	8.00	17.30	14.00	1.20	0.80	0.60

A= 0-15cm, B=16-30cm, C=31-45

AL=Artificial Lake, ABP=Abandoned pit, ACP=Active pit, TL=Tailing

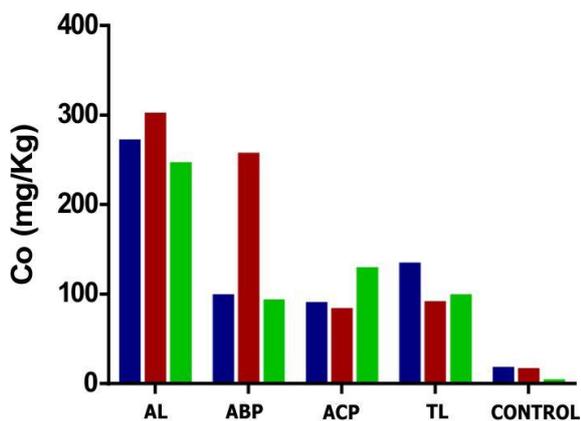


Fig. 1. Cobalt content of soil at various depths at study area and control.

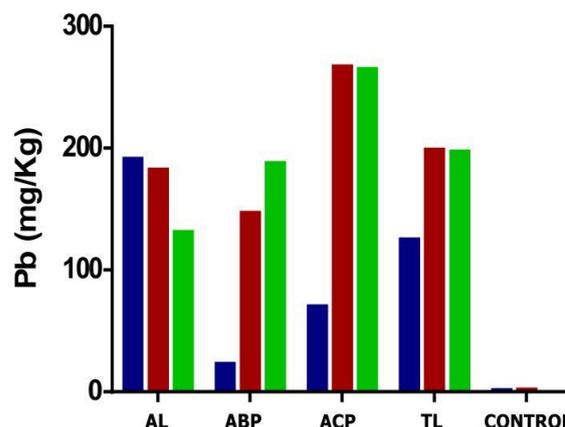


Fig. 2. Lead concentration in soil at various depths.

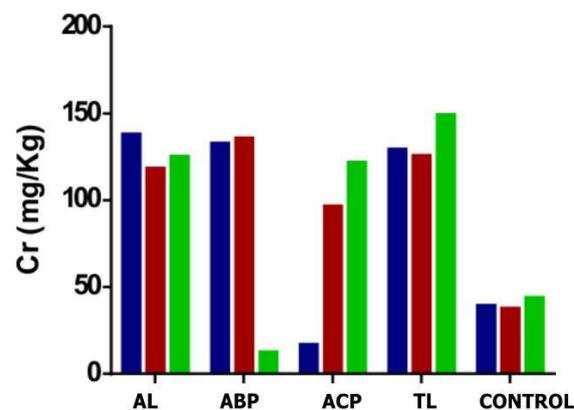
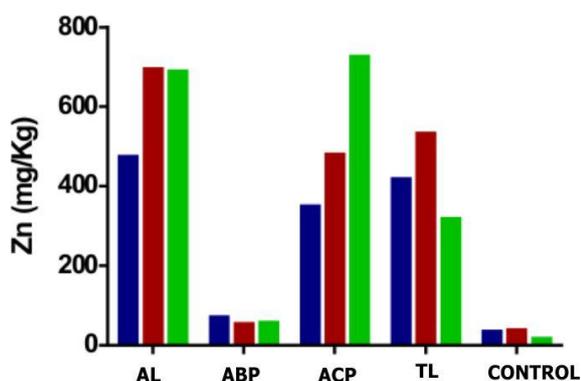


Fig. 4. Chromium concentration in soil at various depths.

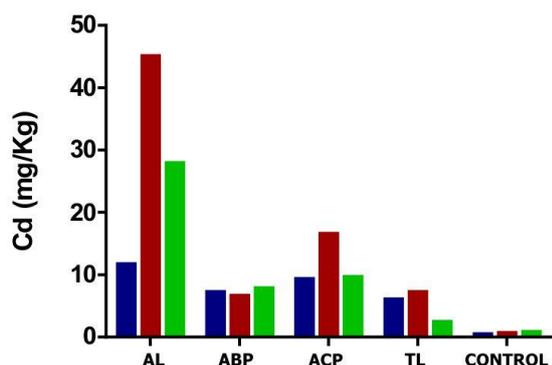


Fig. 5. Cadmium concentration in soil at various depths.

Soil Depth (cm)



AL= Artificial Lake, ABP= Abandoned pit, ACP= Active pit, TL= Tailing

Discussion

Soil pH is the most important property influencing metal mobility and availability in soil. This is because the capacity of metal sorption into soil surface largely depends on it. Soil pH influences all other soil properties including physical, chemical and biological (Brady and Weil, 1999) and along with cation exchange capacity, organic carbon and soil texture, influence metal bioavailability for plant uptake (Jung, 2008). Basta *et al.*, (1993) indicated that lower solubility and higher retention of metal cations occur at high pH.

The lowest pH however was obtained at the mine tailing (TL) at the (31-45cm). The acidic nature of the tailing, imply that heavy metals there are more soluble and bioavailable. There is therefore, a high risk of soil and water contamination by toxic metals at the tailing. The higher values of pH at the mining

area, particularly at the abandoned pit and active pit can be attributed to the higher concentrations of heavy metals there.

