JASEM ISSN 1119-8362

Full-text Available Online at
https://www.ajol.info/index.php/jasem
http://ww.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 22 (9) 1485 –1488 September 2018

Assessment of Pb, Zn, As, Ni, Cu, Cr and Cd in Agricultural Soils around Settlements of Abandoned Lead-Zinc Mine in Mkpuma Ekwoku, South-eastern, Nigeria

***CHUKWU, A; OJI, KK**

Department of Geology, Ebonyi State University, Abakaliki, Nigeria.
**Corresponding Author Email: achukwu1@gmail.com; kelechioji3@gmail.com*

ABSTRACT: This study was carried out to assess the level, distribution and the contamination status of Pb, Zn, As, Ni, Cu, Cr and Cd in agricultural soils around the settlements of Abandoned Lead-Zinc Mine in Nkpuma Ekwoku, South-eastern, Nigeria. The mean concentrations of the heavy metals, Pb, Zn, As, Ni, Cu, Cr and Cd are 109.55, 210, 1.83, 2.34, 8.24, 12.66 and 8.57 mg/kg respectively. The values obtained were compared with the established soil sediment standard by Canadian Council of Ministers of Environment (CCME). Generally most samples around the abandoned Pb/Zn mine show higher concentration of Pb, Zn, Cd, and Cr compare to individual Effect Range Low (ERL) values of the elements while Cu, and Ni were below both Effect Range Low (ERL) and Effect Range Medium values. However, Cd and Cr exceed the Effect Range Medium of the elements. Pollution Load Index (PLI) was found to be generally low in all the locations whereas the contamination factor (CF) values for metals like Pb, Zn and Cd are >1 while CF values of As, Cu, Cr and Ni are <1. The contamination is most probably resulted from the mineralized veins and mining of the ores.

DOI: https://dx.doi.org/10.4314/jasem.v22i9.21

Dates: Received: 28 May 2018; Revised: 27 August 2018; Accepted: 17 September 2018

Keywords: heavy metals; soil contamination; lead-zinc; Mkpuma-Ekwoku

Recently, there have been increasing interests regarding heavy metal contamination in the environment, apparently due to their toxicity and persistence within the environment (Tijani *et al*., 2005). Heavy metal contamination is common in developed and developing countries especially industrial and mineralization areas. Natural and anthropogenic processes including methods of mining and mine waste have remained the major sources of the heavy metals in the environment (Obiora *et al*., 2016a, b, 2018). Lead poisoning which resulted from artisan mining of gold bearing lead ores around parts of Zamfara State, northeastern Nigeria has led to death of 163 people including children between March and June, 2010 (Lo *et al*., 2010). Heavy metals have the ability to accumulate in human body over a period of time before its effect (Paz-Ferreiro *et al*., 2014; Chehregani *et al*., 2005). The soil is the major interface for the exchange of these heavy metals. Due to daily activities of man such as mining, agricultural activities and other developmental activities, there is frequent and continues interaction with soil and direct ingestion of the heavy metals via plants cultivated on the soils (Obiora *et al*., 2016a).

The study area is located within Abakaliki basin (Chukwu and Obiora, 2018), Lower Benue Rift, Nigeria. The basin consists mainly of Albian carbonaceous shale of the Asu River Group (Abakaliki shale) subordinate sandstone, siltstone and limestone. The Cretaceous dark shales host hydrothermal Pb/Zn mineralization (figure 1). Mining of Pb-Zn in the study area has lasted for more 85 years. The waste from the mines has been converted to settlements and farmlands and the mining pits in most localities serve as ponds for domestic water activities by the inhabitants. This present work is aimed to assess the level, distribution and the contamination status of Pb, Zn, As, Ni, Cu, Cr and Cd in agricultural soils around the settlements of abandoned Pb-Zn mines.

MATERIAL AND METHODS

Soil Sampling: Samples of sediments were taking from sixteen stations (covering Mkpuma Ekwoku and its environs) within the period of December - March. A total of 16 samples were collected (0-10cm) from the main sample points covering the study area. The sampling positions were recorded using GPS localization. The collected samples were air dried, crushed in a porcelain mortar and stored in a polyethylene bags for subsequent analysis. The

**Corresponding Author Email: achukwu1@gmail.com; kelechioji3@gmail.com*

concentration of Pb, Zn, Cu, Cd, Ni, As, and Cr were determined in all samples using Atomic absorption Spectrophotometer (FS 240 Varian) with standard solution in similar manner to that described in APHA 1995.

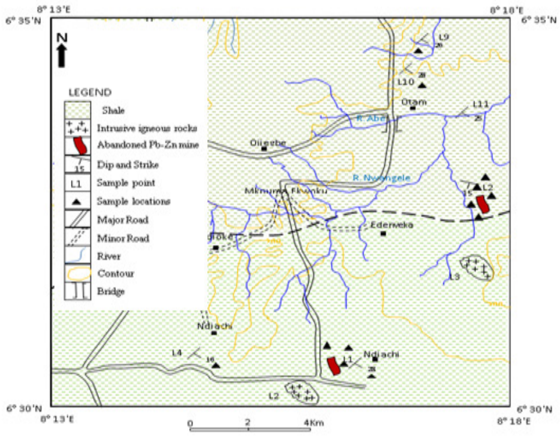

Fig 1: Geologic and sample location map of Mkpuma Ekwoku and its environs

Sediment pollution indices: Geo-accumulation index (I-geo): This was determined by the following equation according to Muller (1996), I-geo = Log 2(C_n/1.5 B_n); Where C_n = measured concentration of heavy metal in Mkpuma Ekwoku, B_n = Geochemical background value in average abundance of shale is used for the possible variations of the background data due to lithological variations. The geo-accumulation index was classified into seven different groups (table 1) according to the severity of contamination (Muller, 1996).

Table 1: Classes of geo-accumulation factor

Class	Value	Soil/Sediment quality
0	I-geo<0	Practically uncontaminated
1	0<I-geo<1	Uncontaminated to moderately contaminated
2	1<I-geo<2	Moderately contaminated
3	2<I-geo<3	Moderately contaminated to heavily contaminated
4	3<I-geo<4	Heavily contaminated
5	4<I-geo<5	Heavily contaminated to extremely contaminated
6	5<I-geo<6	Extremely contaminated

The Pollution Load Index (PLI): The Pollution Load Index (PLI) is obtained as degree of overall contamination using the concentration factors (CF). CF is the quotient obtained by dividing the concentration of each metal with background value. The PLI of the place are calculated by obtaining the n-root from the n- CFs that was obtained for all the metals. Generally pollution load index (PLI) as developed by Tomlinson *et al.,* (1980), which is as follows:

$$CF = \frac{C_{metal}}{C_{background\ value}}$$

$$PLI = n \sqrt{(CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)}$$

Where, CF = contamination factor, n = number of metals, C_{metal} = metal concentration in polluted sediments, $C_{Background\ value}$ = background value of that metal. The PLI value of > 1 is polluted, whereas <1 indicates no pollution (Harikumar *et al.,* 2009). Microsoft excel and ANOVA were used for statistical calculations.

RESULTS AND DISCUSSION

The concentrations of heavy metals in sediments are varied according to the rate of particle sedimentation, the rate of heavy metals deposition, the particle size and the presence or absence of organic matter in the sediments (Saloman *et al.,* 1987). The concentration of Pb, Zn, As, Ni, Cu, Cr and Cd in the sediment of the study area ranges between 33.73 – 166.26, 114.51 – 303.30, 0.00 – 5.10, 0.82 – 4.43, 3.940 – 16.910, 4.97 – 28.32 and 2.00 – 20.22 mg/kg respectively (table 2). Zn has high concentration compared with other heavy metals in the study area, in the order; Zn > Pb > Cr > Cd > Cu > Ni > As. This may be due to the high concentration of this metal in suspended solids and sphalerite bearing ores in the area. Obiora et al. 2016b has also reported high values of Zn, Pb and Cd in soils of lead-zinc mining district of Enyigba in other part of Nigeria.

In characterizing the contaminant level in Mkpuma Ekwoku, the approach described in the United States' Environmental Protection Agency (USEPA) and Mid-Atlantic Integrated Assessment (MAIA), for estuaries 1997-1998 Summary Report (table 2). This was in line with the sediment quality guideline established by Long *et al. (*1995). Metal concentrations in sediments below ERL values are not expected to cause adverse effects, concentrations between the ERL and ERM values represent a range within which effects will occasionally occur while metal concentrations in sediments above ERM are likely to be very toxic (Table 2).

The values of the analysed heavy metals in the study area were within the ERM and ERL allowable limits except for Cd which shows values above allowable limits of ERM and ERL in 60 % sampled points in the area. The maximum concentration of Cd in all sampled locations is 20.22 mg/kg, above the toxic level. Therefore, according to the US –EPA – MAIA 1998, the rest of the tested heavy metals are also below the toxic level. Furthermore, the heavy metal concentrations of the area were compared with the maximum standards set by Canadian Environmental Quality Guideline (CCME, 1999) (Table 2).