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 neutral to basic nature of the artificial lake and abandoned pit may be due to microflora and fauna activities. With increased oxidation occurring, acid forming species or radicals are generated making pH to tend towards acidity.

The pH values are similar to those obtained by Nwaugo *et al.*, (2007) in the Ishiagu mining area.

Electrical conductivity (EC) is a measure of the amount of dissolved salts in soil solution. Results show that EC of the various sites varied significantly, but were generally higher in soils at the mining area. The higher EC values at the mining area can also be attributed to higher concentration of heavy metals there. This suggests that the soil from the study area contain more soluble salts.

CEC controls the portion of total metal available to soils and is therefore an important soil property (Baath, 1989). In addition, it gives a measure of the sum total of the exchangeable cations that can be absorbed by soil. This soil property is crucial for soil metal bioavailability (Jung, 2008) and fertility (Obasi, 2012). The higher CEC values at the mining area were not surprising since CEC correlates positively with the pH and electrical conductivity (Brady and Weil, 1999). The CEC range is similar to that obtained by Abou-Shanah *et al.*, (2007) in mining sites in Egypt. With the mining area having significantly higher values for CEC, it was expected that metal concentration there would also be higher.

Total organic carbon (TOC) is the reservoir of essential and non-essential elements for plant growth and therefore plays a key role in soil productivity (Anikwe and Nwobodo, 2002). It is

also important for metal solubility in soil (Alloway and Ayres, 1997). TOC was observed to have least value at the tailing where higher oxidation occurs as a result of microbial activity. The oxidation of carbon to CO₂, reduces soil carbon content. While TOC is not critical in the soil for plant growth it influences many other soil processes and is indicative of the soil as a rooting environment (Okalebo *et al.*, 1993).

Clay content is the most important textural property affecting metal bioavailability in soils. Clay content was generally higher at the study area. The low porosity of clayey soils hampers metal dissolution. The higher metal levels in soils at the study site imply that metal bioavailability and clay content are expected to be higher there. This agrees with Sizmur (2007).

Heavy metal is a collective term referring to a group of metals or metalloids with atomic density or specific gravity greater than 4g/cm³ Huton and Symon, (1986) and atomic weight greater than 63.54 (Garbarino *et al.*, 1995). The term is also applied to toxic metals (Duffus, 2002). Heavy metal content was observed to be significantly higher in soils at the study area in comparison with the control (table 1.). The concentration of individual metals in soils at the study area (AL, ABP, ACP and TL), with the exception of Zn at the ABP and chromium at ACP (31-45cm) were all above permissible limits for agricultural soil as given by Kabata-Pendias and Pendias (1984). The estimated toxic levels for soil for purposes of agriculture are Pb (60mg/kg), Zn (200mg/kg), Co (20mg/kg), Cd (1.6mg/kg) and Cr (120mg/kg). Agricultural use of soil in the study area is crucial since the inhabitants are essentially farmers and large quantities of yam, rice and okra are produced in the area (Eze and Chukwu, 2010). At the control, heavy metal content of soil was within these limits.

Heavy metal content of soils at the study area generally exceeded the normal soil concentration

given by Alloway (1968). The mean normal concentrations are; Co (8mg/kg), Pb (10mg/kg), Zn (50mg/kg), Cr (100mg/kg) and Cd (0.06mg/kg). Only Co concentration was above that for normal soil at the control. Similar findings have been obtained by Abou- Shanah *et al.*, (2007); Nwaugo *et al.*, 2008 and Eze and Chukwu, (2012).

With the exception of Pb, heavy metal concentration at the study area was also higher than the mean range of different countries given by Kabata – Pendias and Pendias (2000). The mean ranges for the various heavy metal were Co (0.1-70mg/kg); Pb (3-189mg/kg); Zn (17-125mg/kg); Cd (0.6-1.1mg/kg) and Cr (5-120mg/). With respect to lead, concentrations above 100mg/kg are considered high in soil (Kabata –Pendias and Pendias, 2000) and the upper limit of the metal for normal soil was established as 70mg/kg by Davies (1977).

The high levels of heavy metal content at the study area raise serious concerns for environmental quality and human health. There is obviously a high risk of surface and ground water pollution from runoff and percolation as well as increased level of metal laden particulate matter in the ambient atmosphere. This has grave implications for human health. For instance Aroh *et al.*, (2007) reported high levels of metals in streams receiving acid mine drainage from Ishiagu mines while Onwumesi *et al.*, (2011) implicated metal mining activities for pollution of ground water in the Ishiagu.

However, the high levels of pH at the study area may increase the soil retention capacity for these metals. This is because high soil pH is a stabilising factor for toxic metals in soil (Kabata-Pendias, 2000). This interaction between toxic metals and soil pH impedes metal absorption from soil and their consequent uptake by plants. According to Eze and Chukwu (2011) heavy metals in the mining area are linked to a variety of sources. These include mineralised veins, mine dumps, the Asu river shale and the minor basic intrusives.

Small scale, illegal mining activities expose geological materials to intensive weathering aided by rainfall, relief and the clayey- ferralitic nature of the soil. Heavy metal uptake by crops and other plants, pose direct and serious health threats to man. Therefore farming activities in the vicinity of the mining sites should be discouraged. This can be achieved by proper sensitization of the inhabitants on the health implications of heavy metals in human diet.

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