Table 2: Heavy metal concentration (mg/kg) of elements in sediments of Mkpuma Ekwoku and its environs.

Heavy metals	Range	Mean	Std. Dev.	Variance	CCME	ERL	ERM
Pb	33.75-166.26	109.55	20.76	431.3	70	47	220
Zn	114.51-303.3	210	23.8	566.97	200	150	410
As	0.8-5.1	1.83	0.94	0.87	12	34	270
Cu	3.94-16.91	8.24	3.16	10	63	1.2	9.6
Ni	0.82-4.43	2.34	3.39	11.49	50	21	52
Cr	4.97-28.32	12.66	4.27	18.28	64	82	370
Cd	2.0-20.22	8.57	2.76	7.59	1.4	1	3.7

Pb and Zn concentrations in 60 % of the sample points exceeded the values of CCME of 70 mg/kg and 200 mg/kg respectively. Pb shows highest concentration in sample point 1 (166.26 mg/kg) while Zn shows highest concentration in sample point 2 (303.1 mg/kg) above CCME (table 2). The concentrations of Cd across the sample area which ranges from 2.00 to 20.22 mg/kg exceeded the maximum allowable limits of 1.4 mg/kg similar to the ERM and ERL discussed above. These high concentrations could also be attributed to the mining activities in the area and the local geology.

Table 3: Geo-accumulation index (I-geo), Contamination factor (CF) and Pollution load effect (PLI) values for soil of Mkpuma-Ekwoku

		Min	Max.	Mean	Std. dev.
Pb	I-geo	0.333	1.662	1.05	0.45
	CF	1.68	8.31	5.23	2.277102
Zn	I-geo	0.254	0.674	0.467	0.174
	CF	1.27	3.37	2.36	0.88666
As	I-geo	0.001	0.01	0.0034	0.0028
	CF	0.08	0.51	0.18	0.147975
Ni	I-geo	0.0001	0.001	0.00013	0.00033
	CF	0.01	0.06	0.026	0.013636
Cr	I-geo	0.001	0.01	0.0044	0.0025
	CF	0.03	0.52	0.215	0.13024
Cd	I-geo	1.333	13.48	5.69	3.035
	CF	6.67	67.4	28.46	15.17709
	PLI	0.39	0.9	0.55	0.2945

Geo-Accumulation Index: The geo-accumulation index (I-geo) is a quantitative measure of the degree of contamination in sediments (Singh et al. 2005). The geo-accumulation index for the quantification of heavy metal accumulation in the study area is presented in table 3. I-geo grade for the study area sediments varies from metal to metal and site to site (across metals and sites). Following the geo-contamination index values given in table 3, it can be deduced that Cd is moderately contaminated to extremely contaminate with the highest value up to 13.48. Lead and Zinc are within uncontaminated to moderately contaminate in the study area. While I-geo for the other elements (As, Ni and Cr) indicated uncontaminated. The contamination of cadmium in the study area could be as a by-product of the Pb-Zn ore and this may impose serious health issues in future.

Pollution load Index: Result of this study shows that the mean CF values of most of the metals such as As, Cu, Cr and Ni are low (< 1) (Table 3). But the CF values for metals like Pb, Zn, and Cd shows higher (> 1) values. This could be due to external discrete sources like anthropogenic inputs and geogenic sources. The values of the pollution load index were found to be generally low in all the sample area. Pearson's correlation coefficient (r) is used to measure the strength of a linear relationship between any two variables on a scale of -1 (perfect inverse relation) through 0 (no relation) to +1 (perfect sympathetic relation) (Asaah *et al*., 2006).

The correlation coefficients of the mobile concentrations of the heavy metals in the sampled media are shown in Table 4 below. According to Evans (1996), When r is 0.00 - 0.19 = very weak, r is 0.20 - 0.39 = weak, r is 0.40 – 0.59 = moderate, r is 0.60 - 0.79 = strong, r is 0.80 – 1.0 = very strong.

The closer the value is to +1 or –1, the stronger the linear correlation. In the soil sediments sampled for Mkpuma-Ekwoku, the correlation matrix (Table 4) shows very strong correlation of Pb and Cd, Pb and Zn while moderate correlation of Cu and Ni. There is a very weak correlation of As and Cd, As and Cr, As and Ni, Ni and Cd, Ni and Cr while the rest falls in the range of weak correlation. These may be probably due to differences in the dispersion of these metals. However, generally, the result shows that the elements are inter related.

Conclusion: Pb, Zn and Cd contaminations in the area can directly result from the past mining activities in the area and local geology. These have direct effect on soils and water bodies (streams) and interfere with their nutrients uptake. The effect may range from simple ailments to serious changes in sensory perceptions, immune and nervous system impairments, damage of vital internal organs, reduced fertility, spontaneous abortion and ultimately death. Researches are encouraged to avoid future casualties similar to the incident in Zamfara mines in northern, Nigeria.

Table 4: Correlation matrix of eight heavy metals in the soil samples from Mkpuma Ekwoku

	Cd	Cr	Ni	Cu	As	Zn	Pb
Pb	0.863678	-0.25489	0.249083	0.268487	0.379965	0.963655	1
Zn	0.854627	-0.38909	0.24554	0.383461	0.329046	1	
As	0.163518	-0.01901	-0.02649	0.384303	1		
Cu	0.212853	-0.31145	-0.47403	1			
Ni	0.01739	-0.02562	1				
Cr	-0.35000	1					
Cd	1						

Acknowledgement: The authors appreciate the effort of Prof. H.N Ezeh of the Geology Department, Ebonyi State University and Prof. S.C Obiora of Geology Department, University of Nigeria, Nsukka for their encouragements during the research work.

REFERENCE

Asaah, VA; Abimbolu, FA; Such, CE (2006). Heavy metal contamination and distribution in sediment of the Bassa industrial zone, Doula, Cameron. *Arabic J. sci. engine*. 31: 147-158.

Canadian Environmental Council of Ministers of the Environment (1999). Soil Quality Guidelines for the Protection of Environmental and Human Health updated 2006.

Chukwu, A; Obiora, SC (2018). Geochemical constraints on the petrogenesis of the pyroclastic rocks in Abakaliki basin (Lower Benue Rift), Southeastern Nigeria. *J. Afr. Earth Sci*. 141: 207-220

Harikumar, PS; Nasir, UP; Mujeebu Rahma, MP (2009). Distribution of heavy metals in the core sediments of a tropical wetland system, "International Journal. *Environ. Sci. Technol.* 6(2): 225-232.

Lo, Y; Dooyema, CA; Neri, A; Durant, J; Jefferies, T; Medina-Mrino, A; Ravello, L; Thoroughman, D; Davis, L (2010). Childhood Lead poisoning associated with Gold ore processing: a village-level investigation- Zamfara State, Nigeria. *Environ. Health perspect*. 120(10): 1450-1455.

Long, ER; MacDonald, DD; Smith, SL; Calder, FD (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environ. Manage.* 19: 81 – 97.

Muller, G (1969). Index of geo-accumulation in sediments of the Rhine River. *Geol. J*. 2: 109–118.

Saloman, WN; Rooij, H; Bril, J (1987). Sediments as a source for contaminants, *Hydrobiologia*, 149: 13-30.

Singh, VK; Singh, KP; Mohan, D (2005). Status of heavy metals in water and bed sediments of river Gomti – A tributary of the Ganga River, India. *Environ. Monit. Assess*. 105: 43–67.

Tijani, MN; Onodera, S; Adeleye, MA (2005). Environmental implications of adsorbed and total trace metals concentration in bottom-sediments of an urban drainage network in a developing country. *Mater. Geoenviron.* 52(1): 127-130.

Tomlinson, DL: Wilson, JG: Harris, CR: Jeffney, DW (1980). Problems in the assessment of heavy metal levels in estuaries and the formation of a pollution index, Helgol. Wiss. *Meeresunters*, 33: 566-572.

Obiora, SC; Chukwu, A; Davies, TC (2016a). Heavy metals and health risk assessment of arable soils and food crops around Pb-Zn mining localities in Enyigba, southeastern Nigeria. *J. Afr. Earth Sc*. 116, 182-189.

Obiora, SC; Chukwu, A; Toteu, SF; Davies, TC (2016b). Assesment of heavy metal contamination in soils around Lead (Pb) - Zinc (Zn) mining areas in Enyigba, Southeastern Nigeria. *J. Geol. Soc. India*., 87: 453-462.

Obiora, SC; Chukwu, A; Davies, TC (2018). Contamination of the Potable water supply in the Lead-zinc mining communities of Enyigba, southeastern Nigeria. *Mine Wat. Environ.* https://doi.org/10.1007/s10230-018-0550-0.